Theory for structure and bulk modulus determination

Eleni Ziambaras and Elsebeth Schröder*
Applied Physics, Chalmers University of Technology and Göteborg University, SE-41296 Gothenburg, Sweden
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A method for direct evaluation of both lattice parameters, atomic basis, bulk modulus B_0, and bulk-modulus pressure derivative B_0' of solid materials with complex crystal structures is presented. The explicit and exact results presented here permit a multidimensional polynomial fit of the total energy as a function of all relevant structure parameters to simultaneously determine the equilibrium configuration and the elastic properties. The method allows for inclusion of general (internal) structure parameters, e.g., bond lengths and angles within the unit cell, on an equal footing with the unit-cell lattice parameters. The method is illustrated by the calculation of B_0 and B_0' for a few selected materials with multiple structure parameters for which data are obtained by using first-principles density-functional theory.

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I. INTRODUCTION

Calculations of bulk ground-state properties, such as lattice constants, atomic positions, bond lengths, and bulk modulus, play an important role in the physics of condensed matter.[1–6] Bulk calculations help us to understand, characterize, and predict mechanical properties of materials in our surroundings, under extreme conditions, as in geological formations and settings,[7] and for industrial applications.[6,8] Crystalline materials come in many different structures and, in contrast to isotropic materials, the description of the ground state of crystalline materials may in general need multiple lattice parameters and an atomic basis. In this paper we discuss how to determine the equilibrium structure parameters of a (multiparameter) crystalline material while, at the same time, directly determining the bulk modulus and the bulk modulus pressure derivative. We argue and show that for theoretical structure calculations of multiparameter systems this is simpler and more exact[9] than fitting to (semi)empirical equations of state (EOS), such as the Murnaghan or Birch EOS. In particular, with our direct method there is no need to first determine the hydrostatic path of the system. We further discuss how to include the atomic basis in this process in a natural way.

In crystalline materials described by a single lattice parameter (e.g., monatomic cubic phases) the lattice parameter is a simple function of the unit-cell volume, and the equilibrium volume thus uniquely determines the equilibrium structure, i.e., the value of the lattice parameter. This is not the case when multiple lattice parameters characterize the system and a whole range of lattice-parameter values can form the same unit-cell volume. The equilibrium structure of the material must then be found by fitting and minimizing the free energy within the multidimensional space of lattice parameters, given the space group of the material.[2,5,10] Relevant variables describing the atomic basis (e.g., bond lengths or binding angles) may be included among the parameters, and the full set of lattice parameters and internal (atomic basis) parameters are collected into the vector $\boldsymbol{x}$, scaled to dimensionless form. The volume of the unit cell $V(\boldsymbol{x})$ depends in a simple way on the values of the lattice parameters describing the unit cell, but not on the internal atomic configuration. Nevertheless, we here treat the external and internal parameters on an equal footing.

From theory bulk calculations the total energy (per unit cell) $E(\boldsymbol{x})$ is found for a number of structures $\boldsymbol{x}$. The elastic response of typical hard crystalline materials corresponds to small deviations $\delta\boldsymbol{x}=\boldsymbol{x}-\boldsymbol{x}^{(0)}$ of the structural parameters from the equilibrium structure $\boldsymbol{x}^{(0)}$. The observation that the total energy forms a natural potential (hyper)surface in the parameter space of lattice and internal parameters $\boldsymbol{x}$, combined with the accuracy of present-day bulk-calculation methods (such as density-functional theory, embedded atom methods, or effective-medium theory), then makes it possible to fit the corresponding total-energy variation through the multidimensional fit

$$E(\boldsymbol{x})=k+\frac{1}{2}M_{ij}\delta x_i\delta x_j+\frac{1}{3!}\gamma_{ijl}\delta x_i\delta x_j\delta x_l+O(\delta\boldsymbol{x})^4 \tag{1}$$

at controlled accuracy. Here k, M, and γ denote zeroth-, second-, and third-rank tensors of fitting constants respectively. An additional set of fitting constants are the $\boldsymbol{x}^{(0)}$ hidden in $\delta\boldsymbol{x}=\boldsymbol{x}-\boldsymbol{x}^{(0)}$. The polynomial fit (1) gives a transparent description of the materials-structure energy variation and directly determines the equilibrium structure $\boldsymbol{x}^{(0)}$. In this paper we exploit and use the structure calculation, i.e., the multidimensional polynomial fit of the total energy (1) for an additional and direct determination of the zero-pressure bulk modulus $B_0=-V(\boldsymbol{x}^{(0)})(\partial p/\partial V)|_{\boldsymbol{x}=\boldsymbol{x}^{(0)}}$ and its pressure derivative $B_0'=-\partial\{V(\partial p/\partial V)\}/\partial p|_{\boldsymbol{x}=\boldsymbol{x}^{(0)}}$ at zero temperature.

