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Ab initio calculations of the second-order elastic constants of crystals under arbitrary isotropic pressure

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We derive an equation that relates the elastic constants of a single crystal under isotropic pressure to the magnitude of this pressure, the characteristics of a small homogeneous strain, and the second derivative of a specific energy with respect to the magnitude of strain. We also derive two formulas that are valid for cubic, hexagonal, tetragonal, trigonal, and orthorhombic crystals and relate the elastic constants to the bulk modulus and the dependence of lattice parameters on volume. Their use is illustrated by examples.

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I. INTRODUCTION

Elastic constants are the important characteristics of solids whose knowledge is essential to the understanding of many of their properties. In particular, elastic constants determine the elasticity and mechanical stability of crystals. There is a considerable interest in the elastic properties of the high-pressure phases of distinct crystals. An accurate experimental determination of elastic constants under pressure is often rather difficult, and here computer modeling can play an important role in establishing properties of specific phases. However, as mentioned in a classic paper,[1] except when the solid is under zero stress, care is needed both in the definition and the derivation of the elastic constants.

Several methods are currently used for the *ab initio* calculation of second-order elastic constants at an arbitrary isotropic pressure. One of them is based on the calculation of the dependence of specific energy on strain magnitude.[1,2] This method is widely used in practice (see, for example, Refs. 3–12). Also widely used is a method based on the analysis of changes in calculated stresses resulting from changes in the strain.[1,13–17] There is a published approach that used the calculated dependence of Gibbs potential on strain magnitude,[18] but it was subject to criticism.[10,19]

This paper is devoted to the development of the approach described in Ref. 2 and to the derivation of formulas that relate the elastic constants to the bulk modulus and the dependence of lattice parameters on volume. Below, we will use the traditional tensor notation as well as Voigt's matrix notation,[20,21] each time specifying which one is used to exclude misunderstandings.

As shown in Ref. 2, if the homogeneous strain of a crystal at a specific volume V_1 and zero temperature is described by the symmetric matrix

$$\hat{\varepsilon}(\gamma)=\begin{pmatrix}\varepsilon_{11}(\gamma) & \varepsilon_{12}(\gamma) & \varepsilon_{13}(\gamma)\\ \varepsilon_{21}(\gamma) & \varepsilon_{22}(\gamma) & \varepsilon_{23}(\gamma)\\ \varepsilon_{31}(\gamma) & \varepsilon_{32}(\gamma) & \varepsilon_{33}(\gamma)\end{pmatrix}, \tag{1}$$

where

$$\varepsilon_{ij}(\gamma)=s_{ij}\gamma+e_{ij}\gamma^2+\cdots,$$

γ is the magnitude of strain, and $\frac{d^2E[V_1,\hat{\varepsilon}(\gamma)]}{d\gamma^2}\Big|_{\gamma=0}$ is obtained from *ab initio* calculations of a specific energy of the crystal as a function of strain magnitude, then

$$\tilde{C}_{ijkl}=\frac{\partial^2E(V_1,\{\eta_{mn}\})}{\partial\eta_{ij}\partial\eta_{kl}}\bigg|_{\{\eta_{mn}\}=0},$$

or, in Voigt notation,

$$\tilde{C}_{\alpha\beta}=\frac{\partial^2E(V_1,\{\eta_{\nu}\})}{\partial\eta_{\alpha}\partial\eta_{\beta}}\bigg|_{\{\eta_{\nu}\}=0}$$

satisfies the equation

$$\sum_{\alpha,\beta}\xi_\alpha\xi_\beta\tilde{C}_{\alpha\beta}s_\alpha s_\beta=2P(V_1)\sum_{\alpha}(2-\xi_\alpha)e_\alpha+P(V_1)\sum_{\alpha}\xi_\alpha s_\alpha^2+\frac{1}{V_1}\frac{d^2E[V_1,\hat{\varepsilon}(\gamma)]}{d\gamma^2}\bigg|_{\gamma=0}. \tag{2}$$

Here, η_{ij} are Lagrange strain tensor components,

$$\eta_{ij}=\varepsilon_{ij}+\frac{1}{2}\sum_{k}\varepsilon_{ik}\varepsilon_{kj}.$$

η_α, s_α, and e_α are η_{ij}, s_{ij}, and e_{ij} in Voigt notation, and

$$\xi_\alpha=\begin{cases}1 & \text{if } \alpha=1,2,3\\ 2 & \text{if } \alpha=4,5,6.\end{cases}$$

