PHYSICAL REVIEW B VOLUME 40, NUMBER 8 15 SEPTEMBER 1989-I

Anharmonic elastic and phonon properties of Si

David Vanderbilt
Department of Physics, Harvard University, Cambridge, Massachusetts 02138

S. H. Taole*
Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

Shobhana Narasimhan
Department of Physics, Harvard University, Cambridge, Massachusetts 02138

(Received 20 March 1989; revised manuscript received 25 July 1989)

A unified framework is suggested for the discussion of anharmonic phonon coupling constants and anharmonic elastic constants in diamond-structure materials. A summary is given, within this framework, of those anharmonic constants which have previously been determined experimentally or theoretically for silicon. New local-density total-energy calculations for X-point phonons in Si are used to add to this database of known anharmonic constants. It is proposed that empirical models for interatomic potentials should be constrained to fit this database. A generalized Keating model which has been fitted in this way, with two- and three-body couplings of third and fourth order, is presented. It can be used to calculate arbitrary anharmonic phonon couplings through fourth order.

I. INTRODUCTION

Recent years have seen a revival of interest in the development of empirical interatomic potentials to describe structural energies in covalently bonded crystals. Traditionally, these models have usually been obtained by fitting to experimental phonon spectra. Examples include Keating-type models[1,2] and the closely related valence-force-field models,[3-6] bond-charge models,[7,8] and shell models.[9] However, these models are only accurate when the displacements from equilibrium are small enough for the harmonic approximation to hold. Furthermore, they are usually ill defined for radical distortions, such as those involved in defect formation or melting, where the "nearest neighbors" are not easily identified. Many of the models proposed recently, on the other hand, are sufficiently general to handle such cases.[10-14] They are usually fitted to calculated energies for a variety of hypothetical crystal and defect structures, and usually do a poor job of describing infinitesimal deviations from equilibrium. For example, phonon frequencies and elastic constants are often in error by a factor of 2 or more.[15]

Between the extremes of "infinitesimal" and "radical" structural changes is an intermediate regime of "moderate" structural distortions, which lies marginally beyond the domain of applicability of the harmonic approximation. This is the anharmonic regime which can be characterized by third-, fourth-, and higher-order anharmonic terms in the Taylor expansion of the energy. While an extensive database has been established to describe the energies in the harmonic and radical regimes, the anharmonic regime remains poorly characterized. Previous attempts to extend some of the harmonic models into the anharmonic regime[16-18] have suffered from this lack of information, typically containing only one or a few anharmonic parameters fitted to a correspondingly small number of experimental results. Eventually it may be possible to formulate empirical interatomic-potential models which are able to describe both infinitesimal and radical structural changes accurately. If so, it seems likely that such models would also provide a good description of the energies in the intermediate anharmonic regime. However, such models are not currently available.

Our purpose here is twofold. First, we summarize what is known experimentally and theoretically about this intermediate anharmonic regime for the case of silicon. We also present the results of new local-density total-energy calculations for X-point phonons, which add to this database of known anharmonic constants. We argue that this database should be used as a further constraint in developing and fitting model empirical interatomic potentials. Second, we propose a modified Keating-type model which can describe both the harmonic and anharmonic sectors accurately, up to fourth order in the anharmonic expansion. This model should prove extremely useful in the calculation of anharmonic effects in Si, such as phonon lifetimes and frequency shifts. Of course, it is not expected to describe radical structural distortions such as those involving coordination changes. However, it is hoped that this incremental step beyond the harmonic regime will contribute to the eventual formulation of a universally applicable model.

In Sec. II we introduce a unified framework for the discussion of anharmonic elastic constants and zone-center phonon coupling constants in diamond-structure materials, and review the anharmonic constants which have previously been determined either experimentally or theoretically. Section III summarizes the harmonic force constants for phonons at high-symmetry points in the Brillouin zone, while in Sec. IV we present the results of our new frozen-phonon calculations for phonons at the X point of the Brillouin zone. In Sec. V, we propose a new Keating-type force-constant model which has been fitted to the database of anharmonic coupling constants discussed above. Finally, Sec. VI contains a summary and discussion.

II. ZONE-CENTER COUPLING CONSTANTS

We propose here a unified framework for the discussion of the anharmonic elastic constants and the Brillouin-zone–center phonon coupling constants in diamond-structure materials. Actually the elastic constants are also zone-center phonon coupling constants, in the sense that strains may be considered to be acoustic phonons in the long-wavelength (zone-center) limit. We thus focus on the structural degrees of freedom corresponding to long-wavelength acoustic phonons (i.e., uniform strains) and long-wavelength optical phonons (i.e., rigid relative displacement of the two sublattices, sometimes called "internal strains"). The energy of the crystal is Taylor expanded in these two quantities, retaining all terms up to combined fourth order. Specifically, the coordinates of the atoms in the mth unit cell of the distorted crystal are given by a uniform strain ϵ followed by a sublattice shift $\mathbf{u}$,

$$\begin{aligned} \mathbf{x}_{1m} &= (1+\epsilon)\mathbf{a}_{1m} - \mathbf{u} , \\ \mathbf{x}_{2m} &= (1+\epsilon)\mathbf{a}_{2m} + \mathbf{u} , \end{aligned} \tag{2.1}$$

acting on the equilibrium atom positions

$$\begin{aligned} \mathbf{a}_{1m} &= \tau_1 + \mathbf{R}_m , \\ \mathbf{a}_{2m} &= \tau_2 + \mathbf{R}_m . \end{aligned} \tag{2.2}$$

We use the experimental lattice constant $a = 5.43$ Å and take $\tau_2 - \tau_1 = (a/4)(1,1,1)$ for the reference configuration in Eq. (2.2). Following previous authors,[19,20] we use the Lagrangian strain

$$\eta = \epsilon + \tfrac{1}{2}\epsilon^2 \tag{2.3}$$

and go over to the Voigt notation $\epsilon_1 = \epsilon_{xx}$, $\epsilon_4 = 2\epsilon_{yz}$, $\eta_1 = \eta_{xx}$, $\eta_4 = 2\eta_{yz}$, etc. Then the total energy per two-atom unit cell is written in terms of the nine variables

$$E = E(\eta_1, \eta_2, \eta_3, \eta_4, \eta_5, \eta_6, u_x, u_y, u_z) . \tag{2.4}$$

A Taylor expansion is then carried out about $\eta_i = 0$, $u_\alpha = 0$:

$$E = E^{(0)} + E^{(2)} + E^{(3)} + E^{(4)} + \cdots . \tag{2.5}$$

Here, $E^{(2)}$ is the harmonic part of the distortion energy per cell, and $E^{(3)}$ and $E^{(4)}$ are the third- and fourth-order anharmonic contributions.

It is convenient to separate the contributions at each order according to the powers of the η_i ("acoustic" branch) and of the u_α ("optical" branch) variables

$$E^{(2)} = E_{\mathrm{AA}} + E_{\mathrm{AO}} + E_{\mathrm{OO}} , \tag{2.6a}$$

$$E^{(3)} = E_{\mathrm{AAA}} + E_{\mathrm{AAO}} + E_{\mathrm{AOO}} + E_{\mathrm{OOO}} , \tag{2.6b}$$

$$E^{(4)} = E_{\mathrm{AAAA}} + E_{\mathrm{AAAO}} + E_{\mathrm{AAOO}} + E_{\mathrm{AOOO}} + E_{\mathrm{OOOO}} . \tag{2.6c}$$

For example, at harmonic order we have

$$\begin{aligned} E_{\mathrm{AA}} = {} & \tfrac{1}{2}B_{11}(\eta_1^2 + \eta_2^2 + \eta_3^2) + B_{12}(\eta_1\eta_2 + \eta_1\eta_3 + \eta_2\eta_3) \\ & + \tfrac{1}{2}B_{44}(\eta_4^2 + \eta_5^2 + \eta_6^2) , \end{aligned} \tag{2.7}$$

$$E_{\mathrm{AO}} = B_{4x}(\eta_4 u_x + \eta_5 u_y + \eta_6 u_z) , \tag{2.8}$$

$$E_{\mathrm{OO}} = \tfrac{1}{2}B_{xx}(u_x^2 + u_y^2 + u_z^2) . \tag{2.9}$$

Note that B_{xx} is related to the zone-center optical-phonon frequency by $2M\omega_{\mathrm{LTO}}^2(\Gamma) = B_{xx}$, where M is the Si mass. The terms which appear at third order, in Eq. (2.6b), are

$$\begin{aligned} E_{\mathrm{AAA}} = {} & \tfrac{1}{6}B_{111}(\eta_1^3 + \eta_2^3 + \eta_3^3) + \tfrac{1}{2}B_{112}[\eta_1^2(\eta_2 + \eta_3) + \eta_2^2(\eta_1 + \eta_3) + \eta_3^2(\eta_1 + \eta_2)] \\ & + B_{123}\eta_1\eta_2\eta_3 + \tfrac{1}{2}B_{144}(\eta_1\eta_4^2 + \eta_2\eta_5^2 + \eta_3\eta_6^2) \\ & + \tfrac{1}{2}B_{155}[\eta_1(\eta_5^2 + \eta_6^2) + \eta_2(\eta_4^2 + \eta_6^2) + \eta_3(\eta_4^2 + \eta_5^2)] + B_{456}\eta_4\eta_5\eta_6 , \end{aligned} \tag{2.10}$$

$$\begin{aligned} E_{\mathrm{AAO}} = {} & B_{14x}(\eta_1\eta_4 u_x + \eta_2\eta_5 u_y + \eta_3\eta_6 u_z) + B_{45z}(\eta_4\eta_5 u_z + \eta_4 u_y \eta_6 + u_x \eta_5\eta_6) \\ & + B_{15y}[(\eta_1 + \eta_2)\eta_6 u_z + (\eta_1 + \eta_3)\eta_5 u_y + (\eta_2 + \eta_3)\eta_4 u_x] , \end{aligned} \tag{2.11}$$

$$\begin{aligned} E_{\mathrm{AOO}} = {} & \tfrac{1}{2}B_{1xx}(\eta_1 u_x^2 + \eta_2 u_y^2 + \eta_3 u_z^2) + B_{4yz}(\eta_4 u_y u_z + \eta_5 u_x u_z + \eta_6 u_x u_y) \\ & + \tfrac{1}{2}B_{1yy}[(\eta_1 + \eta_3)u_y^2 + (\eta_1 + \eta_2)u_z^2 + (\eta_2 + \eta_3)u_x^2] , \end{aligned} \tag{2.12}$$

$$E_{\mathrm{OOO}} = B_{xyz} u_x u_y u_z . \tag{2.13}$$

The expressions for the fourth-order terms of Eq. (2.6c) are given in the Appendix. By convention we include in each prefactor a factor $1/n!$ for each variable which appears to the nth power. Terms which do not appear are zero by symmetry, as discussed in the Appendix.