For a general set of structure parameters $\boldsymbol{x}$ we expand the volume around the equilibrium configuration $\boldsymbol{x}^{(0)}$ using the gradient $\boldsymbol{g}=\nabla V(\boldsymbol{x})|_{\boldsymbol{x}=\boldsymbol{x}^{(0)}}$ and the Hessian $H=H(V(\boldsymbol{x}))|_{\boldsymbol{x}=\boldsymbol{x}^{(0)}}=[\{\partial^2V(\boldsymbol{x})/(\partial x_i\partial x_j)\}_{ij}]_{\boldsymbol{x}=\boldsymbol{x}^{(0)}}$ of the volume. We note that derivatives of the volume with respect to the internal parameters vanish, by definition. By providing a systematic treatment of the structural changes induced by the pressure $p=-\partial E/\partial V$ we extract from the minimum of the zero-temperature enthalpy

$$\mathcal{H}(\boldsymbol{x},p)=E(\boldsymbol{x})+pV(\boldsymbol{x}) \tag{2}$$

both the bulk modulus

$$B_0=\frac{V(\boldsymbol{x}^{(0)})}{\boldsymbol{g}^T M^{-1}\boldsymbol{g}} \tag{3}$$

and the bulk modulus pressure derivative

$$B_0'=V(\boldsymbol{x}^{(0)})\frac{3\boldsymbol{g}^T M^{-1}HM^{-1}\boldsymbol{g}-\gamma_{ijl}(M^{-1}\boldsymbol{g})_i(M^{-1}\boldsymbol{g})_j(M^{-1}\boldsymbol{g})_l}{(\boldsymbol{g}^T M^{-1}\boldsymbol{g})^2}-1. \tag{4}$$

The algorithm outlined above can also be applied to the corresponding direct determinations of general harmonic[11,12] and anharmonic elastic properties[13] such as the second- and third-order elastic constants C_{ij} and C_{ijk}.

Our results both enhance the theory understanding of the crystalline mechanical properties and simplify the desired testing of theory calculations as they combine the formal determination of the crystalline structure [Eq. (1)] and of the elastic properties [Eqs. (3) and (4)]. The equilibrium volume, the crystallographic parameters, and the bulk modulus, describing the material's resistance to hydrostatic stress, provide simple experimental tests against which we can compare and calibrate our calculations.[14] For example, from Eqs. (1) and (2), we can directly identify which (internal) structure parameters soften the bulk modulus (3) and we may, in turn, strengthen the materials by suitable chemical or structural modification.

Besides the direct relevance of our results for the description of complex materials, our calculations of bulk structure and bulk modulus calculations are also of interest for development of pseudo-potential-based density-functional-theory (DFT) methods and for methods using empirical parameters. There, a first and critical test of the pseudopotential or the empirical parameters is whether the calculations predict a correct materials structure, binding, and elastic properties for the relevant equilibrium configuration. Present DFT scripts[15] can automate some pseudopotential testing for simple materials and symmetries, our formal results generalize such testing of theory accuracy to cases when multiple structural parameters determine the elastic properties.

The outline of this paper is as follows. In Sec. II we discuss the traditional methods of determining the bulk modulus for single-parameter and multiparameter systems. In Sec. III we derive our expressions for the bulk modulus and the bulk modulus derivative, Eqs. (3) and (4), for the simple one-parameter problem (e.g., monoatomic fcc or bcc structures), easily generalized to the n-parameter problem. In Sec. IV we proceed to illustrate and test the algorithm on a number of monoatomic and diatomic materials based on first-principle DFT calculations and comparison to experiments. Comparisons of B_0 and B_0', together with the test of the lattice and structure parameters themselves, represent the typical test of materials-theory accuracy. Section V contains the conclusion.