It is also shown in Ref. 2 that $C_{\alpha\beta}$ related to $\tilde{C}_{\alpha\beta}$ by the relations (in Voigt notation)

$$C_{\alpha\beta}=\tilde{C}_{\alpha\beta}+P\frac{[(2-\xi_\alpha)(2-\xi_\beta)-2\xi_\alpha\delta_{\alpha\beta})]}{\xi_\alpha\xi_\beta} \tag{3}$$

should be treated as the second-order elastic constants of an arbitrary crystal at any pressure. Relation (3) agrees with the definition introduced in Ref. [1,22]. With this definition of elastic constants, the Christoffel equation determining the velocities of elastic waves and the mechanical stability conditions for crystals takes identical forms both at zero pressure and at nonzero pressure.[1,2]

Some disadvantage of Ref. 2 is that Eq. (4) was derived there for the intermediate quantities $\tilde{C}_{\alpha\beta}$, not for the elastic constants. In this paper, the disadvantage is rectified. Also, two formulas are derived, which are valid for cubic, hexagonal, tetragonal, trigonal, and orthorhombic crystals and relate the elastic constants to the bulk modulus and the dependence of lattice parameters on volume.

II. EQUATIONS FOR ELASTIC CONSTANTS

To obtain one of the equations for the elastic constants $C_{\alpha\beta}$ of a single crystal under an arbitrary pressure, we substitute Eq. (3) into Eq. (2). Then, Eq. (2) takes the form

$$\sum_{\alpha,\beta} \xi_\alpha \xi_\beta C_{\alpha\beta} s_\alpha s_\beta = P(V_1) \sum_{\alpha\beta} [(2-\xi_\alpha)(2-\xi_\beta) - 2\xi_\alpha \delta_{\alpha\beta}] s_\alpha s_\beta + P(V_1)\left[2\sum_\alpha (2-\xi_\alpha)e_\alpha + \sum_\alpha \xi_\alpha s_\alpha^2\right] + \frac{1}{V_1} \left. \frac{d^2E[V_1,\hat{\varepsilon}(\gamma)]}{d\gamma^2}\right|_{\gamma=0} .$$

Taking into account that

$$\sum_{\alpha\beta} \xi_\alpha \delta_{\alpha\beta} s_\alpha s_\beta = \sum_\alpha \xi_\alpha s_\alpha^2,$$

$$\sum_{\alpha\beta} (2-\xi_\alpha)(2-\xi_\beta) s_\alpha s_\beta = \left(\sum_\alpha (2-\xi_\alpha) s_\alpha\right)^2 = (s_1+s_2+s_3)^2,$$

$$\sum_\alpha (2-\xi_\alpha) e_\alpha = e_1+e_2+e_3,$$

we obtain the equation

$$\sum_{\alpha,\beta} \xi_\alpha \xi_\beta C_{\alpha\beta} s_\alpha s_\beta = 2P(V_1)(e_1+e_2+e_3+s_1s_2+s_1s_3+s_2s_3-s_4^2-s_5^2-s_6^2) + \frac{1}{V_1} \left. \frac{d^2E[V_1,\hat{\varepsilon}(\gamma)]}{d\gamma^2}\right|_{\gamma=0}, \tag{4}$$

which relates, for the strain matrix [Eq. (1)], the elastic constants of a crystal isotropically compressed to a pressure P, the characteristics of the strain matrix $\hat{\varepsilon}(\gamma)$, and the second derivative of a specific energy with respect to the strain magnitude.

It is known that the number of independent elastic constants is equal to the number of independent strains in the crystal. Therefore, having calculated γ is the magnitude of strain, and $\frac{d^2E[V_1,\hat{\varepsilon}(\gamma)]}{d\gamma^2}|_{\gamma=0}$ and written Eq. (4) for each independent strain of a crystal that has a specific volume V_1, we, in principle, can obtain a system of equations for all elastic constants of the crystal at this specific volume.

However, in practice, the implementation of this approach encounters some technical difficulties. The problem is that for strains that do not preserve volume, an accurate calculation of γ is the magnitude of strain, and $\frac{d^2E[V_1,\hat{\varepsilon}(\gamma)]}{d\gamma^2}|_{\gamma=0}$ requires that the dependence of specific energy on strain magnitude be calculated more accurately compared to the case of volume-preserving strains because a specific energy depends on volume much strongly than on strain. If required accuracy is not achievable, the resulting elastic constants will have an uncontrollable error. In this case, relations that relate the elastic constants to such quantities as the bulk modulus and the volume derivatives of lattice parameters that are easier to calculate with high accuracy are very helpful. For some crystals, specifically cubic, hexagonal and tetragonal, these relations are known[2,7,21] and could be used to replace equations of the type of Eq. (4) for some strains that change volume. For a highly symmetric crystal, this technique makes it possible not to use strains that change volume at all. In this paper, we derive two relations of that type, which are valid for orthorhombic, hexagonal, tetragonal, trigonal, and cubic crystals. The well-known relations are particular cases of these general relations. However, before we start their derivation, let us consider examples of the calculation of the elastic constants from papers[7,8] that are often cited and compare equations used there for the determination of the elastic constants under pressure with those obtained in accord with Eq. (4).

