PHYSICAL REVIEW B VOLUME 52, NUMBER 6 1 AUGUST 1995-II

# Molecular approach to the modeling of elasticity and piezoelectricity of SiC polytypes

A. P. Mirgorodsky and M. B. Smirnov
*Institute for Silicate Chemistry, Russian Academy of Sciences, Odoevskogo Street 24, corpus 2, St. Petersburg 199155, Russia*

E. Abdelmounîm, T. Merle, and P. E. Quintard
*Laboratoire de Matériaux Ceramiques et Traitements de Surface, Faculty of Sciences, 123 Avenue Albert Thomas, F-87060 Limoges, France*

(Received 27 May 1994; revised manuscript received 22 November 1994)

We present the results of a lattice-dynamical treatment of the 3*C*, 2*H*, 4*H*, and 6*H* structures of SiC, performed within the framework of an unified approach. This includes (i) a simple valence force field, whose parameters were in part derived from the quantum-mechanical calculations of the appropriate molecule, in part from a fitting procedure, and (ii) a charge distribution model regarding the electron transfer between bonded atoms as a response to the change of interatomic separation. A conflict exists in the literature about the elastic properties of 3*C*-SiC, and our opinion on the most reliable data is given. Complete sets of elastic and piezoelectric tensor elements derived from the model calculations are presented for all materials under consideration. The chemical regularity in the variation of sign of the $e_{14}$ piezoelectric constants from the I-VII to IV-IV members of the sphalerite family is discussed in light of the present model.

## I. INTRODUCTION

The modern nonempirical quantum-mechanical investigations of molecules are capable of credibly estimating a wide scope of parameters usable in phenomenological models of crystals. The fruitfulness of such a molecular approach to the lattice-dynamical treatments of ionic-covalent IV-VI compounds, namely, *silicon oxide* ($\alpha$-quartz), and of IV-V compounds, namely, *silicon nitride* ($Si_3N_4$) was recently demonstrated in Refs. 1 and 2, respectively. The application of this approach to IV-IV *silicon carbide* compounds, in particular, to a series of SiC polytypes, therefore seems worthwhile.

At least two circumstances argue for this. The first one relates mainly to practice. SiC plays an important role in modern electronics and is also of technological interest as a piezoelectric pressure sensor and an actuator material. One should therefore study its elastic and piezoelectric characteristics. The delay in our detailed knowledge of these values is due to the unavailability of SiC in the form of large single crystals. Thus our first aim is to estimate the above quantities for the series of the simplest SiC polytypes including 3*C* cubic and 2*H*, 4*H*, and 6*H* hexagonal ones by utilizing some separate experimental data obtained for the latter.

This work can also be of fundamental interest since the cubic SiC belongs to the sphalerite family whose role in the lattice-dynamical investigations is comparable to that of *Drosophila* in studies of heredity. Silicon carbide occupies a special position in this family in being the only IV-IV heteropolar lattice and thus attracts considerable interest.

Although many phenomenological models were employed during the past three decades to treat the dynamical properties of SiC,[3–9] all of them, except Ref. 9 which we shall discuss below, were essentially based on the ionic concept assuming the lattice to be made up of point or spherelike entities, interconnected through pair-wise forces. This approximation is not suitable for a substance where covalent bonding effects are not negligible. Thus the second aim of this paper is to reexamine the interatomic forces and the polarization mechanism in SiC lattices within the framework of an approach viewing the crystal as an enormous covalently bonded molecule. Below we present the general scheme which allows us to do this without departing from the direct space of the lattice, unlike the conventional approach (method of long waves) using the abstract **k** space.

The potential function of the lattice is described via valence force fields (VFF) of $SiC_4$ and $CSi_4$ tetrahedra, whose main parameters were derived from quantum-mechanical studies of the appropriate molecule. The charge distribution response to a structure deformation is considered within a model in which the redistribution of electron density is described via the charge transfer from one atom to another inside the chemical bonds, in contrast to all preceding phenomenological model which localized this effect inside the ions. When discussing the results obtained for the different polytypes we provide their comparison by regarding the cubic {111} planes as physically equivalent to the hexagonal planes {0001}. Thus we show that there is a group of elastic and piezoelectric constants of cubic and hexagonal lattices which are very closely related due to the similarity in the local tetrahedral bonding. On the other hand, there exists significant difference between the cubic and hexagonal structures which manifests itself in the magnitudes of tensor elements which are equal to zero for the hexagonal systems but are nonvanishing for the cubic one.

Section II of this paper briefly reviews existing information about the properties in question. Section III presents general considerations, while Sec. IV details the computational scheme and analysis of results. These are summarized and discussed in Sec. V.

0163-1829/95/52(6)/3993(8)/$06.00

## II. OBJECT AND PREVIOUS STUDIES

Silicon carbide forms a great variety of tetrahedral frameworklike lattices which are called polytypes. The origin of the polytypism can be visualized as follows. In Fig. 1, the solid circles represent spheres closely packed in a plane; call this "plane 1." To place another such set of spheres on top of plane 1 as closely as possible, one would place each sphere in the hole between any three neighboring spheres in plane 1 (dotted circles, plane 2). But there is another way of accomplishing this: the dashed circles in plane 3. The order of stacking of the planes determines the types of close-packed structures and their symmetry properties. According to conventional nomenclature, a SiC polytype is represented by the number of Si-C double layers in the unit cell, the appended letter *C*, *H*, or *R* indicating a cubic, hexagonal, or rhombohedral symmetry. For example, the 6*H* hexagonal lattice has six such layers in the primitive cell with the following succession of the above planes: 1,2,3,1,3,2,1,2,3,1,3,2; the 3*C* lattice is built up as 1,2,3,1,2,3; 2*H*-SiC corresponds to 1,2,1,2; and 4*H*-SiC corresponds to 1,2,1,3,1,2,1,3.