II. BACKGROUND

A theory determination of the zero-temperature bulk modulus based on either traditional methods[1,16,17] or our formal result (3) is straightforward when one single structural parameter (e.g., the lattice parameter a) defines the crystalline state. This situation applies for monatomic crystals with simple cubic (sc), face-centered cubic (fcc), and body-centered cubic (bcc) symmetries. Here, the unit-cell volume $V(a)=qa^3$ uniquely determines the lattice parameter a through a dimensionless number q which depends on the crystal symmetry ($q=1$, $q=1/4$, and $q=1/2$ for sc, fcc, and bcc lattices, respectively). All that is required are theory calculations of total energies for a range of a values to determine both the equilibrium structure a_0 and the equilibrium volume $V^{(0)}$. The total energy per unit cell, $E(a)$ [as in Eq. (1)], can then be expressed as a function of the unit-cell volume $E(V)$.

The general approach is illustrated by the example in Fig. 1, which shows the total energy as a function of the lattice parameter a for the zinc-blende phase of SiC (3C-SiC), as found from DFT calculations. A parabola fit to the 15 data points closest to the equilibrium value of a and a fourth-order polynomial fit to all data points are shown. Fits using

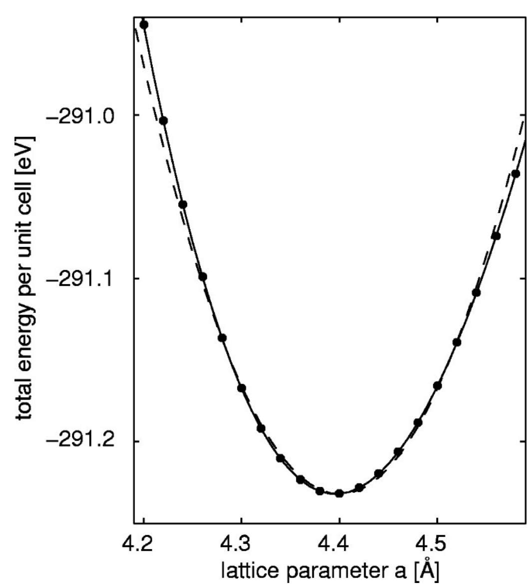

FIG. 1. The total energy per unit cell (two atoms) as a function of the lattice parameter a for the 3C polytype of SiC. The circles are the data points obtained from density-functional-theory calculations. Solid line: Fourth-order polynomial fit as used for the values in Table I. Dashed line: Second-order polynomial fit to the 15 central data points.

TABLE I. Bulk properties calculated from density-functional-theory data obtained directly from Eqs. (3) and (4) via a fourth-order polynomial fit (''Present approach''), available experimental values, and values from fits to Murnaghan's and Birch's equations (5) and (6) along the hydrostatic path. For the internal parameter in $2H$-SiC we find the following value: Si-C distance along the c direction, $u(\text{Si-C})=0.3752c$ or bond length $\ell_{\text{bond}}=1.9031$ Å. [Experiments find[19] $u(\text{Si-C})_{\text{exp}}=0.3760c$, $(\ell_{\text{bond}})_{\text{exp}}=1.8998$ Å] For $4H$-SiC we find $u(\text{Si-C})_1=0.1880c$, $u(\text{Si-C})_2=0.1874c$, $u(\text{Si-Si})=0.2500c$, in good agreement with the calculated values by Bauer *et al.* (Ref. 20), $u(\text{Si-C})_1=0.1881c$, $u(\text{Si-C})_2=0.1874c$, and $u(\text{Si-Si})=0.2500c$. A change of pseudopotentials in Ref. 20 from Bachelet-Hamann-Schlüter type[21] to ultrasoft Vanderbilt pseudopotentials[22] gave the following values for the interatomic distances: $u(\text{Si-C})_1=0.1880c$, $u(\text{Si-C})_2=0.1875c$, and $u(\text{Si-Si})=0.2500c$.