Steinle-Neumann *et al.*[7] calculated the elastic constants of hcp Fe, Co, and Re under pressure. To calculate five independent constants, i.e., C_{11}, C_{12}, C_{13}, C_{33}, and C_{44}, they consider three independent volume-preserving strains,

$$\hat{\varepsilon}_1 = \begin{pmatrix} \gamma & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & \dfrac{1}{(1+\gamma)^2} - 1 \end{pmatrix}, \quad \hat{\varepsilon}_2 = \begin{pmatrix} \gamma & 0 & 0 \\ 0 & -\gamma & 0 \\ 0 & 0 & \dfrac{\gamma^2}{1-\gamma^2} \end{pmatrix},$$

$$\hat{\varepsilon}_3 = \begin{pmatrix} 0 & 0 & \gamma \\ 0 & \dfrac{\gamma^2}{1-\gamma^2} & 0 \\ \gamma & 0 & 0 \end{pmatrix}.$$

The specific energy of the crystal deformed in accord with the matrix $\hat{\varepsilon}_1$ was calculated as a function of the strain magnitude γ and was used in an equation that, in our notation, can be written as

$$2(C_{11}+C_{12}+2C_{33}-4C_{13}) = \frac{1}{V_1}\left.\frac{d^2E(V_1,\hat{\varepsilon}_1)}{d\gamma^2}\right|_{\gamma=0}. \tag{5}$$

Similar results of calculations with the matrix $\hat{\varepsilon}_2$ were used in the equation

$$4\left(\frac{C_{11}-C_{12}}{2}\right) = \frac{1}{V_1}\left.\frac{d^2E(V_1,\hat{\varepsilon}_2)}{d\gamma^2}\right|_{\gamma=0}, \tag{6}$$

and the results of calculations with the matrix $\hat{\varepsilon}_3$ were used in the equation

$$4C_{44} = \frac{1}{V_1}\left.\frac{d^2E(V_1,\hat{\varepsilon}_3)}{d\gamma^2}\right|_{\gamma=0}. \tag{7}$$

Unfortunately, the expansion of energy in terms of γ, which gives Eqs. (5)–(7) is provided without derivation and references.

Consider relations between the elastic constants, which can be obtained from the general equation [Eq. (4)] for strains ε_1, ε_2, and ε_3. For ε_1, we have

$$s_1=1,\quad e_1=0;\quad s_2=1,\quad e_2=0;\quad s_3=-2,\quad e_3=3;$$

$$s_4=s_5=s_6=e_4=e_5=e_6=0. \tag{8}$$

For ε_2,

$$s_1=1,\quad e_1=0;\quad s_2=-1,\quad e_2=0;\quad s_3=0,\quad e_3=1;$$

$$s_4=s_5=s_6=e_4=e_5=e_6=0. \tag{9}$$

For ε_3,

$$s_1=0,\quad e_1=0;\quad s_2=0,\quad e_2=1;\quad s_3=0,\quad e_3=3;$$

$$s_5=1,\quad e_5=0;\quad s_4=s_6=e_4=e_6=0. \tag{10}$$

By successively substituting the values of Eqs. (8)–(10) for s_i and e_i into the general equation [Eq. (4)] obtained here and by using the relations between the elastic constants, which arise from the symmetry properties of hcp crystals, we can easily see that the corresponding equations fully coincide with Eqs. (5)–(7). For two equations that are lacking for the determination of the five independent elastic constants, Steinle-Neumann *et al.*[7] use

$$B = \frac{C_{33}(C_{11}+C_{12})-2C_{13}^2}{C_{11}+C_{12}+2C_{33}-4C_{13}}, \tag{11}$$

$$\frac{d\ln(c/a)}{d\ln V} = \frac{C_{11}+C_{12}-C_{33}-C_{13}}{C_{11}+C_{12}+2C_{33}-4C_{13}}, \tag{12}$$

where B is the bulk modulus, and c and a are lattice parameters for the hcp crystal. As we will see below, these expressions also follow from more general relations.