It is important to note that the strains above are *not* the physical strains that enter the usual definitions of the elastic constants, because they are *uniform* strains which do not include any additional relative displacement of the two sublattices. Let $\tilde{E}(\eta_1,\eta_2,\eta_3,\eta_4,\eta_5,\eta_6)$ be the energy minimized with respect to the internal strain variable $\mathbf{u}$ at a given strain $\boldsymbol{\eta}$. It can be expanded as

$$\tilde{E}=\tilde{E}_{\mathrm{AA}}+\tilde{E}_{\mathrm{AAA}}+\tilde{E}_{\mathrm{AAAA}}+\cdots , \tag{2.14}$$

where, for example,

$$\tilde{E}_{\mathrm{AA}}=\tfrac{1}{2}C_{11}(\eta_1^2+\eta_2^2+\eta_3^2)+C_{12}(\eta_1\eta_2+\eta_1\eta_3+\eta_2\eta_3)+\tfrac{1}{2}C_{44}(\eta_4^2+\eta_5^2+\eta_6^2) . \tag{2.15}$$

The coefficients C that now appear are the physical elastic constants, which are given in terms of the "bare" elastic constants B by

$$C_{11}=B_{11} , \tag{2.16a}$$

$$C_{12}=B_{12} , \tag{2.16b}$$

$$C_{44}=B_{44}-B_{4x}^2/B_{xx} . \tag{2.16c}$$

The last can be rewritten

$$C_{44}=B_{44}+B_{4x}\Gamma_{4x} , \tag{2.17}$$

where

$$\Gamma_{4x}=-B_{4x}/B_{xx} . \tag{2.18}$$

Note that $\Gamma_{4x}=-\xi a/8$, where ξ is the "internal-strain parameter" introduced by Kleinman,[21] and a is the lattice constant. At third order, C_{111}, C_{112}, and C_{123} are identical to B_{111}, B_{112}, and B_{123}, respectively, and, using the above notation,

$$C_{144}=B_{144}+2B_{14x}\Gamma_{4x}+B_{1xx}\Gamma_{4x}^2 , \tag{2.19a}$$

$$C_{155}=B_{155}+2B_{15y}\Gamma_{4x}+B_{1yy}\Gamma_{4x}^2 , \tag{2.19b}$$

$$C_{456}=B_{456}+3B_{45z}\Gamma_{4x}+B_{xyz}\Gamma_{4x}^3 . \tag{2.19c}$$

The relation between the physical and bare fourth-order elastic constants is even more complicated, involving several of the coefficients from Eqs. (2.11) and (2.12) as well as Γ_{4x}, reflecting in some sense the dependence of ξ itself upon strain.

The emphasis here is on the bare coefficients because they are simpler to treat theoretically. For example, suppose one wants to use total-energy calculations on a series of strained structures to obtain the elastic constants. To obtain the bare constants B only one calculation is needed per strain tensor considered, while for the physical constant C several are necessary in order to relax the structure and eliminate the forces. The use of bare coefficients is even more important when fitting empirical interatomic potentials, because such model potentials are typically given by a sum over terms (e.g., two body, three body; first neighbor, second neighbor) with a prefactor for each term. The bare coefficients are linear functions of these prefactors, while the physical, dressed coefficients are not, and therefore it is much simpler to fit to the bare coefficients. Thus, it is suggested that the bare coefficients B be obtained from realistic calculations (e.g., local-density total-energy calculations) or from experiment, and be used as the input for the fitting of empirical interatomic potentials. That is the approach taken here.

We now review some previous experimental and theoretical work which provides values for some of the coefficients B appearing in these equations. Those constants which we consider "known" we collect as a "database" which should be useful for fitting empirical interatomic potentials; this "database" is summarized in the column labeled "Target" in Table VII in Sec. V. For consistency, we will express all of these constants in units of $\mathrm{eV}/\mathrm{\AA}^l$, where l is the number of x, y, and z subscripts of B. Thus, elastic constants (e.g., B_{111}) here have units of energy, not energy per volume, as is more conventional. In general, experimental input is used when it is available and reliable. Otherwise theoretical input, which comes from total-energy calculations carried out within the Hohenberg-Kohn-Sham local-density approximation (LDA), is used.

The harmonic elastic constants are taken from the work of McSkimin and Andreatch;[22] they obtain $C_{11}=41.90$ eV, $C_{12}=16.23$ eV, and $C_{44}=20.07$ eV. The constant B_{xx} may, with caution, be derived from the zone-center optical-phonon frequency, giving $B_{xx}=55.44$ eV (see Sec. III). The internal-strain parameter has been determined experimentally by Cousins *et al.*[23] to be $\xi=0.54\pm0.04$, and theoretically from the LDA calculations of Nielsen and Martin[20] to be $\xi=0.53$. We have adopted the latter value. This leads to $B_{4x}=19.94$ eV/Å and via Eq. (2.16c) to $B_{44}=27.24$ eV.

The third-order anharmonic elastic constants are taken from ultrasonic propagation measurements of McSkimin and Andreatch.[24] Because of the complications of internal-strain relaxation, Eqs. (2.19a)–(2.19c), we only include in our "known database" the bare constants $B_{111}=C_{111}=-206$ eV, $B_{112}=C_{112}=-113$ eV, and $B_{123}=C_{123}=-16$ eV. Nielsen and Martin have calculated[20] $C_{111}=-187$ eV, $C_{112}=-120$ eV, and $C_{123}\approx0$ eV, in good agreement with the experimental values used here. They also obtain $C_{1111}\approx0$ eV and $C_{1112}\approx800$ eV (which are equal to B_{1111} and B_{1112}, respectively). As experimental information on the fourth-order elastic constants appears to be unavailable, these values are adopted here.

The constants B_{1xx}, B_{1yy}, and B_{4yz} are related to the strain derivatives of the zone-center optical-phonon frequencies. Chandrasekhar, Renucci, and Cardona[25] have measured these Raman shifts, and express their results in terms of parameters p, q, and r defined in their Appendix B and related to our parameters via

$$\frac{B_{1xx}}{B_{xx}}=\frac{p}{\omega_0^2} , \tag{2.20a}$$

$$\frac{B_{1yy}}{B_{xx}}=\frac{q}{\omega_0^2} , \tag{2.20b}$$

$$\frac{C_{4yz}}{B_{xx}}=\frac{r}{\omega_0^2} , \tag{2.20c}$$

where internal-strain considerations lead to

$$C_{4yz}=B_{4yz}+\Gamma_{4x}B_{xyz}\ . \tag{2.21}$$

The values they report lead to $B_{1xx}=-80$ eV/Å^2, $B_{1yy}=-106$ eV/Å^2, and $C_{4yz}=-33$ eV/Å^2, which we adopt here. These are in good agreement with the theoretical values calculated by Nielsen and Martin,[20] which (after conversion from their s_{100}, s_{111}, and γ) are $B_{1xx}=-90$ eV/Å^2, $B_{1yy}=-105$ eV/Å^2, and $C_{4yz}=-33$ eV/Å^2. The hydrostatic shift is often expressed in terms of the dimensionless constant $\gamma=-(p+2q)/\omega_0^2$, for which Chandrasekhar *et al.* obtain $\gamma=0.89$, in reasonable agreement with other experiment[26] ($\gamma=0.98$) and theory[27,20] ($\gamma=0.92$ and 0.9, respectively). The value for the bare B_{4yz}, -137 eV/Å^2, is obtained from Eq. (2.21).

Finally, the zone-center optical-phonon coupling constants have been obtained from LDA total-energy calculations of Vanderbilt, Louie, and Cohen.[28] The γ, α, and β of their notation are related to our parameters B_{xyz}, B_{xxxx}, and B_{xxyy} via

$$B_{xyz}=6\gamma,\quad B_{xxxx}=24\alpha,\quad B_{xxyy}=24\beta\ , \tag{2.22}$$

and we obtain the values $B_{xyz}=-290$ eV/Å^3, $B_{xxxx}=-1250$ eV/Å^4, and $B_{xxyy}=410$ eV/Å^4.

III. OTHER HARMONIC COUPLING CONSTANTS

In the preceding section we discussed the zone-center optical and acoustic harmonic coupling constants B_{xx}, B_{4x}, B_{11}, B_{12}, and B_{44}. Before going on to consider other anharmonic coupling constants, we now briefly review the remainder of the harmonic sector, i.e., the couplings for phonons at k points other than the Γ point.