		Present approach				Experiment				Murnaghan		Birch	
		a_0 [Å]	c/a	B_0 [GPa]	B_0'	a_0 [Å]	c/a	B_0 [GPa]	B_0'	B_0 [GPa]	B_0'	B_0 [GPa]	B_0'
Co	fcc	3.531		218	4.80			188.9 [a]		214	4.47	216	4.65
	bcc	2.817		206	5.09					199.4	4.90	205	4.95
	hcp	2.500	1.617	223	4.70	2.507 [b]	1.623 [b]	190.3 [a]	5.07 [c]	217	4.52	219	4.61
SiC	$3C$	4.376		213	3.93	4.3596 [d]		224 [e]	4.0 [f]	212	3.87	213	3.91
	$2H$	3.089	1.642	213	3.92	3.079 [g]	1.641 [g]	223 [h]		208	3.74	211	3.86
	$4H$	3.092	3.274	213	3.93	3.073 [d]	3.271 [d]			212	3.78	213	3.89
C	Diamond	3.565		436	3.71	3.567 [i]		442 [i]	4.07 [j]	432	3.72	435	3.70
Si	Diamond	5.466		88.7	4.35	5.431 [i]		98.8 [i]	4.09 [k]	87.7	4.20	88.3	4.28

[a]Reference 23.
[b]Reference 24.
[c]Reference 25.
[d]Reference 26.
[e]Reference 27.
[f]Reference 28.
[g]Reference 19.
[h]Reference 29.
[i]Reference 30.
[j]Reference 31.
[k]Reference 32.

the traditional Murnaghan equation of state,[16] integrated to give

$$E_{\text{Murn}}(V)=-E_0+\frac{B_0V}{B_0'}\left[\frac{(V^{(0)}/V)^{B_0'}}{B_0'-1}+1\right]-\frac{V^{(0)}B_0}{B_0'-1} \quad (5)$$

or the Birch equation of state,[17] integrated to give

$$\begin{aligned}E_{\text{Bir}}(V)=&-E_0+\frac{9}{8}B_0V^{(0)}[(V^{(0)}/V)^{2/3}-1]^2\\&+\frac{9}{16}B_0V^{(0)}\{B_0'-4\}[(V^{(0)}/V)^{2/3}-1]^3\\&+O[(V^{(0)}/V)^{2/3}-1]^4,\end{aligned} \quad (6)$$

yield, to the eye, curves identical to the fourth-order polynomial fit and are not shown separately. In Murnaghan's and Birch's equations (5) and (6) the quantities B_0, B_0', and $V^{(0)}$, and in some cases also the cohesive energy E_0, are fitted. Other equations of state traditionally used are mentioned in Refs. 1 and 17.

The values of the equilibrium lattice parameter a_0, and of B_0 and B_0' obtained from Eqs. (3) and (4) and from the Murnaghan and Birch fits are included in Table I. Equations (5) and (6) give bulk moduli and bulk modulus derivatives in close agreement with our present direct approach, Eqs. (3) and (4).

We would like to stress that the moduli B_0 and B_0' are formally defined as zero-pressure quantities, and in no way depend on finite-pressure behavior beyond the pressure gradient at $p=0$. If we are able to sample our theory system in a sufficiently dense grid around the zero-pressure structure the values of V_0, B_0, and B_0' in Eqs. (3) and (4) are exact, and can be related to the corresponding exact determination of the elastic constants. Fits to empirical EOS may yield results of V_0, B_0, and B_0' that are in good agreement with experimental observations, but do not *necessarily* ensure a correct determination of the exact quadratic response.

For materials with multiple structure parameters, the procedure of the traditional approaches further becomes quite awkward as it must be supplemented by a separate discussion of how the experimental conditions define the relevant structural constraint at a given volume, the hydrostatic path $\boldsymbol{x}=\boldsymbol{x}(V)$. Moreover, cross-correlations on the n-dimensional energy surface are ignored in traditional fitting procedures. These procedures are basically a one-dimensional fit in the n-dimensional space and they are thus more subject to numerical noise in the data points than our approaches based on the multidimensional least-squares polynomial fit (1).[2]

A simple multiparameter case illustrates this point. Figure 2 both describes the energy surface, Eq. (1), fitted through DFT calculations for Co, and shows the hydrostatic path which must be determined explicitly in the traditional methods.[1,16,17] Our direct approach [Eqs. (3) and (4)] does not require this explicit determination of the hydrostatic path. Materials like Co, which have a nonideal hexagonal-close-packed (hcp) structure, graphite with its layered structure, or the polytypes of SiC (Ref. 2) or alumina,[6] have multiple lattice parameters (plus relevant internal degrees of freedom) which are, of course, no longer uniquely specified by the