Tsuchiya and Kawamura[8] calculated the elastic constants of cubic MgO, CaO, SrO, and BaO under pressure. To calculate three independent elastic constants, i.e., C_{11}, C_{12}, and C_{44}, they used three independent strains,

$$\hat{\varepsilon}_4 = \begin{pmatrix}\gamma & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{pmatrix},\quad \hat{\varepsilon}_5 = \begin{pmatrix}0 & \gamma & \gamma\\ \gamma & 0 & \gamma\\ \gamma & \gamma & 0\end{pmatrix},$$

$$\hat{\varepsilon}_6 = \begin{pmatrix}\gamma & 0 & 0\\ 0 & -\gamma & 0\\ 0 & 0 & 0\end{pmatrix}.$$

The specific energy of the crystal deformed in accord with the matrix $\hat{\varepsilon}_4$ was calculated as a function of the strain magnitude γ and was used in an equation that, in our notation, can be written as

$$C_{11} = \frac{1}{V_1}\left.\frac{d^2E(V_1,\hat{\varepsilon}_4)}{d\gamma^2}\right|_{\gamma=0}. \tag{13}$$

Similar results with $\hat{\varepsilon}_5$ were used in the equation

$$C_{44} = -\frac{P}{2} + \frac{1}{12}\frac{1}{V_1}\left.\frac{d^2E(V_1,\hat{\varepsilon}_5)}{d\gamma^2}\right|_{\gamma=0}, \tag{14}$$

and results obtained with $\hat{\varepsilon}_6$ were used in the equation

$$C_{11}-C_{12} = -P + \frac{1}{2}\frac{1}{V_1}\left.\frac{d^2E(V_1,\hat{\varepsilon}_6)}{d\gamma^2}\right|_{\gamma=0}. \tag{15}$$

Taking into account that for $\hat{\varepsilon}_4$ we have

$$s_1=1,\quad e_1=0;$$

$$s_2=s_3=s_4=s_5=s_6=e_2=e_3=e_4=e_5=e_6=0, \tag{16}$$

for $\hat{\varepsilon}_5$ we have

$$s_4=1,\quad e_4=0;\quad s_5=1,\quad e_5=0;\quad s_6=1,\quad e_6=0;$$

$$s_1=s_2=s_3=e_1=e_2=e_3=0, \tag{17}$$

and for $\hat{\varepsilon}_6$ we have

$$s_1=1,\quad e_1=0;\quad s_2=-1,\quad e_2=0;$$

$$s_3=s_4=s_5=s_6=e_3=e_4=e_5=e_6=0, \tag{18}$$

then by substituting the values of Eqs. (16)–(18) for s_i and e_i into Eq. (4) and using relations between the elastic constants, which arise from the symmetry properties of cubic crystals, we see again that the corresponding equations fully coincide with Eqs. (13)–(15) used in Ref. 8.

III. RELATION OF ELASTIC CONSTANTS TO BULK MODULUS AND VOLUME DEPENDENT LATTICE PARAMETERS

Consider a small uniform and isotropic (hydrostatic) compression of a crystal that is prestressed to a specific volume V_1 by a hydrostatic pressure P. Determine first the components ε_{ij} of the strain matrix corresponding to the small compression. For the hydrostatic compression, the stress tensor is

$$\Delta T_{ij} = -\Delta P\,\delta_{ij}. \tag{19}$$

By Hooke's law,

$$\varepsilon_{ij} = \sum_{lm} S_{ijlm}\Delta T_{lm} = -\Delta P \sum_{lm} S_{ijlm}\delta_{lm}$$
$$= -\Delta P (S_{ij11} + S_{ij22} + S_{ij33}), \tag{20}$$

where S_{ijlm} is the elastic modulus or the elastic compliance constant in accord with current American usage.[21]

For crystals from each crystal class, there are relations between S_{ijlm} that describe the symmetry properties of crystals in the class.[21] By using these relations, we find that for crystals that fall into the cubic, hexagonal, tetragonal, trigonal, and orthorhombic classes, the strain matrix [Eq. (20)] for hydrostatic compression is diagonal,

$$\varepsilon_{ij} = \varepsilon_{ii}\delta_{ij}.$$

For cubic crystals, $\varepsilon_{11}=\varepsilon_{22}=\varepsilon_{33}$; for hexagonal, tetragonal, and trigonal ones, $\varepsilon_{11}=\varepsilon_{22}\neq\varepsilon_{33}$; and for orthorhombic crystals, $\varepsilon_{11}\neq\varepsilon_{22}\neq\varepsilon_{33}$. Just the diagonal form of the strain matrix for hydrostatic compression allows us to obtain for these crystals relatively simple relations relating the elastic constants to the bulk modulus and the volume derivative of lattice parameters. To obtain such relations, we will consider below crystals whose atoms form Bravais lattices, related to the above crystal classes and having an arbitrary basis. It should be emphasized that basis atoms are assumed to completely relax under strain.