One can expect small structural differences to produce small differences in most physical properties of the polytypes, which will facilitate correlation with experiment. Unfortunately, this is not the case. Single crystals of SiC are not available, and the handling of tiny SiC pieces is difficult and an error in measurements easily appears. On the other hand, when the samples are larger, the existence of defects is more probable. Therefore there are no clear reasons why some of the estimates should be taken more seriously than others.

Note first that the situation with regard to the *vibrational spectra* of SiC compounds would appear to be somewhat better than that of elastic and piezoelectric properties. In particular, the difficulty of having different numbers of atoms per unit cell for each structure has been removed according to a concept[10] implying that the modes in a spectrum of any polytype can be assigned to some points of dispersion curves within the Brillouin zone of the cubic SiC. The Raman studies by Feldman *et al.*[11,12] have allowed them to draw the above curves and to verify the existence of a common phonon spectrum for all the SiC family. Since then, those are frequently referred to as "experimental dispersion curves" for 3*C*-SiC along the [111] axis. The investigations by Olego and Cardona[13] enriched this picture with some zone-boundary points for transverse directions.

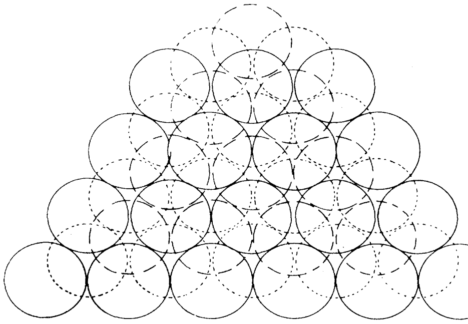

FIG. 1. Schematic diagram of atomic arrangements in the different SiC polytypes (see text).

It is noticeable that the magnitude of the TO-LO splitting of the principal long-wave vibration (795–970 $\mathrm{cm}^{-1}$), and hence a corresponding lattice polarization, seems to be surprisingly large for the compound which, from the chemical standpoint, should be viewed as "significantly covalent." That fact was already discussed in the early works by Tolpygo[14,15] who assumed that it should be attributed to the effect of charge transfer, produced by the stretching vibration and not to large atomic charges in SiC. More recent *ab initio* calculations by Churcher, Kunc, and Heine[16] demonstrate that the valence charge density distribution along the chemical bonds in the SiC lattice is characterized by large anisotropy increasing at outward displacements of atoms. This is typical for ionic compounds. Below we shall treat this topic when discussing the mechanism of the piezoeffect.

The information on the *elastic properties* of SiC is much more inaccurate and confusing. A contemporary detailed analysis of the situation can be found elsewhere.[17] Here we wish to point out that, in contrast to the hexagonal polytypes,[18,19] the elastic constants $C_{11}$, $C_{12}$, and $C_{44}$ of the cubic SiC were never measured by direct experimental methods. Nevertheless, one can find in the literature three complete sets of their values referred to as experimental ones (see Table I). One of them, represented by Lee and Joannopoulos,[20] has a vague origin, as was noted in Ref. 17, and most likely should be viewed as some sort of confusion. The other two were indirectly derived from various experimental characteristics of SiC. The first of them was obtained by Slack[21] via equations including measured magnitudes of the Young modulus, and Poisson and anisotropy ratios. It can be seen from Table I that Slack's value $C_{11}$ drastically contradicts the one calculated previously by Tolpygo,[3] and the results of more recent models.[17,20,22,23] Lambrecht *et al.*[17] have revealed an obvious mistake in the Slack's calculations which, after correction, provided results more in line with the rest. These authors have deduced the third set of the

TABLE I. Elastic and piezoelectric constants of cubic silicon carbide.

| | $C_{11}$ | $C_{12}$ | $C_{44}$ | $e_{14}$ |
|---|---|---|---|---|
| | ($10^{11}$ dyn/cm$^2$) | | | ($10^4$ esu cm$^{-2}$) |
| Ref. 3 | 35.23 | 14.04 | 23.29 | +33.00 |
| Ref. 21 | 54.0 | 18.0 | 25.0 | |
| Ref. 22 | 34.89 | 13.80 | 20.82 | |
| Ref. 20 | 37.1 | 16.9 | 17.6 | |
| Ref. 9[a] | 30.0 | 11.6 | 16.5 | −7.88 |
| Ref. 23 | 42.0 | 12.0 | 26.0 | |
| Ref. 17[b] | 44.4 | 14.8 | 20.7 | |
| Ref. 17[c] | 39.0 | 14.2 | 25.6 | |
| Ref. 17[d] | 42.0 | 12.6 | 28.7 | |
| This work | 42.82 | 16.54 | 24.62 | −10.4 |

[a] Derived by us from parameters of Ref. 9.

[b] Corrected results of Ref. 21.

[c] Derived from measured sound velocities and the bulk modulus.

[d] Results of the *ab initio* calculations.

"experimental" elastic constants (Table I) by using the sound velocities, obtained by Feldman *et al.*,[12] and quite reliable data for the bulk modulus. Moreover, they have made *ab initio* estimates of those values (Table I). The latter are in accord with those estimated from the experimental characteristics and with a series of the theoretical results from the ones by Tolpygo[3] to the contemporary calculations of Tersoff.[23]

However, this seemingly final clarity is debatable, if one assumes the determination of the "true" magnitudes to be a prerogative of experiment. Actually, the authoritative spectroscopic investigations of the subject by Feng, Choyke, and Powell[24] let them conclude that the best available magnitudes of the elastic constants of 3*C*-SiC should be close to those originally obtained by Slack.[21] These authors resolutely classified the corresponding data in Refs. 3, 20, and 22 as unreliable, which, obviously, should equally apply to more recent works.[17,23] Such a situation argues for further studies.

Concerning *the piezoelectricity* of the material under consideration, let us recall that the cubic modification of SiC belongs to the simplest crystalline structures which can be macroscopically polarized by homogeneous deformations. Consequently, it would represent the most favorable case for the model study of the microscopic mechanism of piezoelectricity.