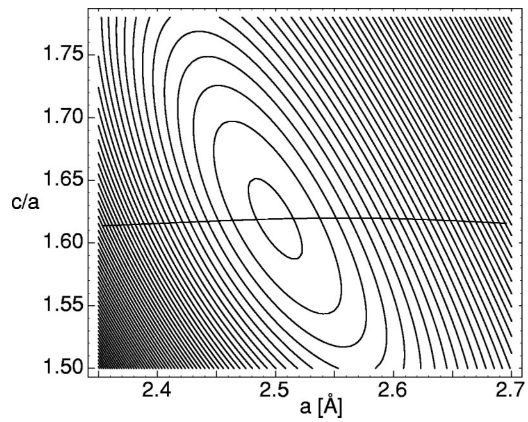

FIG. 2. Contour plot of the fourth-order polynomial fit to the Co hcp total energy, including the hydrostatic path. The hcp unit cell is given by the two independent lattice parameters a and c/a. The contour step is 0.025 eV per unit cell (two atoms).

volume but depend on the general materials conditions. The hydrostatic path defines the system when subject to uniform pressure (as relevant for the bulk modulus measurements). The traditional approaches[16,17] proceed by implementing this complex constraint in the equation of state, Eq. (5) or Eq. (6), to fit the bulk modulus and its derivative. Instead, we present an explicit determination, Eqs. (3) and (4), based directly on Eq. (1) expressed as a function of the underlying crystalline structural parameters.

III. DERIVATION

Our direct bulk modulus evaluations, Eqs. (3) and (4), are the results of using the pressure (instead of the volume) in a formal identification of the hydrostatic path and then invoking a systematic expansion in small pressure for an explicit specification of B_0 and B_0'. Today DFT and other materials-theory bulk calculations are done with high accuracy, and we need only to vary the lattice parameters values slightly around the optimal structure to approximate the total-energy curve by an accurate polynomial fit, Eq. (1). The minimum of the corresponding (zero-temperature) enthalpy (2) can thus be used to directly specify the physically correct structural configuration at any given pressure p. The set of these optimal structure-parameter values, $\boldsymbol{x}_{\text{hydro}}(p)$, traces out the hydrostatic path which, when parametrized by p, is obtained by simply solving the equation

$$\nabla \mathcal{H}(\boldsymbol{x},p) = \nabla E(\boldsymbol{x}) + p \nabla V(\boldsymbol{x}) = 0. \tag{7}$$

We obtain a formal expression for the general (pressure dependent) bulk modulus by taking the derivative along this hydrostatic path

$$B = -V(\boldsymbol{x}_{\text{hydro}}(p)) \left(\frac{\partial V(\boldsymbol{x}_{\text{hydro}}(p))}{\partial p} \right)^{-1}, \tag{8}$$

and finally we extract the explicit results for the zero-pressure bulk modulus B_0 and for its pressure derivative, B_0'.

We illustrate the general derivation by focusing on a one-dimensional parameter space x, e.g., for the fcc or bcc one-atomic structure. Then the total energy can be fitted by the polynomial

$$E(x) = k + \frac{1}{2} M (x - x^{(0)})^2 + \frac{1}{3!} \gamma (x - x^{(0)})^3 + f(x - x^{(0)}) \tag{9}$$

where $f(x - x^{(0)}) = O(x - x^{(0)})^4$ contains higher-order terms. The coefficients k, M, γ, the coefficients of $f(x - x^{(0)})$, as well as the optimal value of the lattice parameter at zero pressure, $x^{(0)}$, are the fitting parameters to be specified, for example, by a set of accurate underlying DFT calculations.

At small pressures, i.e., for lattice and internal parameter values close to the zero-pressure optimal values, the pV term in the enthalpy is small and can be regarded as a perturbation of the system. To proceed we introduce a small, nondimensional and real parameter λ such that we can write the small pressure as $p = \lambda p^{(1)}$ and the lattice-parameter variable as $x = x^{(0)} + \lambda x^{(1)} + \lambda^2 x^{(2)} + O(\lambda^3)$. The variables $x^{(1)}$, $x^{(2)}$, ... are unknown, are functions of the pressure, and must be found in the following.

