Efficient parametrization of high-pressure elasticity

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Since high-pressure physics quite generally involves large deformations, it usually calls for a fully nonlinear description taking physical as well as geometrical nonlinearities (finite strains) accurately into account. In a recent paper [A. Tröster, W. Schranz, and R. Miletich, Phys. Rev. Lett. 88, 55503 (2002)], as a by-product of formulating a Landau theory of high-pressure phase transitions, we have constructed a parametrization of the elastic behavior of crystals of cubic, tetragonal, or orthorhombic symmetry which is customized to purely hydrostatic stresses. Under plausible assumptions this parametrization allows one to simultaneously describe the pressure dependence of the crystal lattice parameters and elastic constants in terms of comparatively simple expansions in powers of the pressure which involve a much smaller number of parameters than needed in, e.g., an approach using nonlinear elastic constants of higher order. In addition, the resulting formulas give rise to certain consistency checks for a set of unit cell parameters and elastic constants, which any such set—obtained from experiments or computer simulations—has to pass without approximation. However, the validity of our assumptions remained to be checked against experimental data. In this work we present detailed derivations of the approach sketched in the paper cited above and show that it can be successfully applied to describe data of recent high-pressure experiments on olivine, fluorite, garnet, magnesium oxide, and stishovite.

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I. INTRODUCTION

Our understanding of materials (minerals, molecular crystals, liquid crystals, complex liquids, biological membranes, etc.) at extreme conditions such as ultrahigh pressures has substantially increased due to the development of in situ diffraction methods. Over the last two decades great effort has been made to measure the elastic properties of materials up to extreme pressures.2 Specifically, the diamond anvil cell for x-ray diffraction allows the determination of the structure and unit cell parameters to pressures up to several tens of gigapascals routinely in the laboratory. Powder diffraction methods using synchrotron radiation can nowadays3 be performed up to more than 200 GPa.4 Clearly such experiments are essential for an understanding of the Earth’s bulk properties, as an accurate knowledge of general material properties both at ambient states and at extremely high pressures and temperatures is important in this context. Also, the behavior of the elements under pressure has been increasingly studied in recent years.5–7 For minerals, there exists a variety of phase transformations, in particular for the case of the group-IV elements. Extensive work has been done for these materials, especially measuring their $P$–$V$ behavior. For an excellent review see Ref. 8.

The theory of elasticity at high pressures is quite involved because of the importance of geometrical and physical nonlinearities. At sufficiently high pressures the pressure behavior of the unit cell volume and lattice parameters starts to develop deviations from simple linear laws. As the volume of a solid becomes smaller the interatomic forces opposing further compression increase. Experimentally, the accessible data frequently allow one to determine the dependence of the crystal’s unit cell parameters $a_i(P)$, $i = 1, 2, 3$, or at least the unit cell volume $v(P)$, on an externally applied hydrostatic pressure $P$, from which the isothermal compressibility $\kappa(P) = -d \log v(P)/dP$, which characterizes the “stiffness” of any solid, can be computed. It is much more difficult to measure the pressure dependence of the complete set of elastic constants. However, such measurements have nowadays been undertaken in a broad pressure range, reaching sometimes beyond 100 GPa for hydrostatic pressure. Yet, systems where the lattice parameters $a_i(P)$ and the Birch coefficients $B_{ij}(P)$ or compliances $S_{ij}(P)$ have been measured under extreme (hydrostatic) pressure are still scarce. In fact, one might ask what—apart from theoretical interest—drives the motivation to study the pressure behavior of individual elastic tensor components. On the one hand, very interesting new insights into high-pressure physics can be gained from computer simulations,9 in which, along with the pressure dependence of the lattice parameters, the elastic tensor components are frequently computed. On the other hand, knowledge of the individual elastic tensor components is crucial in a theoretical description of many high-pressure phase transitions (HPPT’s). In fact, suppose first that no phase transition occurs in a certain pressure interval $[0, P_c]$. Then the hydrostatic pressure dependence of the crystal’s volume $V(P)$ can frequently be fitted to a so-called equation of state (EOS). Of course, the particular type of EOS used depends on the physical details of the system, and in fact various theoretical concepts can be employed to derive an appropriate EOS,10–12 including universality arguments, somewhere a particular form of intermolecular potential or pressure dependence of $\kappa(P)$ and so on. In presence of a HPPT at a critical pressure $P_c$, anomalies usually appear in the pressure dependence of at least one of the lattice parameters $a_i(P)$, $i = 1, 2, 3$, often resulting in an anomaly of $v(P)$ around $P_c$. Frequently, the measured pressure dependence of the volume is simply fitted to a number of differently parametrized EOS’s for each phase.5,6,11 Admittedly, this procedure seems to fit experimental volume data in many cases, and for many strongly first-order phase transitions of reconstructive nature this is probably the best one can do. However, a vast number of
HPPT’s should allow for a more detailed theoretical analysis. Quite obviously, the above piecewise EOS approach is not the best framework to tackle these problems and insufficient for understanding the pressure behavior of individual strain components. A more profound theoretical approach is therefore of vital interest to a broad audience reaching from physicists studying the high-pressure behavior of materials (crystals, liquid crystals, complex liquids, biological membranes, etc.), and would nevertheless also be of considerable interest to, e.g., geologists investigating the Earth’s minerals and bulk properties.

The objective of the theory presented in Ref. 1 was to gain insight into the mechanism of HPPT’s of the group-subgroup type by a Landau type of approach, taking into account its microscopic origin or the symmetry changes involved. Calculating the system’s response within such a theory clearly calls for a tensorial description. In constructing this theory, it was clear from the start that, since the total resulting deformations are large and the externally applied pressures can be of the order of the size of the elastic tensor components, infinitesimal elasticity would be ill designed to describe such HPPT’s. The spontaneous strain resulting from the emergence of a nonzero order parameter is defined with respect to the background reference frame of the “clamped” or “bare” system, which is the hypothetical system resulting from forcing the order parameter to remain zero. While the clamped system may involve a large nonlinear deformation with respect to the zero-pressure state, the spontaneous strain, which is defined in the reference frame of the clamped system, should allow an infinitesimal elastic treatment, in particular in the vicinity of the transition which is close to a continuous one. The applicability of the theory constructed in Ref. 1 therefore rests on a rather precise knowledge of the elastic behavior of the clamped background system. In particular, precise information on the \( P \) dependence of the individual compliance tensor components \( S_{ij}(P) \) is mandatory.