Unfortunately, the piezoelectric studies of SiC are inconclusive. The early attempts[25] to obtain the electromechanical coefficient squared, $k_{13}^2$ and $k_{33}^2$, for the hexagonal samples were made with large uncertainties; the recent measurements of the $k_{31}^2$ value seem to be more reliable.[19,26] The existing estimates related to 3*C*-SiC are exclusively theoretical. The first of them was made by Tolpygo,[3] who computed the $e_{14}$ piezoconstant along with the elastic ones, and obtained a relatively large value for the former ($33\times10^4$ esu cm$^{-2}$). Later, Kunc, Balkanski, and Nusimovici[8] used the calculated results by Tolpygo[3] for a model investigation, but assumed, without explanation, that $e_{14}=0$. Since then, to the best of our knowledge, no steps were made in this direction.

The most elaborate lattice-dynamical model of the cubic SiC is that proposed by Cheng, Kunc, and Heine[9] and termed "the valence overlap shell model" (VOSM). However, in this work, attention was exclusively focused on the eigenfrequency-eigendisplacement problem, which has always been a challenge to lattice dynamics. The *ab initio* frozen-phonon eigenvectors, measured phonon frequencies, and "experimental" elastic constants by Lee and Joannopoulos[20] were included in the fitting procedure. However, the calculated elastic constants were not presented, and the piezoelectric tensor was not treated. Since the model was characterized by the authors as "the most physical among the available;" in Table I we present those values, derived by us from the VOSM parameters given in Ref. 9.

## III. GENERAL CONSIDERATIONS

Vibrational, elastic, and piezoelectric properties of a lattice can be naturally joined together within the framework of the lattice-dynamical theory of homogeneous deformations of crystals.[27] According to this theory, the initial (instant) deformation $U_i$ ($i=1-6$ are Voigt's indices) is followed by two processes minimizing the internal energy density $V$. These are (i) a structural relaxation describable via zone-center normal coordinates $Q_\lambda$ which necessarily belong to any Raman-active representation, and (ii) the variation of the dipole moment density, i.e., the lattice polarization $\Delta\mathbf{P}$, producing the macroscopic electric field $\mathbf{E}$ within the lattice. Thus, the $V$ value can be regarded as a following quadric form (normalization to a unit volume and summation on repeated indices are assumed hereafter):

$$V=\tfrac{1}{2}U_iC_{ik}^0U_k+\tfrac{1}{2}Q_\lambda\omega_\lambda^2Q_\lambda+U_iF_{\lambda i}Q_\lambda-\tfrac{1}{2}E_\alpha\varepsilon_0\varepsilon_{\alpha\beta}^eE_\beta-U_ie_{\alpha i}^0E_\alpha-Q_\lambda Z_{\alpha\lambda}E_\alpha\ , \tag{1}$$

whose coefficients are the second *partial derivatives* of the internal energy density with respect to corresponding variables: $C_{ik}^0$ is a "bare" (nonrelaxed) elastic constant, $\omega_\lambda$ is a frequency of $\lambda$th phonon, $F_{\lambda i}$ is an elastic-optic coupling constant, $\varepsilon_0\varepsilon_{\alpha\beta}^e$ is an electronic dielectric constant (here $\varepsilon_0$ is permittivity of vacuum; $\alpha,\beta=1,2,3$ are indices of the Cartesian axis), $e_{\alpha i}^0$ is a "bare" piezoelectric constant, and $Z_{\alpha\lambda}$ is the Born dynamical charge tensor, associated with normal coordinate $Q_\lambda$.

Via condition $dV/dQ=0$, Eq. (1) can be transformed into the form

$$V=\tfrac{1}{2}U_iC_{ik}U_k-\tfrac{1}{2}E_\alpha\varepsilon_0\varepsilon_{\alpha\beta}^{\mathrm{st}}E_\beta-U_ie_{\alpha i}E_\alpha\ , \tag{2}$$

where

$$C_{ik}=C_{ik}^0-\frac{F_{\lambda i}F_{\lambda k}}{\omega_\lambda^2} \tag{3}$$

is an element of the elastic tensor at constant electric field;

$$\varepsilon_0\varepsilon_{\alpha\beta}^{\mathrm{st}}=\varepsilon_0\varepsilon_{\alpha\beta}^e+\frac{Z_{\alpha\lambda}Z_{\beta\lambda}}{\omega_\lambda^2} \tag{4}$$

represents the static dielectric tensor, and

$$e_{\alpha_i}=e_{\alpha_i}^0-\frac{Z_{\alpha\lambda}F_{\lambda i}}{\omega_\lambda^2} \tag{5}$$

is the element of the piezoelectric tensor.

By applying the condition $dV/dE_\alpha=0$ to expression (2), one gets

$$V=\tfrac{1}{2}U_i\Gamma_{ik}U_k\ , \tag{6}$$

where

$$\Gamma_{ik}=C_{ik}+\frac{e_{\alpha i}e_{\beta k}}{\varepsilon_0\varepsilon_{\alpha\beta}^{\mathrm{st}}} \tag{7}$$

is a piezoelectrically stiffened elastic constant, which can be rewritten as

$$\Gamma_{ik}=C_{ik}(1+k^2)\ . \tag{8}$$

The $k^2$ value describes electromechanical coupling. Its components for $\alpha=\beta$ and $i=k$ are electromechanical coefficients squared, widely used in practice:

$$k_{\alpha i}^2=\frac{e_{\alpha i}^2}{\varepsilon_0\varepsilon^{\mathrm{st}}_{\alpha\alpha}C_{ii}}\ . \tag{9}$$