Inelastic-neutron-scattering experiments have been used to determine the phonon dispersion relations for Si throughout the Brillouin zone. These measured phonon frequencies are frequently used to derive the harmonic coupling constants, but this procedure is only valid if third- and higher-order anharmonic contributions to the phonon frequencies can be neglected. Estimates for the zone-center optical phonons in Si indicate[28] that the bare (harmonic) frequencies differ from the renormalized (physical) frequencies by about 1%. Thus, we have provisionally chosen to follow the common practice, and assume that the anharmonic corrections are negligible. However, it is possible that the anharmonic frequency shifts may turn out to be proportionally much larger for other phonons, such as the soft TA phonons at the X point. It should be possible to calculate these frequency shifts using the model proposed in Sec. V; work in this direction is in progress. If some of the anharmonic corrections do turn out to be important, then it will be necessary to refine the harmonic coupling constants listed below.

With the above proviso, we list in Table I the harmonic coupling constants for phonons at the Γ, X, and L high-symmetry points in the Brillouin zone, as obtained from the neutron data of Dolling.[29] [Recall that the constant $2M\omega_{\rm LTO}^2(\Gamma)=B_{xx}$ of Sec. II.] We have found that this is a large enough sampling of the Brillouin zone for fitting a force-constant model of the type used in Sec. V.

TABLE I. Harmonic force constants for high-symmetry points in the Brillouin zone as determined from inelastic-neutron-scattering data by Dolling (Ref. 29).

k point	Branch(es)	$M\omega^2$ (eV/Å^2)
Γ	LTO	27.715
X	TA	2.317
X	LAO	17.442
X	TO	22.203
L	TA	1.352
L	LA	14.804
L	LO	18.244
L	TO	24.764

IV. CALCULATIONS OF ANHARMONIC COUPLINGS FOR X-POINT PHONONS

In order to enlarge the database of known anharmonic coupling constants for Si, we have carried out frozen-phonon LDA calculations on the four-atom unit cell shown in Fig. 1. Note that the coordinate system in Fig. 1 has been rotated by 45° about the $\hat{\mathbf{z}}$ axis relative to the coordinate system of Sec. II. In this section, x, y, and z refer to these new coordinates, and the symbol E refers to an energy *per four-atom unit cell.* The accessible "zone-center phonons" of this enlarged cell map either to the Γ point or to the X point $(2\pi/a)\hat{\mathbf{z}}$ of the original Brillouin zone. Thus, these frozen-phonon calculations allow us to obtain anharmonic couplings involving both Γ- and X-point phonons.

The energy E can be expanded in terms of the displacement vectors $\mathbf{u}_1$, $\mathbf{u}_2$, $\mathbf{u}_3$, and $\mathbf{u}_4$ of the atoms shown in Fig. 1. However, the three degrees of freedom corresponding to an overall rigid translation of the cell (the acoustic branches at Γ) do not enter, so it is convenient to write E in terms of the remaining nine degrees of freedom $\mathbf{u}$, $\mathbf{v}$, and $\mathbf{w}$ defined by

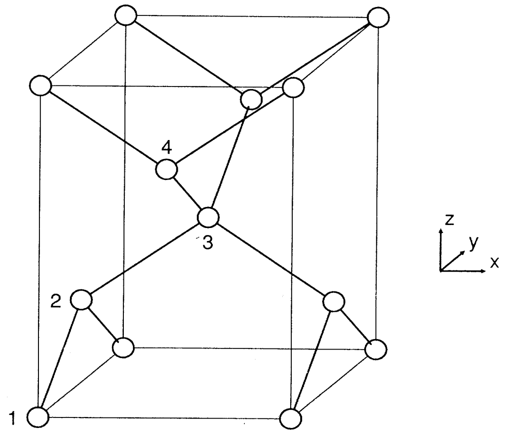

FIG. 1. Geometry of four-atom unit cell used for X-point phonons.

$$\begin{aligned}\mathbf{u}_1&=-\mathbf{u}+\mathbf{v}+\mathbf{w}\ ,\\ \mathbf{u}_2&=+\mathbf{u}+\mathbf{v}-\mathbf{w}\ ,\\ \mathbf{u}_3&=-\mathbf{u}-\mathbf{v}-\mathbf{w}\ ,\\ \mathbf{u}_4&=+\mathbf{u}-\mathbf{v}+\mathbf{w}\ .\end{aligned}\tag{4.1}$$

($\mathbf{u}$ describes the three optical-phonon branches at Γ, while $\mathbf{v}$ and $\mathbf{w}$ describe the six phonon branches at point X.) Furthermore, most of the terms in the expansion of E may be eliminated by the use of symmetry, since E must be invariant under any symmetry operation of the crystal. The only symmetry operations which are useful in this way are those which map the X point along $\hat{\mathbf{z}}$ onto itself; this excludes some operations, such as threefold rotations, from our considerations. The remaining symmetry operations are generated by mirror operations M_x and M_y in the $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ directions, nonsymmorphic inversion I (e.g., atom 1→2, 2→1, 3→4, 4→3), translation T by the original primitive lattice vector (e.g., atom 1→3, 2→4, 3→1, 4→2), and a (nonsymmorphic) 90° rotation C_4^z about $\hat{\mathbf{z}}$ (e.g., atom 1→2, 2→3, 3→4, 4→1). The transformation properties of the nine quantities defined in Eq. (4.1) under these symmetry generators are given in Table II. Any term in the expansion of the energy E must be invariant under each of these generators. Note that invariance under T requires that the X-point variables $(v_x, \ldots, w_z)$ must occur an even number of times in any term, reflecting wave-vector conservation.

TABLE II. Action of the symmetry transformations of the X-point supercell of Fig. 1 upon the structural variables of Eq. (4.1).

Variable	M_x	M_y	I	T	C_4^z
u_x	$-u_x$	u_x	u_x	u_x	$-u_y$
u_y	u_y	$-u_y$	u_y	u_y	u_x
u_z	u_z	u_z	u_z	u_z	u_z
v_x	$-v_x$	v_x	$-v_x$	$-v_x$	$-w_y$
v_y	v_y	$-v_y$	$-v_y$	$-v_y$	w_x
v_z	v_z	v_z	$-v_z$	$-v_z$	$-w_z$
w_x	$-w_x$	w_x	w_x	$-w_x$	v_y
w_y	w_y	$-w_y$	w_y	$-w_y$	$-v_x$
w_z	w_z	w_z	w_z	$-w_z$	v_z

A comprehensive search for invariant terms through fourth anharmonic order results in the following expressions for the expansion of the energy. At harmonic order we can write

$$E^{(2)}=E_{\Gamma\Gamma}+E_{XX}\ ,\tag{4.2}$$

where $E_{\Gamma\Gamma}$ is identically equal to $2E_{\mathrm{OO}}$ of Eq. (2.9) (involving only zone-center optical phonons), and

$$E_{XX}=I_{\underline{aa}}\theta_{\underline{aa}}+I_{\underline{bb}}\theta_{\underline{bb}}+I_{\underline{cc}}\theta_{\underline{cc}}\ ,\tag{4.3}$$

with

$$\begin{aligned}\theta_{\underline{aa}}&=v_x^2+w_y^2\ ,\\ \theta_{\underline{bb}}&=v_y^2+w_x^2\ ,\\ \theta_{\underline{cc}}&=v_z^2+w_z^2\ .\end{aligned}\tag{4.4}$$

[The subscript notation employs x, y, z, a, b, c, d, e, and f to denote a factor u_x, u_y, u_z, v_x, v_y, v_z, w_x, w_y, and w_z, respectively, and an underline (bar) to denote an even (odd) linear combination with respect to the interchange $u_x\leftrightarrow u_y$, $v_x\leftrightarrow w_y$, $v_y\leftrightarrow w_x$, $v_z\leftrightarrow w_z$.] The three coefficients $I_{\underline{aa}}$, $I_{\underline{bb}}$, and $I_{\underline{cc}}$ are identical to $2M\omega_{\mathrm{TO}}^2(X)$, $2M\omega_{\mathrm{TA}}^2(X)$, and $2M\omega_{\mathrm{LAO}}^2(X)$ of Sec. III, respectively. At third order we obtain the anharmonic terms

$$E^{(3)}=E_{\Gamma\Gamma\Gamma}+E_{\Gamma XX}\ ,\tag{4.5}$$

where $E_{\Gamma\Gamma\Gamma}=2E_{\mathrm{OOO}}$ of Eq. (2.13), and

$$\begin{aligned}E_{\Gamma XX}={}&I_{z\overline{aa}}u_z\theta_{\overline{aa}}+I_{z\overline{bb}}u_z\theta_{\overline{bb}}+I_{z\overline{cc}}u_z\theta_{\overline{cc}}\\ &+I_{\overline{xac}}\theta_{\overline{xac}}+I_{\overline{ybc}}\theta_{\overline{ybc}}\end{aligned}\tag{4.6}$$

with

$$\begin{aligned}\theta_{\overline{aa}}&=v_x^2-w_y^2\ ,\\ \theta_{\overline{bb}}&=v_y^2-w_x^2\ ,\\ \theta_{\overline{cc}}&=v_z^2-w_z^2\ ,\\ \theta_{\overline{xac}}&=u_xv_xv_z-u_yw_yw_z\ ,\\ \theta_{\overline{ybc}}&=u_yv_yv_z-u_xw_xw_z\ .\end{aligned}\tag{4.7}$$