As far as the volume-pressure behavior of the background system is concerned, its nonlinearity is usually reflected in the pressure evolution of the corresponding EOS, \( V=V(P) \). A possible way of dealing with the corresponding nonlinearities is to expand the system’s elastic Helmholtz free energy in powers of the Lagrangian strain tensor \( e \) beyond the harmonic approximation. However, it was realized in Ref. 1 that this approach is not very promising for any attempts to describe hydrostatic or almost hydrostatic conditions. In fact, one should keep in mind that for a hydrostatic situation the higher-order nonlinear elastic constants, whose knowledge allows computation of the system’s response to \( \epsilon \) arbitrary deformations, contain much more information than required. In turn, this means that an imposed hydrostatic volume-pressure behavior places extremely complicated restrictions and interdependencies on the corresponding collection of tensor components. From a practical point of view, depending on the basic symmetry of the system, just by including terms up to fourth order in the strain, such an approach generally calls for introducing a large number of unknown third- and higher-order elastic constants. We are therefore faced with a vast number of unknown fit parameters, which are moreover far from being independent of one another, as they collectively should produce the prescribed volume-pressure behavior. The resulting description is, to say the least, extremely cumbersome in practical applications.

For these reasons in Ref. 1 the above approach was replaced by one that was designed to be well suited to problems dealing with systems subject to hydrostatic pressures. We illustrate the idea by a geometric analogy. In principle, one would agree that any three-dimensional geometrical problem can be correctly described using coordinates defined by an arbitrary set of three linearly independent base vectors and an arbitrary choice of its origin. However, for spherically symmetric objects, these coordinates are clearly inadequate, and the resulting coordinate interdependencies are generally so cumbersome that they might not even allow to recognize the underlying “hidden” spherical symmetry. Now consider the case of applied hydrostatic pressure as opposed to arbitrary stress. Quite obviously, to reduce the redundancy of the description, for pressures that do not deviate too far from the hydrostatic regime, one should try to expand the elastic properties around a “generic” hydrostatically compressed reference state, which is chosen to resemble the simplest choice of elastic tensor components which comply to the given volume and axes behavior. As we will show, this background state is uniquely determined purely from the knowledge of the zero-pressure elastic constants and the pressure dependence of the unit cell parameters. Of course, this still leaves plenty of room for the actual behavior of the elastic tensor components. Nevertheless, except in the vicinity of a phase transition, it should be possible to expand these residual tensor deviations in simple Taylor series with respect to \( P \). In applying the resulting theory, this raises the question of where to truncate such an expansion without producing large errors. A natural assumption made in Ref. 1 was that truncation is possible at low (linear or quadratic) orders. It is one of the purposes of the present work to test the validity of this additional hypothesis in a comparison to recent experimental data.

The paper is organized as follows. In Sec. II we introduce the basic notations for the quantities of nonlinear elasticity which will be used subsequently. While the reader should refer to classic textbooks, e.g., Refs. 14–17, for a more complete presentation of general nonlinear elasticity, the derivation of the formulas which we intend to check experimentally is reviewed in a complete and self-contained way and in considerably more detail than was possible in Ref. 1 due to space limitations. We add particular emphasis to the difference between a system’s Birch coefficients and elastic constants which start to play an important role at high pressure. The remaining part of this work is devoted to the comparison of these formulas to a wide range of experimental data. The paper ends with a discussion of the results.

II. NOTATION AND THEORY

The notation used in this work closely follows that of Ref. 1, which can also be consulted for details that are omitted here because of a slightly different focus of the present paper. Nevertheless, for the reader’s convenience below we list the central ingredients used in the subsequent discussion. Let us denote by \( \alpha = (\alpha_{ik}), i,k=1,2,3 \), the matrix of deformation...
gradients. The corresponding Lagrangian strain tensor is defined by \( \varepsilon = \frac{1}{2} (\alpha^* \cdot \alpha - 1) \) with components \( \varepsilon_{ik} = \frac{1}{2} (\Sigma_{n} \alpha_{ni} \alpha_{nk} - \delta_{ik}) \). A deformation is called homogeneous, if all coefficients \( \alpha_{ik}(X) = \alpha_{ik} \) are constants, which is the case we will focus on below. The tensor \( \tau \) of stresses induced by the strain \( \varepsilon \) relative to the undeformed reference state accompanying the deformation, which is physically measured in the deformed state, is known as the Cauchy stress and is isothermally calculated from the free energy \( F(\dot{\varepsilon}) \) in the deformed state as

\[
\tau_{ij} = \frac{1}{V} \frac{\partial F(\dot{\varepsilon})}{\partial \dot{\varepsilon}_{ij}} \bigg|_{\dot{\varepsilon}=0},
\]

(1)

where the Lagrangian strain \( \dot{\varepsilon} \) characterizes a further deformation with respect to the deformed state. Taking an expansion of \( F(\dot{\varepsilon}) \) to second order in \( \varepsilon \) we obtain the elastic constants

\[
C_{ijkl} := \frac{1}{V} \frac{\partial^2 F(\dot{\varepsilon})}{\partial \dot{\varepsilon}_{ij} \partial \dot{\varepsilon}_{kl}} \bigg|_{\dot{\varepsilon}=0}.
\]

(2)

This yields the Taylor series

\[
F(\dot{\varepsilon}) = V \left( \sum_{ij} \tau_{ij} \dot{\varepsilon}_{ij} + \frac{1}{2} \sum_{ijkl} C_{ijkl} \dot{\varepsilon}_{ij} \dot{\varepsilon}_{kl} + O(\dot{\varepsilon}^3) \right).
\]

(3)

Higher-order elastic constants are defined similarly. A Cauchy stress \( \tau \) is said to exert hydrostatic pressure \( P \) if it is diagonal with \( \tau_{ij} = -P \delta_{ij} \). More generally, the hydrostatic component of a Cauchy stress \( \tau \) and its corresponding traceless deviatoric stress \( \tilde{\tau} \) will be defined by \( \tau = -(1/3) \text{tr} \tau \) and \( \tilde{\tau} = \tau + \hat{\tau} \). A Cauchy stress \( \tau \) is termed uniaxial along the axis \( k \) if it can be written \( \tau_{ij} = -P \delta_{ij} \delta_{jk} \) for a suitable choice of rectangular coordinates.