Our model implies that energy $V$ can be decomposed into two parts: a mechanical one, $V^{\mathrm{mec}}$, which includes the first three terms in the right-hand side of Eq. (1), and a polarization one, $V^{\mathrm{pol}}$, formed by the last three terms. Let us focus first on the former. Within the framework of the VFF, it can be presented as

$$V^{\mathrm{mec}}=\tfrac{1}{2}q_m K_{mn} q_n\ , \tag{10}$$

where variables $q_m$ (we call them valence coordinates) describe the changes of interatomic bond lengths and of bond angle magnitudes, and force constants $K_{mn}$ are the parameters of the VFF. By taking the *partial derivatives* of Eq. (10) with respect to $U_i$ and $Q_\lambda$, one gets

$$C^0_{ik}=\frac{d^2V^{\mathrm{mec}}}{dU_i dU_k}=L_{im}K_{mn}L_{kn}\ , \tag{11}$$

$$\omega_\lambda^2=\frac{d^2V^{\mathrm{mec}}}{dQ_\lambda dQ_\lambda}=L_{\lambda m}K_{mn}L_{\lambda n}\ , \tag{12}$$

$$F_{\lambda i}=\frac{d^2V^{\mathrm{mec}}}{dU_i dQ_\lambda}=L_{\lambda m}K_{mn}L_{in}\ , \tag{13}$$

where $L_{im}=dq_m/dU_i$ is a shape of nonrelaxed deformation $U_i$ obtainable from a lattice geometry,[28] and $L_{\lambda m}$ is a shape of the $\lambda$th normal coordinate, i.e., an eigenvector of the dynamical matrix given on the basis of the valence coordinates. The knowledge of quantities involved in Eqs. (11)–(13) is sufficient to evaluate the elastic constants $C_{ik}$ either by using Eq. (3), or via a relation analogous to (11), where, however, the total differentiation is implied:

$$C_{ik}=L^*_{im}K_{mn}L^*_{kn}\ , \tag{14}$$

where

$$L^*_{im}=L_{im}-\frac{L_{\lambda m}F_{\lambda i}}{\omega_\lambda^2} \tag{15}$$

is the *total derivative* $dq_m/dU_i$, that is a shape of the "full" (i.e., relaxed) deformation $U_i$ at constant $\mathbf{E}$.[28]

Note that relationship $\mathbf{q}=\mathbf{B}\Delta\mathbf{r}$ connects the $q$ space of the valence coordinates with a space of atomic Cartesian displacements $\Delta r_{s\alpha}$ ($r_s$ is a vector describing the position of $s$th atom) and allows us to derive the vibrational frequencies from the dynamical matrix in the Cartesian space along with corresponding eigenvectors $L_{\lambda s\alpha}=dr_{s\alpha}/dQ_\lambda$.

Let us now consider the piezoelectric effect. Equations (1) and (5) correspond to a traditional approach[27] implying that quantities $e^0_{\alpha i}$ and $Z_{\alpha\lambda}$ specify two contributions to this effect. These are, respectively, (i) polarization $\Delta P^0(U_i)$, produced by a nonrelaxed homogeneous deformation, and (ii) polarization $\Delta P(Q_\lambda)$, associated with a relevant inner relaxation via the variation of normal coordinates $Q_\lambda$. Thus,

$$e^0_{\alpha i}=dP^0_\alpha(U_i)/dU_i\ , \tag{16}$$

$$Z_{\alpha\lambda}=dP_\alpha(Q_\lambda)/dQ_\lambda\ . \tag{17}$$

From a physicist's point of view it seems desirable to distinguish the microscopic mechanisms that produce the charge density variation in a strained lattice. For a mixed ionic covalent compound two main mechanisms can be proposed.[29] One corresponds to displacements $\Delta r_s$ of the ionic static charges $z_s^0$ from equilibrium positions $r_s^0$, and the other would originate from the intrabond electron charge redistribution, induced by those displacements and leading to changes $\Delta z_s$ of the ionic charges. Thus the polarization $\Delta P$ can be described as

$$\Delta P_\alpha=z_s^0\Delta r_{s\alpha}+r^0_{s\alpha}\Delta z_s\ . \tag{18}$$

In our model $\Delta z_s$ is a linear function of the change of the Si-C bond length $a$. The model contains two independent parameters only: $z^0=z^0(\mathrm{Si})=-z^0(\mathrm{C})$ characterizing the ionic charges $z_s^0$ at equilibrium positions, and $c^0=c_m=dz(\mathrm{Si})/da_m=-dz(\mathrm{C})/da_m$ specifying the dependence of the charges upon the lattice distortion. In view of (18) and the neutrality condition, Eqs. (16) and (17) can be represented as follows:

$$e^0_{\alpha i}=z_s^0 r^0_{s\alpha}+a^0_{m\alpha}c_m L_{mi}\ , \tag{19}$$

$$Z_{\alpha\lambda}=z_s^0 L_{\lambda s\alpha}+a^0_{m\alpha}c_m L_{\lambda m}\ , \tag{20}$$

where $a^0_{m\alpha}=r^0_{s\alpha}-r^0_{t\alpha}$ is the $\alpha$ projection of the $m$th Si-C bond (between atoms $s$ and $t$), and $c_m=c^0$, if $m$ corresponds to a bond-stretching valence coordinate, and is otherwise equal to zero. The first term in the right-hand side of (19) describes a dipole moment density of the strain-free lattice and thus is identical to zero in our case (nonpyroelectric crystal). Consequently, Eq. (5) assumes the form

$$e_{\alpha i}=a^0_{m\alpha}c_m L_{mi}-Z_{\alpha\lambda}F_{\lambda i}/\omega_\lambda^2 \tag{21}$$

and, in view of (20) and (15), one obtains the following expression for the piezoelectric constant:

$$e_{\alpha i}=-z_s^0 L_{\lambda s\alpha}F_{\lambda i}/\omega_\lambda^2+a^0_{m\alpha}c_m L^*_{mi}\ . \tag{22}$$

The first term in the right-hand side of Eq. (22) represents the purely ionic contributions, while the second term relates to the electron flow inside the chemical bonds from one bonded atom to another.

## IV. MODEL AND ANALYSIS OF RESULTS

The simple VFF model used in our calculation consisted of the following seven parameters: one Si-C bond-stretching force constant $K_q$; two bending force constants $K_\gamma$ and $K_\delta$ relating to angles C-Si-C and Si-C-Si, respectively; two off-diagonal constants $H_\gamma$ and $H_\delta$ describing the stretching-stretching interactions via atoms Si and C, respectively; and two off-diagonal constants $A_\gamma$ and $A_\delta$ describing the stretching-bending interactions in angles C-Si-C and Si-C-Si.