Finally, at fourth order

$$E^{(4)}=E_{\Gamma\Gamma\Gamma\Gamma}+E_{\Gamma\Gamma XX}+E_{XXXX}\ ,\tag{4.8}$$

where $E_{\Gamma\Gamma\Gamma\Gamma}=2E_{\mathrm{OOOO}}$ of the Appendix,

$$\begin{aligned}E_{\Gamma\Gamma XX}={}&\tfrac{1}{2}I_{zz\underline{aa}}u_z^2\theta_{\underline{aa}}+\tfrac{1}{2}I_{zz\underline{bb}}u_z^2\theta_{\underline{bb}}+\tfrac{1}{2}I_{zz\underline{cc}}u_z^2\theta_{\underline{cc}}+I_{\underline{xx}\,\underline{aa}}\theta_{\underline{xx}}\theta_{\underline{aa}}+I_{\underline{xx}\,\underline{bb}}\theta_{\underline{xx}}\theta_{\underline{bb}}\\ &+I_{\underline{xx}\,\underline{cc}}\theta_{\underline{xx}}\theta_{\underline{cc}}+I_{\overline{xx}\,\overline{aa}}\theta_{\overline{xx}}\theta_{\overline{aa}}+I_{\overline{xx}\,\overline{bb}}\theta_{\overline{xx}}\theta_{\overline{bb}}+I_{\overline{xx}\,\overline{cc}}\theta_{\overline{xx}}\theta_{\overline{cc}}\\ &+I_{xy\underline{xy}}u_xu_y\theta_{\underline{xy}}+I_{z\underline{xac}}u_z\theta_{\underline{xac}}+I_{z\underline{ybc}}u_z\theta_{\underline{ybc}}\end{aligned}\tag{4.9}$$

and

$$\begin{aligned}E_{XXXX}={}&\tfrac{1}{2}I_{\underline{aa}\,\underline{aa}}\theta_{\underline{aa}}^2+\tfrac{1}{2}I_{\underline{bb}\,\underline{bb}}\theta_{\underline{bb}}^2+\tfrac{1}{2}I_{\underline{cc}\,\underline{cc}}\theta_{\underline{cc}}^2+I_{\underline{aa}\,\underline{bb}}\theta_{\underline{aa}}\theta_{\underline{bb}}+I_{\underline{aa}\,\underline{cc}}\theta_{\underline{aa}}\theta_{\underline{cc}}+I_{\underline{bb}\,\underline{cc}}\theta_{\underline{bb}}\theta_{\underline{cc}}\\ &+\tfrac{1}{2}I_{\overline{aa}\,\overline{aa}}\theta_{\overline{aa}}^2+\tfrac{1}{2}I_{\overline{bb}\,\overline{bb}}\theta_{\overline{bb}}^2+\tfrac{1}{2}I_{\overline{cc}\,\overline{cc}}\theta_{\overline{cc}}^2+I_{\overline{aa}\,\overline{bb}}\theta_{\overline{aa}}\theta_{\overline{bb}}+I_{\overline{aa}\,\overline{cc}}\theta_{\overline{aa}}\theta_{\overline{cc}}\\ &+I_{\overline{bb}\,\overline{cc}}\theta_{\overline{bb}}\theta_{\overline{cc}}+I_{abde}v_xv_yw_xw_y+I_{cf\underline{be}}v_zw_z\theta_{\underline{be}}\ .\end{aligned}\tag{4.10}$$

The θ's are again defined using the conventions given following Eq. (4.4).

In summary, we see that the additional degrees of freedom inherent in the four-atom unit cell allow for the definition of five new third-order anharmonic constants ($I_{z\overline{aa}}$, $I_{z\overline{bb}}$, $I_{z\overline{cc}}$, $I_{\overline{xac}}$, and $I_{\overline{ybc}}$) and 26 new fourth-order constants.

We have carried out local-density[30] pseudopotential calculations of forces and total energies in order to determine three of the third-order constants and five fourth-order constants. The calculations are carried out using norm-conserving pseudopotentials[31] and Wigner exchange correlation[32] with plane waves up to 14 Ry included exactly. We considered five frozen-phonon modes given by (i) $\mathbf{u}=0$, $\mathbf{v}=-\mathbf{w}=t\hat{\mathbf{z}}/\sqrt{2}$; (ii) $\mathbf{u}=\mathbf{w}=0$, $\mathbf{v}=t\hat{\mathbf{z}}$; (iii) $\mathbf{u}=\mathbf{v}=0$, $\mathbf{w}=t\hat{\mathbf{x}}$; (iv) $\mathbf{u}=\mathbf{w}=0$, $\mathbf{v}=t\hat{\mathbf{x}}$; (v) $\mathbf{w}=0$, $-\mathbf{u}=\mathbf{v}=t\hat{\mathbf{z}}/\sqrt{2}$. Modes (i) and (ii) correspond to the two degenerate longitudinal normal modes at point X, (iii) and (iv) correspond to the TA and TO normal modes at point X, respectively, and (v) is a mixed mode having both Γ and X character. For each case, we have calculated forces (more specifically, the quantity $\partial E/\partial u_z$) and total energies for $t=0$, ± 0.04, ± 0.08, and ± 0.12 Å using a set of four k points in the irreducible Brillouin zone. From Eq. (4.6) above, it is easy to show that the leading contributions to the quantity $\partial E/\partial u_z$ are given by $I_{z\overline{cc}}t^2$, $-I_{z\overline{bb}}t^2$, and $I_{z\overline{aa}}t^2$ for modes (ii), (iii), and (iv), respectively. A polynomial fit to the calculated forces then yields the three third-order couplings to be $I_{z\overline{cc}}=46.84$ eV/Å^3, $I_{z\overline{bb}}=-49.12$ eV/Å^3, and $I_{z\overline{aa}}=315.20$ eV/Å^3. In addition, five fourth-order couplings were determined by extracting the fourth derivative $\partial^4 E/\partial^4 t$ from a polynomial fit to the total energies for each of the cases (i)–(v). From Eqs. (4.9) and (4.10), these fourth derivates are, respectively, $12I_{\underline{cc}\,\underline{cc}}$, $12K_{cc}$, $12K_{bb}$, $12K_{aa}$, and $24K_{zc}$, where

$$\begin{aligned} K_{cc}&=I_{\underline{cc}\,\underline{cc}}+I_{\overline{cc}\,\overline{cc}} , \\ K_{bb}&=I_{\underline{bb}\,\underline{bb}}+I_{\overline{bb}\,\overline{bb}} , \\ K_{aa}&=I_{\underline{aa}\,\underline{aa}}+I_{\overline{aa}\,\overline{aa}} , \\ K_{zc}&=\tfrac{1}{96}I_{zzzz}+\tfrac{1}{8}I_{zz\underline{cc}}+\tfrac{1}{8}I_{\underline{cc}\,\underline{cc}}+\tfrac{1}{8}I_{\overline{cc}\,\overline{cc}} . \end{aligned} \tag{4.11}$$

The fit of the total-energy results yields $I_{\underline{cc}\,\underline{cc}}=-75.9$ eV/Å^4, $K_{cc}=-97.2$ eV/Å^4, $K_{bb}=16.1$ eV/Å^4, $K_{aa}=66.0$ eV/Å^4, and $K_{zc}=-104.7$ eV/Å^4. Clearly it would be possible to obtain all of the third- and fourth-order anharmonic coefficients from a sufficiently systematic set of frozen-phonon calculations, but for our purposes the three cubic and five quartic ones obtained here form a representative sample of adequate size.

V. GENERALIZED KEATING MODEL

Our goal here is to develop an empirical model of the interatomic forces which can be fitted to the database developed above. The model should be simple enough to facilitate the evaluation of third and higher derivatives of the energy with respect to atomic displacements needed to calculate anharmonic phonon coupling constants. For this reason we have chosen a form for the interatomic energy similar to that of Keating.[1,16] However, we have modified the model so that it more closely resembles a valence-force-field (VFF) model, specifically the model of Tubino *et al.*,[5] whose six (harmonic) force constants do an excellent job of describing the phonon dispersion relations throughout the Brillouin zone. We then add higher-order terms, in order to fit the anharmonic sector as well.

In the Keating model[1,16] the energy of the crystal is expanded in terms of variables which can be written in dimensionless form

$$\begin{aligned} h_{ii}&=x_i^2/a_{\mathrm{K}}^2-3 , \\ h_{ij}&=\mathbf{x}_i\cdot\mathbf{x}_j/a_{\mathrm{K}}^2+1 . \end{aligned} \tag{5.1}$$

Here i and j label nearest-neighbor bonds, $\mathbf{x}_i$ is the "bond vector" pointing from one atom to its neighbor, and $a_{\mathrm{K}}=a/4$. (The term h_{ij} describes a pair of bonds sharing an atom; in this case both $\mathbf{x}_i$ and $\mathbf{x}_j$ point from the shared atom.) Both h_{ii} and h_{ij} vanish for the equilibrium structure; the first is a measure of bond stretching, while the second is a mixed measure of bond-angle bending and bond stretching. The energy of the crystal is then expanded in a power series in terms of these variables. Keating has suggested for the harmonic sector a two-parameter form[1] involving coefficients for h_{ii}^2 and h_{ij}^2 terms, and for the cubic anharmonic sector an additional three parameters[16] for h_{ii}^3, h_{ij}^3, and $h_{ii}h_{ij}^2$ terms. The five Keating parameters were fitted only to bulk elastic constants, and no convincing justification was given for the choice of terms retained.