Next we recall the dependence of the Cauchy stress \( \tau \) on the Lagrangian strain \( \varepsilon \). To first order in the strain \( \varepsilon \), one has the classical result

\[
\Delta \tau_{ij} = \sum_{kl} B_{ijkl} \Delta \varepsilon_{kl} + O(\Delta \varepsilon^2),
\]

(4)

where \( \Delta \tau_{ij} \) is the difference in Cauchy stresses of the further deformed system from “background” deformed system and the quantities

\[
B_{ijkl} = C_{ijkl} + \Delta_{ijkl}
\]

(5)

with

\[
\Delta_{ijkl} = \frac{1}{2} \left( \tau_{ij} \delta_{kl} + \tau_{ik} \delta_{jl} + \tau_{il} \delta_{jk} - 2 \tau_{ij} \delta_{kl} \right)
\]

(6)

are the Birch coefficients. Note that these are symmetric under the exchange \( i \leftrightarrow j \) and \( k \leftrightarrow l \) and therefore can be written in Voigt notation. However, except for hydrostatic stress \( \tau_{ij} = -P \delta_{ij} \) the resulting Voigt matrix \( B_{ij} \) is generally not symmetric, as the Birch coefficients are manifestly not symmetric under the index pair exchange \((ij) \leftrightarrow (kl)\).

Equation (4) can be formulated in a differential way as

\[
\frac{\partial \tau_{ij}}{\partial \varepsilon_{ij}} \bigg|_{\varepsilon=0} = B_{ijkl}.
\]

(7)

The inverse Birch coefficients, which obey the relations

\[
\sum_{mn} B_{ijmn} S_{mnkl} = \frac{1}{2} (\delta_{ik} \delta_{jl} + \delta_{ij} \delta_{kl})
\]

(8)

and are known as the compliances \( S_{ijkl} \), can consequently also be written in Voigt notation. In the background reference system therefore Hooke’s law

\[
\frac{\partial \delta_{ij}}{\partial \tau_{ij}} \bigg|_{\tau=0} = S_{ijkl}
\]

(9)

holds. Two comments are in order here. First of all, although the content of the preceding derivations is classic and known to theorists for many decades, it is our impression that the appearance of the Birch coefficients instead of the elastic constants in Hooke’s law at finite deformations is still widely overlooked by quite a number of researchers doing high-pressure experiments and computer simulations. The reason for this is obvious from a glance at Eqs. (4)–(6). Suppose that one studies a crystal subject to a hydrostatic pressure \( P \). Then probing Hooke’s law in the corresponding state amounts to measuring the system’s Birch coefficients. In particular this is true for Brillouin scattering measurements, in which the sound velocities are measured for various wave vector directions and polarizations. In the underlying wave equation, at general “background stress” \( \tau \), these velocities are determined by the so-called Huang tensor (see Ref. 15). However, in the case of hydrostatic pressure, the resulting expressions can be shown \( ^{15} \) to be formally identical to those determining the sound velocities in infinitesimal elasticity theory, the Birch coefficients simply replacing the elastic constants. We therefore emphasize that in a Brillouin scattering experiment it is also the Birch coefficients that are determined.

Inspecting the above formulas, we see that the error introduced by accidently confusing \( C_{ijkl} \) and \( B_{ijkl} \), represented by the tensor \( \Delta_{ijkl} \), is linear in \( P \). Bearing in mind that elastic constants in real crystals are of an order of several hundred gigapascals, the difference will therefore only be negligible for experiments in a pressure regime well below these values. However, as soon as the experimentally (or computationally) imposed pressure approaches the order of magnitude of the elastic constants, the distinction of \( C_{ijkl} \) and \( B_{ijkl} \) is of vital importance to obtain a correct interpretation of both computer and experimental data when evaluating Hooke’s law. Theoretically this is related to the fact that it is not the Cauchy stress \( \tau \) that is thermodynamically conjugate to a given deformation \( ^{18} \) but the so-called \( ^{15} \) Piola-Kirchhoff stress \( T_{ij} \) measured with respect to the zero-stress “laboratory” reference state, which is identical to the physically measured Cauchy stress only for infinitesimal deformations.

Finally we recall the definition of the compressibility

\[
\kappa(P) := -\frac{1}{V} \frac{\partial V}{\partial P}
\]

(10)

and record its relation to the compliance coefficients \( ^{15} \)
\[ \kappa(P) = \sum_{i,j=1,2,3} S_{i,j} = \sum_{\alpha,\beta=1,2,3} S_{\alpha\beta}. \] (11)

Its inverse \( K(P) = \frac{1}{\kappa(P)} \) is known as the bulk modulus. We will use the abbreviations \( \kappa_0 = K_0 = \kappa(0) \). Notice that the Voigt indices \( \alpha, \beta=4,5,6 \) do not appear in the above. In what follows we will deal exclusively with crystals of cubic, tetragonal, or orthorhombic symmetry under hydrostatic pressure. Shear degrees of freedom, being invisible to the volume, will therefore be excluded from our considerations.

### A. Birch coefficients and equations of state

High-pressure volume data are usually fitted to an equation of state. Examples include the Murnaghan EOS, the Birch-Murnaghan EOS, or the Vinet EOS. Suppressing a (usually small) temperature dependence, a generic EOS may be written in the form \( V = V(P) \). However, even for such simple symmetry classes as tetragonal or orthorhombic crystals it is quite obvious that from the volume behavior alone it is not possible to obtain a unique pressure dependence of the individual crystal unit cell parameters \( a, b, c \), not to mention that of its Birch coefficients \( B_{ij}(P) \). A partial simplification is offered by cubic systems. In this case, there is only a single unit cell parameter \( a = a(P) \) which is therefore uniquely nailed down to \( a(P) = \frac{V(P)}{V(0)} \) by symmetry. From this we read off the diagonal Lagrangian strains \( e_i[P] = e_i[P] \delta_{ij} \) with

\[ e_i[P] = \frac{1}{2} (a_i^2[P] - 1) = \frac{1}{2} [v^{2/3}(P) - 1], \] (12)

where \( v(P) := V(P)/V(0) \) denotes reduced volume. Differentiation yields

\[ \kappa(P) = -\frac{1}{v(P)} \frac{\partial v(P)}{\partial P} = -\frac{1}{a_1^3(P)} \frac{\partial a_1^3(P)}{\partial P} = -3 \frac{\partial \ln a_1(P)}{\partial P}, \] (13)

which is solved by

\[ a_1(P) = e^{-\kappa(P)/3}. \] (14)

But by symmetry in cubic systems

\[ \kappa(P) = 3[S_{11}(P) + 2S_{12}(P)] = 3S_1(P). \] (15)