Theoretically, the *ab initio* magnitudes of these parameters could be deduced from the VFF's of molecules containing $SiC_4$ and $CSi_4$ units. Unfortunately, no corresponding quantum-mechanical calculations are known. To the best of our knowledge, the most appropriate for the goals of this work are the force constants obtained for trimethylsilanol $(CH_3)_3SiOH$ with empirical correction by a so-called scaling procedure based on experimental frequencies.[30]

Among the above force constants, four were adopted from Ref. 30, namely, $K_q = 3$ mdyn/Å, $K_\gamma = 0.9$ mdyn,

$$H_\gamma = 0.05 \text{ mdyn/Å} , \quad A_\gamma = 0.175 \text{ mdyn Å} .$$

They were kept fixed. The remaining constants were found by fitting the zone-center TO frequencies and the elastic constants of SiC-6*H* to the corresponding experimental magnitudes[12,18] which led us to $K_\delta = 0.45$ mdyn, $H_\delta = 0.05$ mdyn/Å, and $A_\delta = 0.525$ mdyn Å. These seven force constants were employed as a unified set of the VFF parameters to all SiC polytypes involved in our considerations. They provided quite satisfactory agreement with the set of TO frequencies measured for various SiC polytypes.

The tensor properties of the cubic and hexagonal polytypes are presented in Tables I and II, respectively. It is known[17] that a comparison of the two tensors is made possible by transforming the coordinate system of 3*C*-SiC to a set of Cartesian axes with the *z* axis along the (111) direction. This implies that it is possible to consider the direction orthogonal to Si-C layers physically equivalent in all the polytypes. For this goal in mind we recalculated the properties of 3*C*-SiC in regarding it as a trigonal lattice whose space group was $C_{3v}^1$ (a subgroup of $T_d^2$). It is labeled $3C^{\text{tri}}$ in Table II.

It can be seen from Table I that the above interatomic potentials automatically provide $C_{11}$, $C_{12}$, and $C_{44}$ values for the cubic lattice close to those found by various methods in Refs. 17 and 23. Table II shows us that the cubic elastic tensor when being transformed into the trigonal one provides $C_{11}$, $C_{33}$, $C_{12}$, $C_{13}$, $C_{44}$, and $C_{66}$ elements very closely related to the properties of the hexagonal polytypes. In considering this result with respect to the problem of selecting the most reliable elastic constants of SiC-3*C* (see Sec. II) we have come to an opinion diametrically opposed to that found in Ref. 24.

TABLE II. Elastic and piezoelectric constants of $3C^{\text{tri}}$, 2*H*, 4*H*, and 6*H* SiC structures (in units of Table I).

| | Experiment | | | Model (this work) | | | |
|---|---|---|---|---|---|---|---|
| | $6H^{\text{a}}$ | $6H^{\text{b}}$ | $4H^{\text{c}}$ | $3C^{\text{tri d}}$ | $2H$ | $4H$ | $6H$ |
| $C_{11}$ | 50.2 | | | 54.32 | 52.00 | 53.72 | 52.50 |
| $C_{33}$ | 56.5 | | 60.52 | 58.15 | 58.52 | 60.50 | 58.30 |
| $C_{12}$ | 9.5 | | | 12.71 | 14.52 | 15.60 | 14.42 |
| $C_{13}$ | | | | 8.88 | 8.91 | 10.85 | 8.88 |
| $C_{14}$ | | | | 5.42 | $\equiv 0$ | $\equiv 0$ | $\equiv 0$ |
| $C_{44}$ | 16.9 | | | 16.97 | 17.00 | 17.01 | 17.00 |
| $C_{66}$ | 20.3 | | | 20.80 | 18.37 | 19.07 | 19.10 |
| $e_{15}$ | | | | $-5.92$ | $-6.05$ | $-5.90$ | $-5.94$ |
| $e_{31}$ | | ±6.0 | | $-5.93$ | $-5.98$ | $-5.95$ | $-6.00$ |
| $e_{33}$ | | | | $+11.85$ | $+11.89$ | $+10.23$ | $+11.95$ |
| $e_{22}$ | | | | $+8.38$ | $\equiv 0$ | $\equiv 0$ | $\equiv 0$ |

[a] Reference 18.

[b] Derived from the electromechanical coupling estimated in Ref. 19.

[c] Reference 19.

[d] 3*C* lattice is regarded as the trigonal structure having the $C_{3v}^1$ symmetry with the *Z* axis along (111).

Before discussing the piezoelectricity of SiC structures, let us recall that the simplest of them belongs to the sphalerite family which contains a wide scope of compounds ranging from the presumably ionic I-VII with noble metal cations, such as CuCl, through the classic II-VI's such as ZnS, to III-V's such as InSb, and, if one allows the two atoms in the sphalerite structure to be identical, also including purely covalent materials such as Si or C. In this number, since it is a IV-IV compound, cubic SiC would occupy position immediately preceding the latter, and thus may be intuitively estimated as the most covalent among the heteropolar structures. On the other hand, a great difference in the ionic radii of Si and C would lead to essential asymmetry in the valence electron distribution inside the bond, which is typical for largely ionic compounds.

Experimentally the above mentioned magnitude of the TO-LO splitting is frequently interpreted as argumentation for large ionicity of SiC. Theoretically, the *ab initio* study[16] of the electron structure of this compound has also shown an ionic rather than covalent character of the SiC bond. Thus the microscopic mechanism of the piezoelectricity in silicon carbide is also of chemical interest. and quantities $z^0$, $F_{\lambda i}$, $c^0$, and $L_{mi}^*$ are worthy of a more detailed consideration.