The Keating model has the advantage that the energy is simply a polynomial in the atomic displacements. For example, the term h_{ii}^2 in the energy introduces quadratic, cubic, and quartic, but not higher, terms in the atomic displacements. This is not typically true of VFF models, which involve terms like $(x_i-x_i^0)^2$ and $(\theta_{ij}-\theta_{ij}^0)^2$; the square roots and inverse trigonometric functions introduce terms at all higher orders in the Taylor expansion of energy in atomic displacements, and considerably complicate the evaluation of third and fourth derivatives. This is an important advantage of a Keating-type model when it comes to evaluating anharmonic phonon coupling constants. However, the Keating model has the disadvantage that the variable h_{ij} is not a pure bond-angle–bending term. We therefore define instead

$$\begin{aligned} \tilde{h}_{ii}&=h_{ii}=x_i^2/a_{\mathrm{K}}^2-3 , \\ \tilde{h}_{ij}&=(\mathbf{x}_i\cdot\mathbf{x}_j+\tfrac{1}{6}x_i^2+\tfrac{1}{6}x_j^2)/a_{\mathrm{K}}^2 . \end{aligned} \tag{5.2}$$

With this definition, $\tilde{h}_{ij}$ is stationary with respect to bond length changes at the equilibrium structure. When the energy of the crystal is expanded in terms of the $\tilde{h}_{ii}$ and $\tilde{h}_{ij}$, we retain the polynomial simplicity of the Keating form, but we can more easily make contact with VFF models which already provide an excellent description of the harmonic sector.

Specifically, we adopt the form of the six-parameter VFF model of Tubino *et al.*,[5] which provides an excellent fit to the phonon dispersion relations. In our notation, the energy of the crystal is, for this model,

$$E^{[2]}=\sum_{i}\tfrac{1}{2}k_{rr}\tilde{h}_{ii}^{2}+\sum_{\langle i<j\rangle}[\tfrac{1}{2}k_{\theta\theta}\tilde{h}_{ij}^{2}+k_{r\theta}(\tilde{h}_{ii}+\tilde{h}_{jj})\tilde{h}_{ij}+k_{rr'}\tilde{h}_{ii}\tilde{h}_{jj}]$$
$$+\sum_{\langle i<j<k\rangle}k_{\theta\theta'}(\tilde{h}_{ij}\tilde{h}_{ik}+\tilde{h}_{ij}\tilde{h}_{jk}+\tilde{h}_{ik}\tilde{h}_{jk})+\sum_{\langle i;j<k\rangle}k_{\theta\theta^{*}}\tilde{h}_{ij}\tilde{h}_{ik}\ . \tag{5.3}$$

Here, $\langle i<j\rangle$ indicates a sum over all pairs of nearest-neighbor bonds (NNB's) sharing an atom, $\langle i<j<k\rangle$ indicates a sum over triplets of NNB's sharing an atom, and $\langle i;j<k\rangle$ represents a sum over chains of three NNB's arranged end to end, with i sharing one of its atoms with j and the other with k, in a 180° dihedral-angle configuration. The superscript "[2]" in Eq. (5.3) indicates a set of terms which are quadratic in the variables r and θ or $\tilde{h}_{ii}$ and $\tilde{h}_{ij}$, but which may contribute to the third-, fourth-, and higher-order anharmonic energies $E^{(3)}, E^{(4)}, \ldots$. This expression (5.3) is identical with the VFF model[5] as far as its contribution to the harmonic Hamiltonian $E^{(2)}$, but differs in its contribution to the anharmonic sector $E^{(3)}$ and $E^{(4)}$. After appropriate unit conversions and insertions of numerical prefactors, our parameters k_{rr}, $k_{\theta\theta}$, $k_{r\theta}$, $k_{rr'}$, $k_{\theta\theta'}$, and $k_{\theta\theta^{*}}$ are identical to the parameters K_R, H_Λ, $F_{R\Lambda}$, F_R, $F_{\Lambda'}$, and $F_{\Lambda'''}$ of Tubino *et al.*[5]

We now wish to generalize this model to include cubic and quartic terms in $\tilde{h}_{ii}$ and $\tilde{h}_{ij}$. A really systematic generalization including the triplets $\langle i<j<k\rangle$ and $\langle i;j<k\rangle$ would generate a huge number of terms, whose coefficient would have to be determined. Instead, we restrict ourselves to terms involving only one NNB or a pair of atom-sharing NNB's; this corresponds to retaining only nearest-neighbor two-body and three-body interactions in the anharmonic sector. The parameters k_{rr}, $k_{\theta\theta}$, $k_{r\theta}$, and $k_{rr'}$ already exhaust all possible quadratic terms in this restricted space of interactions.[33] We now systematically include all possible cubic and quartic terms in this space as well:

$$E^{[3]}=\sum_{i}\tfrac{1}{6}k_{rrr}\tilde{h}_{ii}^{3}+\sum_{\langle i<j\rangle}[\tfrac{1}{2}k_{rr\theta}(\tilde{h}_{ii}^{2}+\tilde{h}_{jj}^{2})\tilde{h}_{ij}+\tfrac{1}{2}k_{r\theta\theta}(\tilde{h}_{ii}+\tilde{h}_{jj})\tilde{h}_{ij}^{2}+\tfrac{1}{6}k_{\theta\theta\theta}\tilde{h}_{ij}^{3}+\tfrac{1}{2}k_{rrr'}(\tilde{h}_{ii}+\tilde{h}_{jj})\tilde{h}_{ii}\tilde{h}_{jj}+k_{rr'\theta}\tilde{h}_{ii}\tilde{h}_{jj}\tilde{h}_{ij}]\ , \tag{5.4}$$

$$E^{[4]}=\sum_{i}\tfrac{1}{24}k_{rrrr}\tilde{h}_{ii}^{4}+\sum_{\langle i<j\rangle}[\tfrac{1}{6}k_{rrr\theta}(\tilde{h}_{ii}^{3}+\tilde{h}_{jj}^{3})\tilde{h}_{ij}+\tfrac{1}{4}k_{rr\theta\theta}(\tilde{h}_{ii}^{2}+\tilde{h}_{jj}^{2})\tilde{h}_{ij}^{2}+\tfrac{1}{6}k_{r\theta\theta\theta}(\tilde{h}_{ii}+\tilde{h}_{jj})\tilde{h}_{ij}^{3}+\tfrac{1}{24}k_{\theta\theta\theta\theta}\tilde{h}_{ij}^{4}$$
$$+\tfrac{1}{6}k_{rrrr'}(\tilde{h}_{ii}^{2}+\tilde{h}_{jj}^{2})\tilde{h}_{ii}\tilde{h}_{jj}+\tfrac{1}{4}k_{rrr'r'}\tilde{h}_{ii}^{2}\tilde{h}_{jj}^{2}+\tfrac{1}{2}k_{rrr'\theta}(\tilde{h}_{ii}+\tilde{h}_{jj})\tilde{h}_{ii}\tilde{h}_{jj}\tilde{h}_{ij}+\tfrac{1}{2}k_{rr'\theta\theta}\tilde{h}_{ii}\tilde{h}_{jj}\tilde{h}_{ij}^{2}]\ . \tag{5.5}$$

It can be seen that this introduces six new cubic parameters and nine new quartic parameters into the model, in addition to the original six quadratic ones. It is this 21-parameter model that we propose to fit to the database of harmonic and anharmonic constants determined in the earlier sections.

In order to carry out the fitting, it was first necessary to determine the contribution from each of the 21 terms in our model potential to each of the 31 constants in our "database" of known anharmonic coupling constants. Because the contributions are all linear, the problem reduces to determining a matrix of proportionality coefficients, which are given in Tables III–VI. While it is possible to work out these coefficients by hand, we have developed an automated procedure for obtaining them, thereby greatly reducing both the effort involved and the chances of error.

Specifically, a computer program was written to calculate, for the 21-term model potential, the energy, force, and stress tensor for a given input geometry. It also calculates the contributions to the energy, force, and stress due to each of the 21 terms separately (assuming a unit

TABLE III. Matrix of proportionality coefficients relating harmonic properties to second-order parameters of the generalized Keating model. Units of the coefficients are given in the last column.

Property	k_{rr}	$k_{\theta\theta}$	$k_{rr'}$	$k_{r\theta}$	$k_{\theta\theta'}$	$k_{\theta\theta^{*}}$	Units
$M\omega^2_{\mathrm{LTO}}(\Gamma)$	17.36	30.87	−34.73	92.61	0.00	61.74	Å^{-2}
$M\omega^2_{\mathrm{TA}}(X)$	0.00	17.36	0.00	0.00	0.00	0.00	Å^{-2}
$M\omega^2_{\mathrm{LAO}}(X)$	8.68	19.29	17.36	23.15	−23.15	30.87	Å^{-2}
$M\omega^2_{\mathrm{TO}}(X)$	17.36	1.93	−34.73	23.15	0.00	0.00	Å^{-2}
$M\omega^2_{\mathrm{TA}}(L)$	0.00	8.68	0.00	0.00	−8.68	0.00	Å^{-2}
$M\omega^2_{\mathrm{LA}}(L)$	4.34	30.87	17.36	23.15	0.00	30.87	Å^{-2}
$M\omega^2_{\mathrm{LO}}(L)$	13.02	0.00	0.00	0.00	0.00	0.00	Å^{-2}
$M\omega^2_{\mathrm{TO}}(L)$	17.36	16.40	−34.73	57.88	−8.68	30.87	Å^{-2}
B_{11}	16.00	42.67	96.00	0.00	−85.33	85.33	none
B_{12}	16.00	−21.33	96.00	0.00	42.67	−42.67	none
B_{44}	16.00	7.11	−32.00	−42.67	0.00	14.22	none
B_{4x}	23.57	−20.95	−47.15	31.43	0.00	−41.91	Å^{-1}

TABLE IV. Matrix of proportionality coefficients relating cubic and quartic anharmonic properties to second-order parameters of the generalized Keating model. Units of the coefficients are given in the last column.