We conclude that for cubic symmetry the row sum \( S_{11}(P) + 2S_{12}(P) \) of the compliance matrix, which is equal to the axial compressibility

\[ \kappa = -\frac{\partial \ln a_1(P)}{\partial P}, \] (16)

is completely determined from knowledge of \( v(P) \). We conclude that, given \( v(P) \) and the zero-pressure elastic constants \( C_{11}(0), C_{12}(0) \) which are usually known, all smooth functions \( S_{11}(P), S_{12}(P) \) that satisfy the conditions

\[ S_{11}(P) + 2S_{12}(P) = \frac{\kappa(P)}{3}, \] (17a)

\[ S_{11}(P) - S_{12}(P) > 0, \] (17b)

represent possible compliances of cubic systems at hydrostatic pressures \( P \). Obviously these equations do not determine a unique solution for \( S_{11}(P), S_{12}(P) \). The “canonical” possibility to satisfy these equations is

\[ S_{11}(P) = \frac{\kappa(P)}{\kappa_0} S_{11}(0), \quad S_{12}(P) = \frac{\kappa(P)}{\kappa_0} S_{12}(0). \] (18)

As a possible parametrization of the general solution we write

\[ S_{1\beta}(P) = \frac{\kappa(P)}{\kappa_0} [(S_{1\beta}(0) + \kappa_1 \beta(P))], \quad \beta = 1, 2, \] (19)

where the reduced compliances \( \kappa_1^*(P), \kappa_2^*(P) \) have to satisfy the single constraint

\[ \kappa_1^*(P) + 2\kappa_2^*(P) = 0 \quad \forall P. \] (20)

Probably the best one can do at this point is to set up a Taylor expansion for

\[ \kappa_1^*(P) = -2\kappa_2^*(P) = \sum_n \kappa_1^n P^n \] (21)

since the corrections to the canonical \( P \) dependence are expected to be smooth.

### B. Generalization to tetragonal and orthorhombic systems

Things are slightly more subtle in the tetragonal and orthorhombic cases, since the different components \( a_i(P) \) are not constrained to be identical by symmetry any longer. However, for hydrostatic pressure we are still able to deduce the most general form of \( S_{ij}(P) \) from a certain system of partial differential equations, which is deduced for general Cauchy stress \( \tau \). We argue as follows.

Recalling that in the formulation (9) of Hooke’s law, the small quantity \( d\hat{e} \) denotes a differential additional strain measured with respect to the already deformed reference state \( \hat{e} = 0 \) due to the presence of a differential additional stress \( d\tau \). Let \( e_{ij} = e_{ij}[\tau] \) denote the strain of this state measured with respect to the unstrained laboratory state at vanishing Cauchy stress \( \tau = 0 \). By the classical nonlinear superposition formula for strains

\[ e_{ij}[\tau + d\tau] = e_{ij}[\tau] + \sum_{mn} \alpha_{mn}[\tau] \hat{e}_{mn}(d\tau) \alpha_{nj}[\tau] \] (22)

holds for general strains \( \hat{e}_{mn} \) and \( e_{ij} \) and deformations \( \alpha_{ij} \) measured with respect to the laboratory and deformed states, respectively. For \( \alpha_{mn}(s) := \delta_{mn} / \delta \eta_{ss} \) this implies

\[ \frac{\partial e_{ij}[\tau]}{\partial \tau_l} = \frac{d}{ds} \left( e_{ij}[\tau] + \sum_{mn} \alpha_{mn}[\tau] \hat{e}_{mn}(s) \alpha_{nj}[\tau] \right) = \sum_{mn} \alpha_{mn}[\tau] \alpha_{nj}[\tau] \frac{d \hat{e}_{mn}[\alpha(s)]}{ds} \bigg|_{s=0} \] (23)

which by the chain rule expands to
The equations for the three directions are completely decoupled, depending only on the row sums of the upper quadrant of the compliance tensor. Inserting therefore the left-hand sides of these equations represent the axial compressibilities

\[
\kappa_i(P) := -\frac{d \ln \alpha_i(P)}{d P} = S_i(P) \tag{33}
\]

which are thus indeed given by the row sums of the compliance matrix in Voigt notation. Summarizing the situation, as in the cubic case, the quantities \(S_i(P)\) are fully determined once the axis data \(\alpha_i(P)\) are known. In particular, we reobtain

\[
\kappa(P) = -\sum_i \frac{d \ln \alpha_i(P)}{d P} = \sum_{ik} S_{ik}(P) \tag{34}
\]
as it should be. Therefore, also in view of the cubic case considered in the preceding section, we are led to the following ansatz:

\[
S_{ij}(P) = \frac{\kappa(P)}{\kappa_0} [\kappa_0^j + \kappa_0^j(P)], \tag{35}
\]

where \(\kappa_0^j = \kappa_0^j = S_{ij}(0)\), and the reduced compliances \(\kappa_0^j(P)\) are constrained by the relations

\[
\sum_{ij} \kappa_0^j(P) = 0 \quad \forall \ P, \quad \kappa_0^j(0) = 0, \quad i,j = 1,2,3, \tag{36}
\]

which guarantee that \(\kappa(P) = \sum_{ij} \kappa_0^j(P) \forall P\) holds. Comparison of coefficients of the Taylor expansions

\[
\kappa_{ij}^n(P) = \sum_{n=0}^{\infty} \kappa_{ij}^n P^n \tag{37}
\]
in powers of \(P\) yields the conditions

\[
\sum_{ij} \kappa_{ij}^n = 0 \quad \forall \ n \in \mathbb{N}. \tag{38}
\]

Altogether we have

\[
S_{ij}(P) = \frac{\kappa(P)}{\kappa_0} \sum_{n=0}^{\infty} \kappa_{ij}^n P^n \tag{39}
\]

subject to the constraints

\[
\sum_{ij} \kappa_{ij}^n = \begin{cases} \kappa_0, & n = 0, \\ 0, & n = 1,2,3,\ldots. \end{cases} \tag{40}
\]

We also define the corresponding row sums

\[
k_n^j := \sum_{i=1}^{3} \kappa_{ij}^n, \quad n \in \mathbb{N}, \tag{41}
\]

and recognize that

\[
\sum_{i} k_n^j = \begin{cases} \kappa_0, & n = 0, \\ 0, & n = 1,2,3,\ldots. \end{cases} \tag{42}
\]

Notice that up to this point some simplifications due to symmetry were used, but apart from that no approximations were used. Our construction thus represents the most general parametrization of any possible \(P\) dependence of the compliance coefficients of orthorhombic crystals that are in agreement with the given equation of state \(\rho = \rho(P)\) and the set of \(q_2\) zero-pressure non shear elastic constants \(C_{ij}(0)\). From this construction and symmetry arguments it is clear that at each additional power \(n\) of \(P\) this parametrization gives rise to \(q\) unknown coefficients \(k_n^j(P)\). However, since these are subject to the constraints (40), up to order \(n\) there is a total of \((q_2-1)n\) unknown \(\kappa\) parameters.