Note, that $L_{mi}^* = 0$ corresponds to the "traditional" Jaffe model implying that the interatomic bonds are absolutely rigid.[31] In such a case, according to Eq. (22), the polarization would originate from displacements of charges $z^0$ solely, and correspond to the positive $e_{14}$ (see a description of the polarization mechanism in Sec. V). Another particular case $F_{\lambda i} = 0$ can occur if the stretching pair-wise forces are canceled by the three-body interactions. This corresponds to a purely electronic mechanism of the piezoeffect whose sign would be determined by that of coefficient $c^0$. However, normally $L_{\lambda i}^* \neq 0$ and $F_{\lambda i} < 0$, and the $e_{14}$ value can have any sign depending upon the relationship between magnitudes and signs of $z^0$ and $c^0$.

Within the model adopted in this paper, case $c^0 = 0$ would imply that the electron overlap is absent, thus specifying a purely ionic lattice. So, an increasing role of the second term in the right-hand side of Eq. (22) can be associated with increasing covalency. The positive sign of $c^0$ means that the ionic charge $z$ increases along with increase of the interatomic separation. This would manifest a predisposition of the lattice to dissociate into an ensemble of charged ions. The alternative, i.e., a negative value of $c^0$, cannot be ruled out. This would mean a decrease in the charges at bond lengthening, which can be interpreted as a tendency of the lattice to dissociate into a set of neutral atoms. Note that the latter is what would be anticipated for the extremely covalent lattice as diamond.

Thus neither the TO-LO splitting nor the $e_{\alpha i}$ magnitude alone can characterize the type (ionic or covalent) of the compound, since they cannot tell us which of the mechanisms dominates in the polarization effect. If $c^0<0$, the electron flow term can cancel the ionic one in Eq. (20), thus reducing to zero the TO-LO splitting while providing a large piezoelectric effect. On the other hand, as will be shown below, for $c^0>0$ a large oscillator strength can be accompanied by zero piezoelectricity.

Such a variety of changeable factors (i.e., depending on structural and chemical peculiarities) makes the piezoelectric effect a very subtle phenomenon, poorly predictable from the qualitative considerations even in a series of such simple isostructural compounds as sphalerites. In connection with this, more detailed considerations of the estimation of the charge distribution parameters $z^0$ and $c^0$ can be instructive.

To find these, we have used two experimental values, $Z_{\alpha\lambda}=\pm2.7e$ which follows from Eq. (4) (with $\varepsilon^e=6.7$, $\varepsilon^{\rm st}=10.0$, and $\omega=796\ \mathrm{cm}^{-1}$), and $e_{31}=\pm6\times10^4$ esu cm$^{-2}$, deduced for 6*H*-SiC from the data of Refs. 19 and 18 with the help of Eq. (9). By putting these values in the left-hand sides of Eqs. (20) and (22), respectively, one obtains a system of equations leading to four versions for the above mentioned parameters depending on the adopted signs of $Z_{\alpha\lambda}$ and $e_{31}$. They are presented below along with the corresponding values $e_{14}$ calculated for the 3*C* polytype:

| | I | II | III | IV |
|---|---|---|---|---|
| $Z_{\alpha\lambda}(e)$ | 2.7 | 2.7 | $-2.7$ | $-2.7$ |
| $e_{31}(10^4\ \mathrm{esu\,cm}^{-2})$ | 6.0 | $-6.0$ | 6.0 | $-6.0$ |
| $z^0(e)$ | 1.24 | 0.42 | $-0.42$ | $-1.24$ |
| $c^0(e/\text{Å})$ | 0.58 | 0.91 | $-0.91$ | $-0.58$ |
| $e_{14}(10^4\ \mathrm{esu\,cm}^{-2})$ | 10.4 | $-10.4$ | 10.4 | $-10.4$ |

It can be seen from these results that versions I, III, and IV either provide the physically unrealistic negativity of the $z^0$ charge, or contradict the sign of the $e_{14}$ value dictated by results of Ref. 9; only case II appears to provide the meaningful quantities. Significantly, this implies that the signs of two terms in the right-hand side of Eq. (22) are essentially different for 3*C*-SiC. Note that $c^0>0$ would mean that the center of the intrabond electron cloud moves to the negative ion at the Si-C bond elongation, which is in qualitative compliance with the *ab initio* results of Ref. 16. In other words, this confirms the "ionic" type of the charge distribution response to the deformation of the SiC lattice.

On the other hand, within this version, Eqs. (20) and (22) for 3*C*-SiC assume the following numerical views (in corresponding units), $2.7=0.42+2.28$ and $-10.4=7.3-17.7$, respectively, thus demonstrating that the ionic contributions to the Born charge and to the piezoelectric tensor are much smaller than those related to the intrabond electron flow effect which dominates. The piezoelectric constants of the different SiC polytypes calculated with version II are presented in Tables I and II.

## V. SUMMARY AND DISCUSSION

In this paper we have analyzed elastic and piezoelectric properties of 3*C*, 2*H*, 4*H*, and 6*H* polytypes of SiC within a simple unified model.

First, we considered a controversial situation existing in the literature relating to the elastic constants of the cubic SiC lattice. In our opinion, the above results provide strong support for the theoretical estimates of these values made in Refs. 17 and 23. Correspondingly, it is highly likely that the magnitudes claimed in Ref. 24 to be the best available, are, in fact, not the most satisfactory.

Then we concentrated on the piezoelectric properties of SiC polytypes. While reproducing the experimental values of the squared Born dynamical charge for 3*C*-SiC and the squared electromechanical coupling coefficient $k_{31}^2$ for the hexagonal lattice, the model provided a quantitative description of piezoelectric effect in the cubic SiC in reasonable compliance with the estimate derived from the parameters of Ref. 9. Our results confirm the validity of the $e_{31}^{\rm hex}=-\frac{1}{2}e_{33}^{\rm hex}$ relation mentioned in Ref. 32 for the hexagonal structures. However, they drastically contradict the equation $e_{14}^{\rm cub}=+(\sqrt{3}/3)e_{33}^{\rm hex}$ deduced in Ref. 32. According to our considerations, the relationship between these values is $e_{14}^{\rm cub}=-(\sqrt{3}/2)e_{33}^{\rm hex}$, which would imply that the value $e_{14}=-7.88\times10^4$ esu cm$^{-2}$, derived from parameters of Ref. 26, was underestimated by about 20%.