Property	k_{rr}	$k_{\theta\theta}$	$k_{rr'}$	$k_{r\theta}$	Units
B_{111}	0.00	0.00	0.00	0.00	none
B_{112}	0.00	0.00	0.00	0.00	none
B_{123}	0.00	0.00	0.00	0.00	none
B_{xyz}	0.00	0.00	0.00	0.00	Å^{-3}
B_{1xx}	173.65	246.97	−69.46	1018.74	Å^{-2}
B_{1yy}	34.73	0.00	208.38	277.84	Å^{-2}
B_{4yz}	69.46	123.48	−138.92	370.45	Å^{-2}
$I_{z\overline{cc}}$	−76.75	−90.96	−51.17	−477.56	Å^{-3}
$I_{z\overline{bb}}$	−25.58	−45.48	51.17	−136.45	Å^{-3}
$I_{z\overline{aa}}$	−25.58	−45.48	51.17	−136.45	Å^{-3}
B_{xxxx}	226.15	1206.15	1356.92	3618.44	Å^{-4}
B_{xxyy}	75.38	402.05	452.30	1206.15	Å^{-4}
B_{1111}	0.00	0.00	0.00	0.00	none
B_{1112}	0.00	0.00	0.00	0.00	none
$I_{\underline{cc}\,\underline{cc}}$	9.42	37.69	56.54	75.38	Å^{-4}
K_{cc}	18.85	35.60	37.69	125.64	Å^{-4}
K_{bb}	18.85	35.60	37.69	125.64	Å^{-4}
K_{aa}	18.85	35.60	37.69	125.64	Å^{-4}
K_{zc}	21.20	75.65	80.10	248.14	Å^{-4}

prefactor for each term). One version of the program calculates these energies and forces for a two-atom cell with a given relative sublattice displacement **u** and a given Lagrangian strain η, while a second version calculates them for the four-atom cell of Fig. 1. For the four-atom cell, the program was subjected to exactly the same set of displaced input geometries as were used in the LDA calculations of Sec. IV, and the coefficients of $I_{z\overline{cc}}$, $I_{z\overline{bb}}$, $I_{z\overline{aa}}$, $I_{\underline{cc}\,\underline{cc}}$, K_{cc}, K_{bb}, K_{aa}, and K_{zc} were determined by precisely the same polynomial-fitting procedure (see discussion in last paragraph of Sec. IV). For the two-atom cell, the following sets of input geometries were used (only the nonzero quantities are given): (i) $u_x=t$; (ii) $u_x=u_y=u_z=t/\sqrt{3}$; (iii) $\eta_1=t$; (iv) $\eta_1=\eta_2=t$; (v) $2\eta_1=2\eta_2=\eta_6=2t$; (vi) $\eta_1=\eta_2=\eta_3=t$; (vii) $2\eta_1=2\eta_2=2\eta_3=\eta_4=\eta_5=\eta_6=2t$. For the sets (i) and (ii), t ranged from

TABLE V. Matrix of proportionality coefficients relating cubic and quartic anharmonic properties to third-order parameters of the generalized Keating model. Units of the coefficients are given in the last column.

Property	k_{rrr}	$k_{rr\theta}$	$k_{r\theta\theta}$	$k_{\theta\theta\theta}$	$k_{rrr'}$	$k_{rr'\theta}$	Units
B_{111}	32.00	0.00	512.00	56.89	576.00	0.00	none
B_{112}	32.00	0.00	0.00	−28.44	576.00	0.00	none
B_{123}	32.00	0.00	−256.00	56.89	576.00	0.00	none
B_{xyz}	102.33	818.67	0.00	0.00	−614.01	−818.67	Å^{-3}
B_{1xx}	69.46	370.45	740.90	164.64	138.92	740.90	Å^{-2}
B_{1yy}	69.46	370.45	0.00	−82.32	138.92	185.23	Å^{-2}
B_{4yz}	69.46	277.84	0.00	0.00	−416.76	−277.84	Å^{-2}
$I_{z\overline{cc}}$	−51.17	−272.89	−545.78	−121.29	−102.33	−545.78	Å^{-3}
$I_{z\overline{bb}}$	0.00	0.00	0.00	0.00	0.00	0.00	Å^{-3}
$I_{z\overline{aa}}$	−102.33	−409.34	0.00	0.00	614.01	409.34	Å^{-3}
B_{xxxx}	904.61	12 061.48	9649.18	2144.26	1809.22	2412.30	Å^{-4}
B_{xxyy}	301.54	4020.49	3216.40	714.75	603.07	804.10	Å^{-4}
B_{1111}	0.00	0.00	0.00	0.00	0.00	0.00	none
B_{1112}	0.00	0.00	0.00	0.00	0.00	0.00	none
$I_{\underline{cc}\,\underline{cc}}$	37.69	251.28	502.56	78.18	376.92	50.26	Å^{-4}
K_{cc}	75.38	452.30	804.10	184.27	452.30	603.07	Å^{-4}
K_{bb}	0.00	0.00	150.77	25.13	0.00	0.00	Å^{-4}
K_{aa}	150.77	703.59	50.26	2.79	−301.54	−402.05	Å^{-4}
K_{zc}	84.81	848.07	879.48	207.31	282.69	490.00	Å^{-4}

TABLE VI. Matrix of proportionality coefficients relating quartic anharmonic properties to fourth-order parameters of the generalized Keating model. Units of the coefficients are given in the last column.

Property	k_{rrrr}	$k_{rrr\theta}$	$k_{rr\theta\theta}$	$k_{r\theta\theta\theta}$	$k_{\theta\theta\theta\theta}$	$k_{rrrr'}$	$k_{rrr'r'}$	$k_{rrr'\theta}$	$k_{rr'\theta\theta}$	Units
B_{xxxx}	301.54	3216.40	6432.79	5718.04	953.01	−2412.30	5427.67	9649.18	6432.79	Å^{-4}
B_{xxyy}	301.54	3216.40	2144.26	0.00	0.00	−2412.30	603.07	−3216.40	−2144.26	Å^{-4}
B_{1111}	64.00	0.00	2048.00	910.22	227.56	1536.00	1152.00	0.00	2048.00	none
B_{1112}	64.00	0.00	512.00	−113.78	−113.78	1536.00	1152.00	0.00	512.00	none
$I_{\underline{cc}\,\underline{cc}}$	12.56	67.01	335.04	208.47	42.19	100.51	226.15	201.02	335.04	Å^{-4}
K_{cc}	25.13	134.02	603.07	461.61	80.66	201.02	150.77	804.10	536.07	Å^{-4}
K_{bb}	0.00	0.00	0.00	0.00	25.13	0.00	0.00	0.00	0.00	Å^{-4}
K_{aa}	100.51	268.03	67.01	7.45	0.31	−804.10	603.07	0.00	0.00	Å^{-4}
K_{zc}	28.27	234.53	628.20	534.20	89.50	−25.13	320.38	954.87	586.32	Å^{-4}

−0.12 to 0.12 Å in increments of 0.02 Å, while for sets (iii)–(vii) t ranged from −0.3 to 0.3 in increments of 0.05. Polynomial-fitting routines were used to obtain the first through fourth derivatives of the energy, and the first through third derivatives of the forces and stresses, with respect to t, for each set and for each of the 21 terms in the potential model. (Double-precision arithmetic was used throughout, and we have checked that the numerical and polynomial-fitting errors are negligible.) The relation between these derivatives and the anharmonic constants (the B's) follows from the expressions given by Eqs. (2.6)–(2.13) and in the Appendix. For example, for case (i) it follows that $\partial E/\partial u_x = B_{xx}t + \frac{1}{6}B_{xxxx}t^3$, $\partial E/\partial u_y = \partial E/\partial u_z = 0$, $\sigma_1 = \frac{1}{2}B_{1xx}t^2$, $\sigma_2 = \sigma_3 = \frac{1}{2}B_{1yy}t^2$, $\sigma_4 = B_{4x}t + \frac{1}{6}B_{4xxx}t^3$, $\sigma_5 = \sigma_6 = 0$, and $E = \frac{1}{2}B_{xx}t^2 + \frac{1}{24}B_{xxxx}t^4$. (Here $\sigma_1, \ldots, \sigma_6$ is the stress in Voigt notation, e.g., $\sigma_1 = \sigma_{xx}$, $\sigma_4 = \sigma_{yz}$.) In order to obtain similar expressions reliably for all cases (i)–(vii), we have used the symbolic manipulation program SMP. The cases (i)–(vii) are sufficient to determine (redundantly in many cases) all of the 15 B coefficients. Finally, a third version of the program was written to calculate phonon frequencies at arbitrary wave vectors at the equilibrium geometry, and was used to determine the coefficients of the phonon frequencies $M\omega^2_{\text{LTO}}(\Gamma), \ldots, M\omega^2_{\text{TO}}(L)$. We have checked this procedure carefully in many ways, e.g., by verifying that redundant determinations agree and that terms which should vanish do so, and by calculating some representative coefficients by hand.