What have we gained? The answer to this question obviously depends on the order of \(P^n\) at which the above expan-
visions may be truncated without considerable loss of accuracy. For example, in the case of tetragonal symmetry, \( q_2 = 4 \) since \( C_{11}(0), C_{12}(0), C_{13}(0), \) and \( C_{33}(0) \) are independent. Therefore, if we can truncate the series at \( n = 1 \), this leads to three additional \( \kappa \) parameters, which may be chosen as \( \kappa_{11}' \), \( \kappa_{12}' \), \( \kappa_{13}' \). Let us compare this to an approach using higher-order elastic constants to describe the nonlinear elastic behavior. In a general tetragonal system one has \( q_3 = 6 \) third-order and \( q_4 = 8 \) fourth-order nonlinear elastic constants, leading to a total of \( q_3 + q_4 = 14 \) unknown parameters at fourth order. The disadvantage of using such an approach is obvious from comparing these numbers, since, after all, it is difficult to predict the accuracy of both approaches at this stage. The values \( q_2, q_4, q_5, q_6 \) for up to orthorhombic symmetry can be found in Table I of Ref. 1.

From a general point of view, our parametrization is expected to be far superior to a nonlinear elastic constants approach if one is allowed to truncate the series at sufficiently low order. The reason that supports this conjecture is two-fold. On the one hand, an expansion of the elastic energy in terms of nonlinear elastic constants, which is capable of reproducing the systems reaction to any tensorial stresses or strains applied to the system, requires far more information than needed to compute the system’s behavior under merely hydrostatic stress. On the other hand, in contrast to a blind expansion of the elastic energy in terms of nonlinear elastic constants, our parametrization is able to incorporate the volume information supplied by the equation of state to factorize out the major expected \( P \) dependence of the compliance components, leaving hopefully small additional corrections. These expectations will be checked in the subsequent sections.

C. General solution

The system (32) of uncoupled ordinary differential equations allows for simultaneous explicit solutions, which we write in the form

\[
\ln \alpha_i(P) = - P \int_0^1 dt S_i(tP).
\]

Using the ansatz (35), we get

\[
\ln \alpha_i(P) = \frac{1}{\kappa_0} \sum_{n=0}^{\infty} \kappa_n^2 f_n(P),
\]

where

\[
f_n(P) := - P^{n+1} \int_0^1 dt \kappa(Pr)^n.
\]

In terms of reduced volume \( \kappa(Pr) = - \frac{1}{P} \frac{d}{dt} \ln v(Pr) \) holds. We obtain

\[
f_0(P) = \ln v(Pr)
\]

for \( n = 0 \) and, applying partial integration,

\[
f_n(P) = P^n \left[ \frac{d}{dt} \ln v(Pr)^n \right] - nP^n \int_0^1 dt \ln v(Pr)^{n-1}
\]

\[
= P^n \ln v(Pr) - nP^n \int_0^1 dt \ln v(Pr)^{n-1}
\]

for \( n > 0 \). Altogether this yields

\[
a_\epsilon(P) = \exp \left[ \sum_{n=0}^{\infty} \left( \ln v(Pr)^n \kappa_0(P) \right) - nP^n \frac{\kappa_n^2}{\kappa_0} \int_0^1 dt \ln v(Pr)^{n-1} \right]
\]

\[
= \prod_{n=0}^{\infty} \left[ v(Pr)^{n \ln(P)} \left( - n \int_0^1 dt \ln v(Pr)^{n-1} \right) \right]^{P^n \kappa_n^2/\kappa_0},
\]

where of course \( S_i^0 = \sum_{j} \beta_{ij}^0 \). Factorizing out the terms with \( n = 1 \), we therefore have

\[
a_\epsilon(P) = v(1/\kappa_0)(S_i^0 + P \kappa_i^0)(P) \exp \left( - \frac{\kappa_i^0 P}{\kappa_0} \int_0^1 dt \ln v(Pr) \right)
\]

\[
\times \prod_{n=2}^{\infty} \left[ v(Pr)^{n \ln(P)} \left( - n \int_0^1 dt \ln v(Pr)^{n-1} \right) \right]^{P^n \kappa_n^2/\kappa_0}.
\]

Notice that for cubic systems \( S_i^0 = 1/3 \) and from (42), since \( \kappa_1^0 = \kappa_2^0 = \kappa_3^0 \forall n \), we immediately realize that \( \kappa_n^0 = 0, n > 0 \). Therefore, in this case (49) collapses to \( a_\epsilon(P) = \sqrt{v(P)} \), \( i=1,2,3 \), as expected.

III. COMPARISON TO EXPERIMENTAL RESULTS

To check the validity and accuracy of the above theoretical formulas, one can compare the corresponding predictions to published high-pressure data, which in principle include both measurements and simulation results. However, our focus on nonlinear aspects and the symmetry assumptions that we used in developing our theory place some restrictions on data eligible for a comparison. Consequently we were looking for data on cubic, tetragonal, and orthorhombic crystals using hydrostatic pressure in a range exceeding at least 10 GPa. Volume data, raw data, or published parameters of a high-quality fit using any EOS are in principle sufficient for cubic systems, since our theory makes no explicit use of any particular form of EOS. In the noncubic case, volume data are not sufficient as they yield no direct information on the pressure dependence of the unit cell parameters. For tetragonal and orthorhombic crystals, we therefore searched for data on individual lattice parameters subject to hydrostatic pressure. Most important, corresponding data on elastic constants or Birch coefficients should be available at a number of pressure points (preferably isothermal) in the given range.

The number of published experimental data satisfying these criteria and providing adequate data for our purposes is limited. There are several reasons for this. On the one hand,
it has only become possible in recent times to explore the pressure range in question experimentally. Still, experiments that determine not only the unit cell parameters but also the elastic tensor components under pressure are quite elaborate and costly (Brillouin spectroscopy, x-ray diffraction). On the other hand, published \textit{ab initio} calculations very often include elastic tensor components up to 100 GPa. Furthermore, it sometimes turns out to be difficult to retrace if it were the thermodynamic elastic constants or the Birch coefficients that have been calculated (see, e.g., the discussions recorded in Refs. 23 and 24). As we already pointed out, the differences between these tensor components are negligible at low pressures. As it is thus common to identify them at low pressures, we suspect that some workers tend to overlook the importance of this distinction, which does become crucial at ranges of external pressures that represent a sizable fraction of the elastic constant components.