It can be seen from Table II that all nonvanishing elastic and piezoelectric constants of the hexagonal polytypes are very closely related to the corresponding values of the cubic one. Within our model, this can be attributed to the similarity of chemical bonding in their basic structural units, namely $\mathrm{SiC_4}$ (or $\mathrm{CSi_4}$) tetrahedra forming Si-C layers in the lattices. Theoretically, it is possible to consider the cubic SiC as the lattice having the $C_{3v}^1$ symmetry. But its piezoelastic properties can hardly be characterized as pseudohexagonal: tensor elements $C_{15}$ and $e_{22}$ intrinsic for the trigonal symmetry are too large (see Table II). This can be attributed to the different tetrahedron arrangement of the lattices in question, which dictates the difference in their symmetries and thus the different structures of the elastic and piezoelectric tensors.

From the theoretical side, in part this paper has been concerned with dressing up old ideas in new clothing. Really, the notion of chemical bonds as polarizable entities of largely covalent lattices was apparently presented in the early paper by Birman.[33] Several years later, Kleinman and Spitzer[29] employed the same idea when calculating the oscillator strengths of lattice vibrations, and underlined the chemical sense of the above parameter *c*. As a parallel to this, Tolpygo[14,15] has repeatedly claimed that the interatomic charge transfer could play an important role in the polarization mechanism of largely covalent crystals, and thus their lattice-dynamical model essentially had to be that of ions with variable charges. As concerns the VFF model, its status as the most natural description of interatomic forces in such compounds has been well known for years,[34] and the convenience of its application to the theory of homogeneous deformations has been emphasized in Ref. 36. However, although more than three active decades of lattice dynamics have passed since these topics had been discussed, the above ideas were never employed to silicon carbide.

To our belief, the main accomplishment of the present paper is to bring these ideas together in considering the elastic and piezoelectric properties jointly in the least complicated form. A point is the decomposition of the lattice polarization into purely electronic and purely ionic parts [Eq. (22)], which we perform by introducing the notion of the shape of the macroscopic homogeneous deformation. This differs from a conventional scheme[27,35] originating from the decomposition of macroscopic homogeneous deformations into their external and internal components. This scheme leads to Eq. (5) [or, in this particular case, to Eq. (21)], and implies that the second term in its right-hand side *by definition* tends to cancel the first one independent of chemical or structural peculiarities of the lattice. Thus it cannot tell us anything of the detailed nature of the phenomenon in question, and has mathematical rather than physical (and much less chemical) significance.

In contrast, the relative magnitudes and signs of two terms in the right-hand side of Eq. (22) visualize the roles of the two above mentioned mechanisms of lattice polarization. In particular, the variation of the sign of the $e_{14}$ value experimentally found in the series of sphalerite structures ranging from I-VII to III-V (see, e.g., Table I in Ref. 35) receives the following explanation.

Recall first that from the chemical standpoint, the cubic SiC seems to be the most covalent among sphalerite-like structures. However, the positive sign of parameter $c^0$ obtained in our study indicates the ionic character of the electronic redistribution in its lattice at distortions, which corresponds to a paper by Churcher, Kunc, and Heine.[16] This parameter should remain positive (or be equal to zero) for the other sphalerite-type compounds, since they are more ionic than silicon carbide.

Now let us consider a detailed mechanism of piezoelectricity in sphaleritelike lattices *within this model.* A positive ion has coordinates (000) and a negative one occupies $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. The $U_4$ strain decreases the angle between $Y$ and $Z$ axes (Fig. 2), and in the first instant (corresponding to an external part of the uniform strain[27]) this does not displace any ion in the $X$ direction. So the ionic component in the $e_{14}^0$ value [Eq. (19)] equals zero, and only the electronic one arises due to "instant" changes $L_{mi}$ of the bond lengths: an elongation of bonds 5-1, 5-2 and a shortening of bonds 5-3, 5-4. Consequently, the electron charge would flow to ion 5 in the former, and to atoms 3 and 4 in the latter, thus producing a negative polarization along $X$. So the $e_{14}^0$ value is negative. Besides, the stretching forces which arose in every bond would cause positive atoms in Fig. 2 to move upward and negative ones downward, thus producing a positive polarization (and minimizing the internal energy). At the same time, this would decrease the bond length changes from initial $L_{mi}$ to final (relaxed) $L_{mi}^*$ magnitudes and diminish the negative polarization.

Thus the piezoeffect consists of two competitive contributions—ionic (positive) and electronic (negative), which correspond to two terms in the right-hand side of Eq. (22). This means that the sign of the $e_{14}$ value would depend on the character of the electron bonding in the lattice. In particular, the predominance of the first (ionic) term in the case of largely ionic I-VII compounds would account for the positive sign of the $e_{14}$ value, measured for those compounds. On the other hand, the increase of the second term in the case of much more covalent III-V substances explains why this value is negative for most if not all these substances. Consequently, II-VI structures correspond to an intermediate case when both contributions can be mutually canceled, which can clarify the origin of a very small (almost null) piezoelectric effect, for example, in CdTe. Thus the negative sign of the piezoeffect in 3*C*-silicon carbide obtained in our calculations (and derived from parameters of Ref. 9), seems to be quite natural.

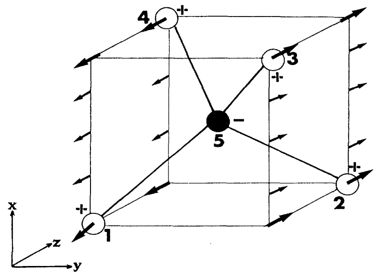

FIG. 2. Fragment of the sphalerite lattice containing one tetrahedron. The "instant" $U_4$ shear strain, shown schematically by arrows, does not displace atoms along the $X$ axis, but changes the interatomic bond lengths and valence angles thus producing forces acting on positive and negative atoms in opposite directions orthogonal to the $Z$-$Y$ plane.