Once the coefficients of Tables III–VI are in hand, it is straightforward to carry out a linear least-squares-fitting procedure to determine the 21 parameters that enter into our model potential. This was done in three stages. First, the six quadratic parameters $(k_{rr}, \ldots, k_{\theta\theta^*})$ were determined by fitting to the 12 harmonic constants $[M\omega^2_{\text{LTO}}(\Gamma), \ldots, B_{11}]$ using Table III. Second, the six cubic parameters $(k_{rrr}, \ldots, k_{rr'\theta})$ were determined by fitting to the nine third-order anharmonic constants $(B_{111}, \ldots, I_{z\overline{aa}})$ using Table V, after accounting for the contributions from the four quadratic parameters $(k_{rr}, k_{\theta\theta}, k_{rr'}, k_{r\theta})$ using Table IV.[33] Finally, the nine quartic parameters $(k_{rrrr}, \ldots, k_{rr'\theta\theta})$ were determined by fitting to the nine quartic anharmonic constants $(B_{xxxx}, \ldots, K_{zc})$ using Table VI, after accounting for the contributions from the quadratic and cubic parameters $(k_{rr}, \ldots, k_{rr'\theta})$ using Tables IV and V. (The quartic fit is not perfect because the 9×9 matrix of Table VI is actually rank deficient, with rank of 7.) The weights used in the linear least-squares fitting are listed in Table VII; those for the phonon frequencies were obtained from the experimental error estimates,[29] while the others were some-

TABLE VII. Comparison of target values (from Secs. II and III) and fitted values (from generalized Keating model) of harmonic and anharmonic properties of Si.

Constant	Weight	Target	Fit	Units
$M\omega^2_{\text{LTO}}(\Gamma)$	1.22	27.72	27.50	eV/Å^2
$M\omega^2_{\text{TA}}(X)$	16.67	2.32	2.38	eV/Å^2
$M\omega^2_{\text{LAO}}(X)$	1.75	17.44	17.39	eV/Å^2
$M\omega^2_{\text{TO}}(X)$	1.04	22.20	21.22	eV/Å^2
$M\omega^2_{\text{TA}}(L)$	25.00	1.35	1.30	eV/Å^2
$M\omega^2_{\text{LA}}(L)$	1.28	14.80	12.74	eV/Å^2
$M\omega^2_{\text{LO}}(L)$	1.08	18.24	17.83	eV/Å^2
$M\omega^2_{\text{TO}}(L)$	0.99	24.76	24.47	eV/Å^2
B_{11}	2.50	41.90	42.29	eV
B_{12}	2.50	16.23	15.98	eV
B_{44}	2.50	27.24	26.99	eV
B_{4x}	2.50	19.94	20.37	eV/Å
B_{111}	0.25	−206	−210	eV
B_{112}	0.25	−113	−105	eV
B_{123}	0.25	−16	−19	eV
B_{xyz}	0.10	−290	−285	eV/Å^3
B_{1xx}	0.25	−80	6	eV/Å^2
B_{1yy}	0.20	−106	−112	eV/Å^2
B_{4yz}	0.50	−137	−153	eV/Å^2
$I_{z\overline{cc}}$	1.00	47	54	eV/Å^3
$I_{z\overline{bb}}$	1.00	−49	−29	eV/Å^3
$I_{z\overline{aa}}$	1.00	315	313	eV/Å^3
B_{xxxx}	0.10	−1250	−1233	eV/Å^4
B_{xxyy}	0.10	410	410	eV/Å^4
B_{1111}	0.10	0	132	eV
B_{1112}	0.10	800	800	eV
$I_{\underline{cc}\,\underline{cc}}$	0.50	−76	−127	eV/Å^4
K_{cc}	0.50	−97	−102	eV/Å^4
K_{bb}	0.50	16	16	eV/Å^4
K_{aa}	0.50	66	66	eV/Å^4
K_{zc}	0.50	−105	−96	eV/Å^4

what arbitrarily chosen in a manner designed to reflect the magnitude of the anharmonic constant to be fitted. For the most part, the fit is rather insensitive to the choice of these weights (but see below). The resulting fitted parameters are listed in Table VIII.

TABLE VIII. Values of fitted parameters of the generalized Keating model. All units are in eV.

Parameter	Value
k_{rr}	1.369
$k_{\theta\theta}$	0.137
$k_{rr'}$	0.030
$k_{r\theta}$	−0.077
$k_{\theta\theta'}$	−0.013
$k_{\theta\theta^*}$	0.124
k_{rrr}	−3.684
$k_{rr\theta}$	0.278
$k_{r\theta\theta}$	−0.249
$k_{\theta\theta\theta}$	0.267
$k_{rrr'}$	0.035
$k_{rr'\theta}$	0.140
k_{rrrr}	2.465
$k_{rrr\theta}$	−1.419
$k_{rr\theta\theta}$	1.749
$k_{r\theta\theta\theta}$	−2.095
$k_{\theta\theta\theta\theta}$	0.987
$k_{rrrr'}$	−0.275
$k_{rrr'r'}$	0.484
$k_{rrr'\theta}$	0.698
$k_{rr'\theta\theta}$	−1.007

The quality of the fit of the harmonic sector is excellent, as can be seen from the first 12 lines of Table VII, despite the fact that it is highly overdetermined (six parameters for 12 constants). The fitted parameters (first six lines of Table VIII) are very close to those obtainable from Tubino *et al.*[5] The fits of the cubic and quartic sectors (rest of Table VII) are also generally good, with the exception of the third-order quantity B_{1xx} which corresponds to a certain strain derivative of the zone-center optical-phonon frequency. By adjusting the fitting weights, it is possible to reduce the fitting error for B_{1xx} significantly, but only at the expense of introducing significantly larger errors into the X-point phonon coupling constant $I_{z\overline{cc}}$. The latter was deemed more important for potential applications such as calculation of optical-phonon lifetimes, for which processes involving one zone-center optical phonon and two acoustic phonons in the vicinity of the X point are quite typical.[34] The difficulty in obtaining a fully satisfactory fit can presumably be traced to the fact that only nearest-neighbor two-body and three-body terms are included in the Keating-model energy. Further-neighbor interactions may be important; these could have their physical origin in long-range Coulomb forces, in which case a model which includes such Coulomb forces[6–9] might provide a better fit. However, our model has the advantage of simplicity, and the overall quality of the fit in Table VII is quite good.

VI. SUMMARY AND DISCUSSION

We have developed a fairly extensive database consisting of 31 harmonic and anharmonic elastic and phonon properties for Si. This database should be useful in developing and fitting empirical interatomic potential models. Two classes of models are anticipated: (i) general models for evaluating total energies and forces, e.g., for use in molecular-dynamics simulations, and (ii) models designed for use in calculating anharmonic phonon interactions. For case (ii), it is important that the functional form of the model facilitate the calculation of third and fourth derivatives of the energy with respect to lattice displacements. We have proposed a 21-parameter Keating-type model of this kind. Ideally, of course, one hopes that a model which captures the essential physics should be able to fit the database of harmonic and anharmonic constants with a much smaller number of parameters. Models which include Coulomb forces, e.g., bond-charge models,[7,8] would be interesting candidates for investigation in this respect. However, for the purposes of case (ii) such models may not turn out to be appropriate, as the analytic calculation of higher derivatives could be quite cumbersome.

A natural extension of the present work would be to other tetrahedrally bonded semiconductors, such as Ge, C, and GaAs. Unfortunately, the database of known anharmonic constants is smaller for these materials than it is for Si. Further experimental work and LDA calculations could remedy this situation. In the meantime, it is suggested that the current model could tentatively be extended to Ge and C by using the quadratic constants of Tubino *et al.*[5] for the harmonic sector, and scaling the cubic and quartic parameters of Si following the scaling relations noted in Vanderbilt *et al.*[28] The extension to polar semiconductors such as GaAs is of considerable importance and poses interesting challenges.

ACKNOWLEDGMENTS

Primary support for this work was provided by the Harvard University Materials Research Laboratory under National Science Foundation NSF Grant No. DMR-86-14003. Supercomputer time for the calculations in Sec. IV was provided at the Purdue University Computer Center under NSF Grant No. DMR-85-14638. One of us (S.T.) wishes to thank the Harvard University–South Africa Fellowship Program for its support We also wish to thank M. Cardona for pointing out the necessity of Eq. (2.21).

APPENDIX

The terms which appear at fourth order in the Taylor expansion of the energy, Eq. (2.6c), are

$$\begin{aligned}E_{\mathrm{AAAA}}={}&\tfrac{1}{24}B_{1111}(\eta_1^4+\eta_2^4+\eta_3^4)+\tfrac{1}{6}B_{1112}[\eta_1^3(\eta_2+\eta_3)+\eta_2^3(\eta_1+\eta_3)+\eta_3^3(\eta_1+\eta_2)]\\&+\tfrac{1}{4}B_{1122}(\eta_1^2\eta_2^2+\eta_1^2\eta_3^2+\eta_2^2\eta_3^2)+\tfrac{1}{2}B_{1123}\eta_1\eta_2\eta_3(\eta_1+\eta_2+\eta_3)+\tfrac{1}{4}B_{1144}(\eta_1^2\eta_4^2+\eta_2^2\eta_5^2+\eta_3^2\eta_6^2)\\&+\tfrac{1}{4}B_{1155}[\eta_1^2(\eta_5^2+\eta_6^2)+\eta_2^2(\eta_4^2+\eta_6^2)+\eta_3^2(\eta_4^2+\eta_5^2)]\\&+\tfrac{1}{2}B_{1244}[\eta_1\eta_4^2(\eta_2+\eta_3)+\eta_2\eta_5^2(\eta_1+\eta_3)+\eta_3\eta_6^2(\eta_1+\eta_2)]\\&+\tfrac{1}{2}B_{1266}(\eta_1\eta_2\eta_6^2+\eta_1\eta_3\eta_5^2+\eta_2\eta_3\eta_4^2)+B_{1456}(\eta_1+\eta_2+\eta_3)\eta_4\eta_5\eta_6\\&+\tfrac{1}{24}B_{4444}(\eta_4^4+\eta_5^4+\eta_6^4)+\tfrac{1}{4}B_{4455}(\eta_4^2\eta_5^2+\eta_4^2\eta_6^2+\eta_5^2\eta_6^2)\ ,\end{aligned}\tag{A1}$$