Our comparison of these data to the predictions of our model always followed an identical scheme. Regardless of the crystal’s structure, we first attempted to fit a suitable EOS to the volume data \([V(P)\text{ or }\rho(P)]\). As a rule it turns out that in most cases a fit by a simple Murnaghan\cite{24} EOS

\[
v(P) = \left(1 + \frac{K_0}{K_0^*}P\right)^{-\frac{1}{n}},
\]

where \(K_0\) denotes the bulk modulus and \(K_0^*\) is independent of \(P\), does the job well enough to carry out the further steps of our procedure (see also Ref. 25), while the effort of using a more complex EOS is not justified by the comparatively small increase of accuracy. From this fit, the compressibility \(\kappa(P) = \frac{-1}{P}v'(P)\) is immediately obtained.

Next, we checked the nature of the published elastic constants and moduli, analyzing carefully the relations used during the published calculations and measurements to identify whether the elastic constants, the Birch coefficients, or the Huang tensor components were determined. Inverting the matrix of Birch coefficients according to Eq. (8), we obtain the desired part of the compliance matrix \(S_{ij}(P)\), \(i,j = 1,2,3\). On the other hand, from the measured pressure dependence of the lattice parameters the axial compressibilities \(\kappa_i(P)\) can be determined. At this stage of the investigation, we could check the consistency of these data with the row sums of the compliance data as stated in Eq. (33). This consistency condition serves to check the credibility of the results. Unfortunately these tests are rarely applied to most published data. Of course, for a cubic system these individual checks reduce to a single comparison of the measured compressibility and the sum over all \(S_{ij}(P)\), \(i,j = 1,2,3\). If one of these tests fails this may for one of several reasons. For instance, the Birch coefficients may have been accidentally confused with components of a different tensor. Other than that, a disagreement could signal an error or internal inconsistency of the measured data that had not been recognized in the published values. On the other hand, if the above checks are passed with satisfying accuracy, we could carry on with confidence to test the remaining predictions of our theory.

The question we were interested in is whether one can get away with truncating the Taylor expansions (40) of the reduced compliances

\[
\kappa^*_ij(P) = \frac{K_0}{\kappa(P)}S_{ij}(P) - S_{ij}(0)
\]

at low, if possible even linear, powers of \(P\) without unacceptable loss of accuracy. In order to check this assertion we calculated \(\kappa^*_ij\) for all measured pressure points and all components \((i,j)\) and inspected the corresponding plots. A linear behavior signals that we can truncate our approximation at \(n=1\), while the observation of pronounced residual nonlinearities in the values \(\kappa^*_ij\) forces one to include at least the \(n=2\) terms in our parametrization. In a preliminary fit we tried to obtain reasonable values for \(\kappa^*_ij, \kappa^*_ij, \ldots\). Finally we attempted to fit the \(n\)-truncated parametrization to the experimentally determined Birch coefficients and axis deformations, using the previously determined coefficients as starting values. For cubic systems this implies a single fit using Eq. (51) under the constraint of (40). For noncubic systems the total fit involves both fits to the set of measured Birch coefficients as well as simultaneous fits to the measured axial deformation data using the truncation of Eq. (49) at the chosen power \(n\), respectively.

\[
\begin{align*}
\text{FIG. 1. Volume fit for San Carlos olivine. Ordinate } v \text{ represents the reduced unit cell volume, squares symbolize data, the line is the Murnaghan EOS. Uncertainties are partially smaller than symbol size.}
\end{align*}
\]

\[
\begin{align*}
\text{FIG. 2. Consistency tests for San Carlos olivine. Symbols are axial data, lines are reduced unit cell parameter functions } \alpha_i(P) \text{ computed from Eq. (43), and error bars represent the simple standard deviations from Ref. 26.}
\end{align*}
\]
As a result of the above requirements and checks, we are led to report our findings for five substances: San Carlos olivin, fluorite, garnet, magnesium oxide, and stishovite.

A. San Carlos olivine

San Carlos olivine (\(\text{Mg}_{1-x}\text{Fe}_x\text{SiO}_4\)) with \(x=0.1\) is an important, possibly dominant mineral of the Earth's upper mantle. Seismic discontinuities within the upper mantle at 410 and 660 km depth are due to phase transitions and disproportionation processes of olivine.

In 1998 Zha et al. explored the elastic high-pressure behavior of San Carlos olivine between 2.5 and 32.5 GPa using Brillouin spectroscopy. Their publication provides Birch coefficients at several pressure points as well as the pressure behavior of individual axes, measured via x-ray diffraction.

Zha et al. published axis and volume data measured at eight pressure points and fitted a third-order Birch-Murnaghan EOS, obtaining \(K_0=129.9\pm0.6\) GPa. Using the numerical data from Table 1 of Ref. 26, we attempted to fit a simple Murnaghan EOS and obtained the values \(K_0=129.6\) GPa and \(K'_0=3.52\). As Fig. 1 shows, this EOS also describes the volume data quite precisely. The quantities given as “elastic moduli” in Table 2 of Ref. 26 were determined by Brillouin scattering and are therefore interpreted as Birch coefficients.

To test the consistency of this assumption, we computed the resulting axial deformations from applying Eq. (43) to smooth interpolations of the three functions \(S_{ij}(P)\).

<table>
<thead>
<tr>
<th>(i)</th>
<th>(j)</th>
<th>(\kappa_{ij}^*) (GPa(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td></td>
<td>49.1 \times 10^{-6}</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>73.6 \times 10^{-6}</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>62.6 \times 10^{-6}</td>
</tr>
<tr>
<td>12</td>
<td>11</td>
<td>-27.3 \times 10^{-6}</td>
</tr>
<tr>
<td>12</td>
<td>13</td>
<td>-24.2 \times 10^{-6}</td>
</tr>
<tr>
<td>13</td>
<td>12</td>
<td>-41.1 \times 10^{-6}</td>
</tr>
</tbody>
</table>
10.3 GPa), the agreement is quite good, which supports our confidence in having correctly identified the Birch coefficients.

We go on to investigate the possible nonlinear behavior of the quantities \( \kappa_{ij} \). Computing those quantities and plotting them in diagrams indicates that all components display a linear \( P \) dependence within the error bars (see Figs. 3 and 4). This observation suggested to truncate the expansions used in the following fit procedure at \( n=1 \). The simultaneous fit of Eqs. (35) and (49) yields the values listed in Table I which were used to calculate the Birch coefficients and compared to the experimentally determined coefficients in Figs. 5 and 6.

**B. Fluorite**

As the first of three cubic systems we found some adequate data for fluorite (CaF\(_2\)). Speziale and Duffy’s work on CaF\(_2\) from 2002 provides high-pressure elastic constants, measured via Brillouin scattering, and density data measured up to 9.5 GPa.\(^{27}\) The experiments showed the onset of a high-pressure structural phase transition at about 9 GPa. We also used these data to check if our considerations are influenced by some precursor effects of this phase transition. To the density data given in Table 3 of Ref. 27 we fitted a Murnaghan EOS, obtaining \( \rho_0=3.186 \text{ g/cm}^3 \), \( K_0=82.6 \pm 0.7 \text{ GPa} \), and \( K_0''=4.53\pm0.13 \). These values are in good agreement with data from literature.\(^{32}\) The Murnaghan EOS describes the density data with sufficient accuracy, as Fig. 7 shows.