By calling our approach to the lattice-dynamical treatment of SiC structures "molecular," we wished to emphasize the difference of VFF we used for those employed to sphalerite and wurzitelike structures in early works (see Ref. 34 and references therein). These works implied that the Coulomb interactions were extracted from the short-range force constants, i.e., that the parameters of the VFF described the non-Coulomb forces only. Consequently, this would lead to a conceptual problem of compatibility of the point-ion approximation with the essentially delocalized distribution of the valence electron cloud inside the chemical bonds in largely covalent lattices.[37] In contrast, the molecular VFF taken from the theory of molecular vibrations involves all types of interactions participating in interatomic bonding, thus necessarily including the Coulomb ones.

By using this approach we attempt to allow chemical bonds play the central role both in lattice mechanics and in the polarization effect. In spite of the neglect of electrostatic forces between distant atoms, which is an evident shortcoming of the model, the values of its parameters very frequently survive transplantation from molecules to solids. According to the results of the present work, silicon carbide belongs to this category, which encourages the further quantum-mechanical investigation of the related molecules and clusters.

## ACKNOWLEDGMENTS

A.P.M. would like to thank Professor B. Frit for his invitation to visit laboratory LMCTS, where the main results of this work were obtained. The authors would also like to express appreciation to S. de Barbuat and V. Bitther for their encouragement and help in preparing the paper.

---

[1] A. N. Lazarev and A. P. Mirgorodsky, Phys. Chem. Miner. **18**, 231 (1991).

[2] J. A. Wendel and W. A. Goddard III, J. Chem. Phys. **97**, 5048 (1992).

[3] K. B. Tolpygo, Fiz. Tverd. Tela (Leningrad) **2**, 2655 (1960) [Sov. Phys. Solid State **2**, 2367 (1961)].

[4] J. F. Vetelino and S. S. Mitra, Phys. Rev. **178**, 1349 (1969).

[5] C. Carabatos, D. Sc. thesis, Strasbourg, 1971.

[6] T. H. Singh, S. S. Kushwaha, and G. Singh, Solid State Commun. **13**, 1393 (1973).

[7] R. Banerjee and Y. P. Varshni, J. Phys. Soc. Jpn. **30**, 1015 (1971).

[8] K. Kunc, M. Balkanski, and M. A. Nusimovici, Phys. Status Solidi B **72**, 229 (1975).

[9] C. Cheng, K. Kunc, and V. Heine, Phys. Rev. B **39**, 5892 (1989).

[10] Lyle Patrick, Phys. Rev. **167**, 809 (1968).

[11] D. W. Feldman, J. H. Parker, Jr., W. J. Choyke, and Lyle Patrick, Phys. Rev. **170**, 698 (1968).

[12] D. W. Feldman, J. H. Parker, Jr., W. J. Choyke, and Lyle Patrick, Phys. Rev. **173**, 787 (1968).

[13] D. Olego and M. Cardona, Phys. Rev. B **25**, 1151 (1982).

[14] K. B. Tolpygo, Usp. Fiz. Nauk **74**, 2969 (1961).

[15] K. B. Tolpygo, in *Chemical Bonding in Semi-conductor and Semi-metal Crystals* (Nauka i Tekhnika, Minsk, 1973) (in Russian), p. 196.

[16] N. Churcher, K. Kunc, and V. Heine, J. Phys. C **19**, 4413 (1986).

[17] W. R. Lambrecht, B. Segal, M. Methfessel, and M. van Schilgaarde, Phys. Rev. B **44**, 3685 (1991).

[18] G. Arlt and G. R. Schodder, J. Acoust. Soc. Am. **37**, 384 (1965).

[19] S. Karmann, R. Helbig, and R. A. Stein, J. Appl. Phys. **66**, 3922 (1989).

[20] D. H. Lee and J. D. Joannopoulos, Phys. Rev. Lett. **48**, 1846 (1982).

[21] G. A. Slack, J. Appl. Phys. **35**, 3960 (1964).

[22] M. Miura, H. Murata, Y. Shiro, and K. Lishi, J. Phys. Chem. Solids **42**, 931 (1981).

[23] J. Tersoff, Phys. Rev. B **39**, 5566 (1989).

[24] Z. C. Feng, W. J. Choyke, and J. A. Powell, J. Appl. Phys. **64**, 6827 (1988).

[25] H. J. Van Daal, Philips Res. Rep. (Suppl.) **3**, 76 (1965).

[26] R. Helbig, S. Karmann, and R. A. Stein, The Electrochemical Society, Conf. Report 89 (Hollywood, Florida, 1989), p. 718.

[27] M. Born and Huang Kun, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).

[28] M. B. Smirnov and A. P. Mirgorodsky, Solid State Commun. **70**, 915 (1989).

[29] D. A. Kleinman and W. G. Spitzer, Phys. Rev. **125**, 16 (1962).

[30] I. S. Ignatyev and T. F. Tenisheva, *Vibrational Spectra and Electronic Structures of Molecules with Carbon-Oxygen and Silicon-Oxygen Bonds* (Nauka, Leningrad, 1991) (in Russian).

[31] H. Jaffe, Phys. Rev. **66**, 357 (1944).

[32] G. Arlt and P. Quadflieg, Phys. Status Solidi **25**, 323 (1968).

[33] J. L. Birman, Phys. Rev. **111**, 1510 (1958).

[34] R. Martin, Phys. Rev. B **1**, 4005 (1970).

[35] R. Martin, Phys. Rev. B **5**, 1607 (1972).

[36] M. Lax, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, Oxford, 1965), p. 583.

[37] A. N. Lazarev, A. P. Mirgorodsky, and M. B. Smirnov, Solid State Commun. **58**, 371 (1986).