$$\begin{aligned}E_{\mathrm{AAAO}}={}&\tfrac{1}{2}B_{114x}(\eta_1^2\eta_4u_x+\eta_2^2\eta_5u_y+\eta_3^2\eta_6u_z)+\tfrac{1}{2}B_{115y}[(\eta_1^2+\eta_2^2)\eta_6u_z+(\eta_1^2+\eta_3^2)\eta_5u_y+(\eta_2^2+\eta_3^2)\eta_4u_x]\\&+B_{124x}[\eta_1\eta_4u_x(\eta_2+\eta_3)+\eta_2\eta_5u_y(\eta_1+\eta_3)+\eta_3\eta_6u_z(\eta_1+\eta_2)]\\&+B_{126z}(\eta_1\eta_2\eta_6u_z+\eta_1\eta_3\eta_5u_y+\eta_2\eta_3\eta_4u_x)+B_{156x}(\eta_1\eta_5\eta_6u_x+\eta_2\eta_4\eta_6u_y+\eta_3\eta_4\eta_5u_z)\\&+B_{145z}[(\eta_1+\eta_2)\eta_4\eta_5u_z+(\eta_1+\eta_3)\eta_4\eta_6u_y+(\eta_2+\eta_3)\eta_5\eta_6u_x]+\tfrac{1}{6}B_{444x}(\eta_4^3u_x+\eta_5^3u_y+\eta_6^3u_z)\\&+\tfrac{1}{2}B_{445y}[(\eta_4^2+\eta_6^2)\eta_5u_y+(\eta_4^2+\eta_5^2)\eta_6u_z+(\eta_5^2+\eta_6^2)\eta_4u_x]\ ,\end{aligned}\tag{A2}$$

$$\begin{aligned}E_{\mathrm{AAOO}}={}&\tfrac{1}{4}B_{11xx}(\eta_1^2u_x^2+\eta_2^2u_y^2+\eta_3^2u_z^2)+\tfrac{1}{4}B_{11yy}[\eta_1^2(u_y^2+u_z^2)+\eta_2^2(u_x^2+u_z^2)+\eta_3^2(u_x^2+u_y^2)]\\&+\tfrac{1}{2}B_{12xx}[\eta_1(\eta_2+\eta_3)u_x^2+\eta_2(\eta_1+\eta_3)u_y^2+\eta_3(\eta_1+\eta_2)u_z^2]\\&+\tfrac{1}{2}B_{12zz}(\eta_1\eta_2u_z^2+\eta_1\eta_3u_y^2+\eta_2\eta_3u_x^2)+B_{14yz}(\eta_1\eta_4u_yu_z+\eta_2\eta_5u_xu_z+\eta_3\eta_6u_xu_y)\\&+B_{15xz}[(\eta_1+\eta_3)\eta_5u_xu_z+(\eta_1+\eta_2)\eta_6u_xu_y+(\eta_2+\eta_3)\eta_4u_yu_z]\\&+\tfrac{1}{4}B_{44xx}(\eta_4^2u_x^2+\eta_5^2u_y^2+\eta_6^2u_z^2)+\tfrac{1}{4}B_{44yy}[\eta_4^2(u_y^2+u_z^2)+\eta_5^2(u_x^2+u_z^2)+\eta_6^2(u_x^2+u_y^2)]\\&+B_{45xy}(\eta_4\eta_5u_xu_y+\eta_4\eta_6u_xu_z+\eta_5\eta_6u_yu_z)\ ,\end{aligned}\tag{A3}$$

$$\begin{aligned}E_{\mathrm{AOOO}}={}&B_{1xyz}(\eta_1+\eta_2+\eta_3)u_xu_yu_z+\tfrac{1}{6}B_{4xxx}(\eta_4u_x^3+\eta_5u_y^3+\eta_6u_z^3)\\&+\tfrac{1}{2}B_{4xyy}[\eta_4u_x(u_y^2+u_z^2)+\eta_5u_y(u_x^2+u_z^2)+\eta_6u_z(u_x^2+u_y^2)]\ ,\end{aligned}\tag{A4}$$

$$E_{\mathrm{OOOO}}=\tfrac{1}{24}B_{xxxx}(u_x^4+u_y^4+u_z^4)+\tfrac{1}{4}B_{xxyy}(u_x^2u_y^2+u_x^2u_z^2+u_y^2u_z^2)\ .\tag{A5}$$

The terms retained above are the only ones allowed by symmetry. They have been enumerated by systematically considering all possible terms and symmetrizing them with respect to a set of generators of the rotational symmetries of the crystal. A convenient set of generators is $\{M_x,M_y,M_z,M_{xy},C_3\}$. Here M_x is the nonsymmorphic mirror operation which takes $x\rightarrow -x$ and interchanges atoms 1 and 2, so that $u_y\rightarrow -u_y$, $u_z\rightarrow -u_z$, $\eta_5\rightarrow -\eta_5$, and $\eta_6\rightarrow -\eta_6$ (with the others, e.g., u_x, unchanged), and M_y and M_z are defined analogously. M_{xy} is the symmorphic mirror operation which takes $x\leftrightarrow y$ and therefore $u_x\leftrightarrow u_y$, $\eta_1\leftrightarrow\eta_2$, and $\eta_4\leftrightarrow\eta_5$. Finally, C_3 is the symmorphic 120° rotation which takes $x\rightarrow y\rightarrow z$ and therefore $u_x\rightarrow u_y\rightarrow u_z$, $\eta_1\rightarrow\eta_2\rightarrow\eta_3$, and $\eta_4\rightarrow\eta_5\rightarrow\eta_6$. For example, the term $u_x\eta_4$ when symmetrized under C_3 becomes $(u_x\eta_4+u_y\eta_5+u_z\eta_6)$, which is then invariant with respect to M_x, M_y, M_z, and M_{xy} and is therefore an allowed term. However, the term $u_x\eta_1$ when symmetrized under C_3 becomes $(u_x\eta_1+u_y\eta_2+u_z\eta_3)$, which is odd under M_x (i.e., it vanishes when symmetrized with respect to M_x), and it is therefore not an allowed term.

---

[*] Permanent address: University of Bophuthatswana, Postal Bag X2046, Mafikeng 8670, Republic of Bophuthatswana.

[1] P. N. Keating, Phys. Rev. **145**, 637 (1966).

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

[3] H. L. McMurray, A. W. Solbrig, J. K. Boyter, and C. Noble, J. Phys. Chem. Solids **28**, 2359 (1967).

[4] B. D. Singh and B. Dayal, Phys. Status Solidi B **38**, 141 (1970).

[5] R. Tubino, L. Piseri, and G. Zerbi, J. Chem. Phys. **56**, 1022 (1972).

[6] K. H. Wanser and R. F. Wallis, J. Phys. (Paris) Colloq. **42**, C6-128 (1981).

[7] W. Weber, Phys. Rev. B **15**, 4789 (1977).

[8] O. H. Nielsen and W. Weber, Comput. Phys. Commun. **18**, 101 (1979).

[9] See, e.g., W. Cochran, Rep. Prog. Phys. **26**, 1 (1963).

[10] E. Pearson, T. Takai, T. Halicioglu, and W. A. Tiller, J. Cryst. Growth **70**, 33 (1984).

[11] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).

[12] R. Biswas and D. R. Hamann, Phys. Rev. Lett. **55**, 2001

(1985).

[13] J. Tersoff, Phys. Rev. Lett. **56**, 632 (1986).

[14] M. I. Baskes, Phys. Rev. Lett. **59**, 2666 (1987).

[15] E. R. Cowley, Phys. Rev. Lett. **60**, 2379 (1988).

[16] P. N. Keating, Phys. Rev. **149**, 674 (1966).

[17] S. L. Altmann, A. Lapiccirella, K. W. Lodge, and N. Toamssini, J. Phys. C **15**, 5581 (1982).

[18] E. Haro, M. Balkanski, R. F. Wallis, and K. H. Wanser, Phys. Rev. B **34**, 5358 (1986).

[19] F. Birch, Phys. Rev. **71**, 809 (1947).

[20] O. H. Nielsen and R. M. Martin, Phys. Rev. B **32**, 3792 (1985).

[21] L. Kleinman, Phys. Rev. **128**, 2614 (1962).

[22] H. J. McSkimin and P. Andreatch, J. Appl. Phys. **35**, 2161 (1964).

[23] C. S. G. Cousins *et al.*, J. Phys. C **20**, 29 (1987).

[24] H. J. McSkimin and P. Andreatch, J. Appl. Phys. **35**, 3312 (1964).

[25] M. Chandrasekhar, J. B. Renucci, and M. Cardona, Phys. Rev. B **17**, 1623 (1978).

[26] B. A. Weinstein and G. J. Piermarini, Phys. Rev. B **12**, 1172 (1975).

[27] M. T. Yin and M. L. Cohen, Phys. Rev. Lett. **45**, 1004 (1980).

[28] D. Vanderbilt, S. G. Louie, and M. L. Cohen, Phys. Rev. **33**, 8740 (1986).

[29] G. Dolling, *Inelastic Scattering of Neutrons in Solids and Liquids* (IAEA, Vienna, 1963), Vol. II, p. 37.

[30] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[31] D. Vanderbilt, Phys. Rev. B **32**, 8412 (1985).

[32] E. P. Wigner, Phys. Rev. **36**, 1002 (1934).

[33] The terms with prefactors $k_{\theta\theta'}$ and $k_{\theta\theta^*}$ are not allowed to contribute to the anharmonic energies $E^{(3)}$ and $E^{(4)}$ in our model. In any case, their contribution would be small, and their inclusion would hardly affect the fitted values in Table VIII.

[34] Shobhana Narasimhan and David Vanderbilt (unpublished).