As CaF\(_2\) is of cubic structure, one can only test the consistency of volume and elastic data. Consequently we calculated the compliance matrices by inverting the matrices of the Birch coefficients, built the sum over all entries for every pressure point of the measurement after Eq. (11) and com-
pared the result to the compressibility derived from the fitted Murnaghan EOS. Figure 8 shows the result. We see that the sum over the compliances is slightly too small for lower pressures. However, this deviation is small /H20849 max. 3% /H20850, which we illustrated by deliberately extending the left-hand scale of Fig. 8 down to /H9260 P /H20850 =0. Furthermore, there seems to be a small kink going upward at 8 GPa, which one could be tempted to associate with the phase transition fluorite is known to undergo at 9.5 GPa. However, a closer analysis shows that this kink is only based on very small statistical deviations of all /Bij downward at this pressure point see Fig. 4 in Ref. 27. The inversion of the matrices of the Birch coefficients enlarges this effect. We therefore cannot accredit this kink to the precursor of the phase transition.

In the case of cubic symmetry we focus on the two compliance components /S11 and /S12. As for the San Carlos olivine, we calculated the quantities /ij after Eq. (35) for every pressure point. Visual inspection indicated that both /k11 and /k12 are linear functions of /P (see Fig. 9), so once again we were led to truncating our expansions at order n =1. Fitting the analytical expression for both /B11(P) and /B12(P) yields the value

\[ \kappa_{11}^1 = 22.1 \times 10^{-5} \text{ GPa}^{-2} \]  

for the single free parameter /k11. Figure 10 shows the comparison of the Birch coefficients calculated with this parameter to the experimentally determined ones.

C. Garnet

The elastic properties of garnet—with the general formula /A3B2(SiO4)3 where /A and /B are metals—are of interest not only because of their geological relevance, but also due to their myriad technological applications.33 In 1997 Chai and Brown explored the elastic moduli of a pyrope-grossular-almandine garnet up to 20 GPa. Their data include Birch coefficients up to 20 GPa and a fitted Murnaghan EOS for the whole pressure regime. The Birch coefficients are given in the form of linear fits of the experimental data in Table 1 of Ref.28. We chose to compute values for the two Birch coefficients /B11 and /B12 at ten particular pressure points along the given linear fits and tested their consistency in the next step. The result is shown in Fig. 11. The Birch coefficients appear to be consistent with the volume data. Moreover the given “elastic moduli” can clearly be identified as Birch coefficients. The quantities /ij are observed to behave nearly linearly in /P see Fig. 12, again justifying truncation of our formulas at order n =1. The corresponding fit determines the single free parameter

\[ \kappa_{11} = 13.5 \times 10^{-6} \text{ GPa}^{-2} \]  

are displayed in Fig. 13.

D. Magnesium oxide

The salt MgO crystallizes in the cubic NaCl lattice type. Together with FeO and perovskite (Mg,Fe)SiO3 it is the most abundant mineral of the lower mantle. There are comparatively many publications dealing with the elastic high-
pressure properties of MgO, so we took the one that achieved the highest pressure so far by experimental means, which is Ref. 29. This work was done by Zha et al. in 2000. By Brillouin scattering and x-ray diffraction in a diamond anvil cell they investigated the density and elastic moduli of MgO up to 55 GPa.

The density data of the measurements are given by a fitted Birch-Murnaghan EOS of third order. Due to the fact that a simple Murnaghan EOS clearly diverges from a Birch-Murnaghan EOS of third order,

\[ P(v) = \frac{3K_0}{2} \left( \frac{v}{v_0} \right)^{7/3} - \left( \frac{v}{v_0} \right)^{5/3} \right] \left[ 1 + \frac{3}{4} \left( K_0 - 4 \right) \left( \frac{v}{v_0} \right)^{2/3} - 1 \right] \]

from 40 GPa on, we use the latter with the parameters \( K_0 = 160.2 \) GPa and \( K_0' = 4.03 \). Numerical inversion of the EOS and comparison of the resulting function \( v(P) \) to Fig. 3 of Ref. 29 provided exact concordance. The experimental results for the Birch coefficients of MgO are given in Table I of Ref. 29 in the form of quadratic fits. We chose to calculate the coefficients \( B_{11} \) and \( B_{12} \) at 17 pressure points along these fits. To check the nature of these elastic moduli and their compatibility with the measured volume behavior, we tested if Eq. (11) is satisfied. Figure 14 illustrates a comparison of the compressibility \( \kappa(P) \) to the sum of the compliances \( S_{ij} \) for each pressure point. We noticed obvious nonlinearities for \( \kappa_{11}(P) \) and \( \kappa_{12}(P) \), but they were covered by the \( n=2 \)

<table>
<thead>
<tr>
<th>( \kappa_{ij}^{\prime} )</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \kappa_{11}^{\prime} )</td>
<td>( -35.4 \times 10^{-6} ) GPa(^{-2} )</td>
</tr>
<tr>
<td>( \kappa_{12}^{\prime} )</td>
<td>( 17.7 \times 10^{-6} ) GPa(^{-2} )</td>
</tr>
<tr>
<td>( \kappa_{11}^{\prime} )</td>
<td>( 8.5 \times 10^{-7} ) GPa(^{-3} )</td>
</tr>
<tr>
<td>( \kappa_{12}^{\prime} )</td>
<td>( -4.3 \times 10^{-7} ) GPa(^{-3} )</td>
</tr>
</tbody>
</table>

FIG. 13. \( n=1 \) fit of the Birch coefficients of garnet. Symbols are points chosen along the experimental data of Ref. 28; lines represent the \( n=1 \) truncated theory using the parameter value (53).

FIG. 14. Volume consistency for MgO. Points are sums of the \( S_{ij} \) after Eq. (11), line is compressibility \( \kappa(P) \), and uncertainties are 1σ calculated from data.

FIG. 15. Reduced compliances \( \kappa_{ij}^{\prime} \) of magnesium oxide computed after Eq. (51); uncertainties are 1σ, and lines are quadratic fits.

FIG. 16. \( n=2 \) fit of Birch coefficients of MgO. Symbols are points chosen along the experimental data of Ref. 29, lines use the parameter values of Table II, and uncertainties are 1σ.