The bulk modulus expression requires calculation of the volume $V(x)$ and its pressure derivative. We write the volume in a Taylor expansion around the zero-pressure solution $x^{(0)}$ as

$$V(x) = V(x^{(0)}) + \lambda g x^{(1)} + \lambda^2 \left(x^{(2)} g + \frac{1}{2!} (x^{(1)})^2 H \right) + O(\lambda^3) \tag{10}$$

with $g = dV/dx|_{x=x^{(0)}}$ and $H = d^2V/dx^2|_{x=x^{(0)}}$. Here, the pressure dependence enters through the variables $x^{(1)}$, $x^{(2)}$, ... The pressure derivative of the volume is thus

$$\frac{\partial V(x)}{\partial p} = g \frac{\partial x^{(1)}}{\partial p^{(1)}} + \lambda \left(g \frac{\partial x^{(2)}}{\partial p^{(1)}} + \frac{\partial x^{(1)}}{\partial p^{(1)}} H x^{(1)} \right) + O(\lambda^2) \tag{11}$$

and we determine the variables $x^{(1)}$, $x^{(2)}$, ... by solving the condition on the enthalpy given by Eq. (7):

$$0 = \lambda (M x^{(1)} + p^{(1)} g) + \lambda^2 \left(M x^{(2)} + \frac{1}{2} \gamma (x^{(1)})^2 + p^{(1)} H x^{(1)} \right) + O(\lambda^3). \tag{12}$$

The identity (12) must hold for every order and we thus obtain a formal pressure dependence of the lattice parameter:

$$x^{(1)} = -p^{(1)} M^{-1} g, \tag{13}$$

$$x^{(2)}=(p^{(1)})^2\left\{M^{-1}HM^{-1}g-\frac{1}{2}M^{-1}\gamma M^{-1}gM^{-1}g\right\}. \tag{14}$$

Finally, introducing these solutions into Eq. (11) we find for $\lambda=0$ the isothermal zero-pressure bulk modulus

$$B_0=-V(x^{(0)})\left(\frac{\partial V}{\partial p}\right)^{-1}_{x=x^{(0)}}=\frac{V(x^{(0)})}{gM^{-1}g}, \tag{15}$$

and taking the derivative of $-V(\partial V/\partial p)^{-1}$ with respect to $p=\lambda p^{(1)}$ we find at $\lambda=0$,

$$B_0'=V(x^{(0)})\frac{3gM^{-1}HM^{-1}g-\gamma M^{-1}gM^{-1}gM^{-1}g}{(gM^{-1}g)^2}-1, \tag{16}$$

in the case when one (lattice) parameter suffices to describe the unit cell and its atom basis.

The above derivation is straightforwardly generalized to materials systems in which n independent lattice and internal parameters determine the structure and the bulk moduli Eqs. (3) and (4), which is our main result. Thus, given a multidimensional fit (1) to the data, B_0 and B_0' can be evaluated directly from the expressions (3) and (4). We stress that B_0 and B_0' are evaluated at zero pressure and thus the results are exact in spite of the perturbation. B_0 depends directly on the second order and B_0' on the second and third order coefficients of the energy fit (M and γ). We observe that the coefficients of $f(x-x^{(0)})$ [as defined in Eq. (9)] do not enter the expression for the bulk modulus (3) or the pressure derivative of the bulk modulus (4). However, their presence may improve the fit (9), and thereby affect also the coefficients M and γ, and thus B_0 and B_0'. Internal parameters, which describe the positions of the atoms within the unit cell, naturally do not enter the expression of the volume, and thus not the volume derivatives $\boldsymbol{g}$ and H either, but do affect B_0 and B_0' through M^{-1}.

Higher pressure derivatives of the bulk modulus may be found by taking into account the higher orders of λ in the Taylor expansions of $\boldsymbol{x}$ and the volume. The pressure derivatives will depend on successively higher orders in the polynomial fit. The derivation is straightforward if somewhat tedious.

IV. EXAMPLES OF APPLICATIONS

As an example of the use of the algorithm for determining B_0 and B_0' we evaluate the structure and bulk modulus of a selection of one- and two-species materials. We fit data obtained from DFT calculations, described in further detail below, to fourth-order polynomials of the form (1) in n-dimensional space, where $n=1$, 2, 3, or 5.

The pseudopotentials used in DFT calculations may be optimized for various purposes, but should generally yield consistent and transferable accuracy and results. Here, we have used some of the predefined pseudopotentials[18] of the open-source DFT program DACAPO.[15] The values that we find for the lattice constants, for B_0, and for B_0', are collected in Table I. For reference, the experimental values are also included, as well as the bulk moduli from a Murnaghan and Birch fit along the hydrostatic path.

We have calculated the structure and bulk modulus for three multiparameter systems, as well as for a number of related one-parameter systems: the two-parameter hcp phase of Co, the three-parameter (one internal) wurtzite phase of SiC ($2H$), the five-parameter (three internal parameters) hexagonal $4H$ polytype of SiC, and the one-parameter bcc and fcc phases of Co, the zinc-blende ($3C$) phase of SiC and the diamond phases of C and Si.

For the DFT calculations we used the plane-wave DACAPO code[15] with the generalized gradient approximation. For the calculations of the $2H$ and $4H$ polytype of SiC we used $8\times8\times8$ and $8\times8\times4$ k points, respectively, to describe the Brillouin zone. For all other calculations $10\times10\times10$ k points were used. A uniform energy cutoff of 400 eV, and a conservative choice of fast-Fourier transform grid was used. For each evaluation of the optimal structure we calculated by DFT a number of data points for the lattice parameter(s) approximately within $\pm10\%$ from the expected optimal value(s) of the lattice parameter(s). In the one-parameter systems we calculated 20–30 data points, for the Co hcp structure 120 data points, for the $2H$ polytype of SiC 140 data points, and for $4H$-SiC we calculated 7500 data points. The Co calculations were spin-polarized, yielding realistic values of the spin polarization over the range of lattice-parameter values considered here.

The traditional method that involves finding the structural minimum first, then determining the hydrostatic path, and then from a fit to the hydrostatic path reading off the bulk modulus and the bulk modulus pressure derivative, in principle needs the same number of total-energy calculations as the method presented here, but the latter gives numerically more accurate results. With the same set of total-energy calculations as input (for example, p^n data points for an n-parameter system) the bulk moduli can be calculated either way. However, finding the local energy variation is more accurately done by one n-dimensional fit to all p^n data points, as in the present method, than the traditional method of using p separate $(n-1)$-dimensional fits each to $p^{(n-1)}$ data points, followed by one one-dimensional fit to the approximate minima of those p fits. This last one-dimensional fit is often semiempirical (Murnaghan, Birch, or similar). Thus, in addition to being conceptually more correct than the traditional method, our method also provides numerically more accurate results.

The possibility of treating the external and internal parameters collectively is important. For example, the variation of internal bond length with pressure might be as important for the total energy as the change in (external) lattice parameters. Often, relaxation of the internal parameters is done with a steepest-descent (or similar) search minimizing the Hellmann-Feynman forces to a certain cutoff at fixed lattice parameters. Although in practice the atomic relaxation will often be a convenient way of obtaining the optimal position of the atoms within the unit cell, the approach has two shortcomings: it introduces a random residual lattice strain, which in turn affects the total energy, and further, the Hellmann-

Feynman forces have a nontrivial dependence on the pressure acting on the unit cell and therefore a constant cutoff on the force will not correspond to a constant accuracy of the total energy with varying pressure. Thus a better accuracy—and a consistent choice of accuracy—can be obtained by treating the lattice and internal parameters on an equal footing. This is here done for the $2H$ and the $4H$ polytype of SiC. The results are shown in Table I. For the Murnaghan and Birch values of B_0 and B_0' we need to explicitly calculate the hydrostatic path [in $(a,c/a,u)$ and $(a,c/a,u_1,u_2,u_3)$ space] before obtaining the fit. In contrast, we stress that when using Eqs. (3) and (4) there is no need to explicitly calculate the hydrostatic path, which is here done purely for illustrational purposes.

V. CONCLUSION

In summary, we have presented a direct algorithm for a combined determination of structure and bulk moduli B_0 and B_0'. The lattice constants of a multiparameter system are best found in a least-squares polynomial fit, as previously noticed for the SiC hexagonal polytypes.[2] We show (a) how to exploit this polynomial fit for a direct determination of the zero-pressure bulk modulus B_0 and its pressure derivative B_0', avoiding the calculation of the hydrostatic path and the subsequent one-dimensional fit to this path. We further show (b) how to consistently include internal parameters, such as bond lengths or bonding angles, in the formalism along with the external lattice parameters. In addition, we have evaluated these formal results in explicit cases within our approach, based on DFT calculations.

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*Corresponding author.
Electronic address: schroder@fy.chalmers.se

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