FIG. 17. Weighted volume fit of stishovite. Ordinate \( v \) represents the reduced unit cell volume, symbols are data from Ref. 30, and line is the fitted Murnaghan EOS with \( K_0 = 311.0 \) GPa and \( K_0' = 4.21 \). Uncertainties are smaller than symbol size.
truncation of Eq. (35), which is shown in Fig. 15. Figure 16 displays the results for the four fitting parameters \( \kappa_{11}, \kappa_{12}, \kappa_{13}, \) and \( \kappa_{12} \) from Table II. The agreement is very good.

### E. Stishovite

Stishovite SiO\(_2\) is a model system among minerals that are important in geology and technology. The tetragonal high-pressure phase of quartz (SiO\(_2\)) was explored by Carpenter et al.\(^{31}\). They analyzed the phase transition to the orthorhombic CaCl\(_2\) Structure and in the course of this work developed equations for the Birch coefficients up to 50 GPa. For axis and volume data we used results of Andrault et al.\(^{30}\) in 2003.\(^{30}\) Table 2 in Ref. 30 provides volume data of stishovite up to 47 GPa, which we used to fit a Murnaghan EOS (see Fig. 17). The parameters we found by doing so are \( K_0 = 311.0 \) GPa and \( K_0' = 4.21 \) and thus nearly identical with those found by Andrault et al. by fitting a Birch-Murnaghan EOS of third order. Comparing Fig. 17 to Fig. 2 of Ref. 30 shows exact accordance.

For the elastic data we used Ref. 31. Carpenter et al. calculated elastic constants of stishovite based on work of Karki et al.\(^{34}\). They published “bare elastic constants” composed of zero pressure elastic constants \( C_{ij}^0 \) and a pressure-dependent part which is linear in \( P \) up to 50 GPa (see Table 2 in Ref. 31). We interpreted these quantities as Birch coefficients and calculated them at 14 freely chosen pressure points. Stishovite has tetragonal structure, so there are four independent nonshear entries \( B_{ij} \). One can see that \( B_{11} \) and \( B_{12} \) always show the same inclination, so the stability criterion \( B_{11} - B_{12} > 0 \) (Born stability, see Ref. 15) is satisfied for the whole pressure range.

Since volume and axis data are taken from different publications, the consistency test is very important in this case. As Fig. 18 indicates, the axis data from Table 2 in Ref. 31 are indeed consistent with the compliances computed from the above bare elastic constants when interpreted as Birch coefficients.

Finally we report that all components besides \( \kappa_{33} \) display linear \( P \) behavior. Component \( \kappa_{33} \) is accurately represented by a quadratic polynomial, but nevertheless the deviation from a linear behavior is small enough to warrant an \( n=1 \)

<table>
<thead>
<tr>
<th>( \kappa_{ij} )</th>
<th>( 10^6 ) GPa(^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \kappa_{11} )</td>
<td>13.2</td>
</tr>
<tr>
<td>( \kappa_{33} )</td>
<td>10.5</td>
</tr>
<tr>
<td>( \kappa_{12} )</td>
<td>-14.3</td>
</tr>
<tr>
<td>( \kappa_{13} )</td>
<td>-2.1</td>
</tr>
</tbody>
</table>

This table contains the parameters \( \kappa_{ij} \) for stishovite.

![FIG. 18. Consistency test for stishovite. Symbols and error bars represent data from Ref. 30; lines are axial deformations \( \alpha_i(P) \) after Eq. (43).](image1)

![FIG. 19. Reduced compliances \( \kappa_{ij}^* \) of stishovite computed after Eq. (51). Lines are linear fits.](image2)

![FIG. 20. \( n=1 \) fit of Birch coefficients of stishovite. Symbols are points chosen along the bare elastic constants of Ref. 31, and lines use the parameter values of Table III.](image3)
truncation [see Fig. 19(a)]. The fit procedure yields values for the four fit parameters $\kappa_{11}^1$, $\kappa_{12}^1$, $\kappa_{13}^1$ and $\kappa_{33}^1$ (see Table III) which we used to calculate the corresponding Birch coefficients. Figure 20 compares these calculated quantities with those from the measurements in Ref. 31.

**IV. DISCUSSION**

In this work we have reviewed five measurements of important minerals, which are common in the Earth’s crust and mantle to test the resulting inverted Birch coefficients (compliances) within the framework of our theory, which was based on the assumption that the main nonlinearity of the Birch coefficients or compliances with respect to pressure is determined by the nonlinearity of the compressibility and a Taylor expansion of the rest can be truncated at low (linear or quadratic) powers of $P$. Indeed, for the orthorhombic San Carlos olivine and the tetragonal stishovite, each reduced compliance component $\kappa_{ij}^c(P)$ is observed to follow a linear $P$ behavior. A simultaneous $n=1$ fit of our theory to both crystal axes $a_j(P)$ and compliance $S_j(P)$ data for both systems provides functions $B_{ij}(P)$ which are in perfect agreement with the experimentally determined or calculated Birch coefficients from literature. For the cubic systems fluorite and garnet the reduced compliances $\kappa_{ij}^c$ show a linear or a slight quadratic behavior, which can be neglected without any loss of accuracy. Magnesium oxide, whose measurements go up to 55 GPa, clearly calls for a quadratic expansion. However, all tested cubic systems allow the suggested parametrization of their Birch coefficients with at most two parameters. Summarizing the results, the fundamental ansatz (51) of our high-pressure theory has thus been shown to represent an extremely efficient parametrization of the hydrostatic high-pressure behavior for all five materials. In particular, the main requirement for the construction of a high-pressure Landau-type free energy as proposed in Ref. 1 is satisfied in all cases. The theory is therefore expected to be well suited for the systematic study of pressure-induced phase transitions in a wide pressure range.

Finally, we would like to draw attention to the apparent loss of symmetry of $B_{ij}$ for nonhydrostatic stress $\tau$. In particular, Eq. (6) shows that the asymmetry depends solely on the imposed stress tensor components. In fact, while it can be extremely hard to guarantee that an externally imposed stress acts hydrostatically on a specimen in an experiment, it is usually in principle easy to observe the behavior of systems at nonhydrostatic conditions in computer experiments. Taking, e.g., the case of principal stresses

$$\tau_{ij} = \tau_{i}\delta_{ij}$$

one obtains for $\alpha, \beta = 1, 2, 3$ the equations

$$B_{\alpha\beta} - B_{\beta\alpha} = 2(\tau_{\beta} - \tau_{\alpha}).$$

We stress that these relations of the above type, which result entirely from the nonlinear geometric structures of the theory, do not rely on any approximations. Therefore they could serve to perform both additional consistency and accuracy checks of simulation data obtained by probing Hooke’s law.

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