The primitive lattice vectors of the deformed Bravais lattice $(\vec{R}_1', \vec{R}_2', \vec{R}_3')$ relate to the corresponding vectors $(\vec{R}_1, \vec{R}_2, \vec{R}_3)$ of the undeformed Bravais lattice as

$$\vec{R}_i' = (\hat{I} + \hat{\varepsilon})\vec{R}_i, \quad i = 1,2,3. \tag{21}$$

Here, $\hat{I}$ is a unit matrix. The specific volume V_1' of the deformed crystal can be obtained if we take the absolute value of the vector-scalar product of vectors [Eq. (21)]. For cubic, hexagonal, tetragonal, trigonal, and orthorhombic crystals under hydrostatic pressure, we obtain (taking into account that their strain matrices are diagonal)

$$V_1' = |\vec{R}_1' \cdot \vec{R}_2' \times \vec{R}_3'| = (1+\varepsilon_1)(1+\varepsilon_2)(1+\varepsilon_3)|\vec{R}_1 \cdot \vec{R}_2 \times \vec{R}_3|$$
$$= V_1(1+\varepsilon_1)(1+\varepsilon_2)(1+\varepsilon_3). \tag{22}$$

Here, ε_i are components of the strain matrix in Voigt notation. Assuming that the strains are small and limiting to the first-order strain terms, we obtain

$$\Delta V = V_1' - V_1 = (\varepsilon_1 + \varepsilon_2 + \varepsilon_3)V_1. \tag{23}$$

Let us calculate the bulk modulus of a crystal that has a specific volume V_1 from the definition

$$B = -V_1 \lim_{\Delta V \to 0} \frac{\Delta P}{\Delta V}. \tag{24}$$

For this end, we use Hooke's law, which relates strains and associated stresses as

$$\Delta T_{ij} = \sum_{kl} C_{ijkl}\varepsilon_{kl}. \tag{25}$$

Here, ΔT_{ij} are stress components and C_{ijkl} are elastic constants. Taking into account Eq. (19) and the fact that the strain matrix is diagonal, Eq. (25) gives the following system of equations for strains resulting from the increase of pressure by ΔP:

$$\sum_k C_{ijkk}\varepsilon_{kk} = -\Delta P \delta_{ij}.$$

The system contains nine-equations. By using the symmetry properties of the elastic constants,[21] one can easily show that for cubic, hexagonal, tetragonal, trigonal, and orthorhombic crystals, six of these equations satisfy identically and three others in Voigt notation take the form

$$C_{11}\varepsilon_1 + C_{12}\varepsilon_2 + C_{13}\varepsilon_3 = -\Delta P,$$
$$C_{21}\varepsilon_1 + C_{22}\varepsilon_2 + C_{23}\varepsilon_3 = -\Delta P,$$
$$C_{31}\varepsilon_1 + C_{32}\varepsilon_2 + C_{33}\varepsilon_3 = -\Delta P. \tag{26}$$

After solving simultaneous equations [Eq. (26)], we obtain

$$\varepsilon_1 + \varepsilon_2 + \varepsilon_3 = -\Delta P \frac{D_1 + D_2 + D_3}{D}, \tag{27}$$

where

$$D = C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2,$$
$$D_1 = C_{22}C_{33} + C_{12}C_{23} + C_{13}C_{23} - C_{23}^2 - C_{12}C_{33} - C_{13}C_{22},$$
$$D_2 = C_{11}C_{33} + C_{12}C_{13} + C_{13}C_{23} - C_{13}^2 - C_{11}C_{23} - C_{12}C_{33},$$
$$D_3 = C_{11}C_{22} + C_{12}C_{23} + C_{13}C_{12} - C_{12}^2 - C_{11}C_{23} - C_{13}C_{22}.$$

By substituting Eq. (27) into Eq. (23) and by using the resulted equality in Eq. (24), we obtain a relation between the bulk modulus and the elastic constants, which is valid for cubic, hexagonal, tetragonal, trigonal, and orthorhombic crystals,

$$B = \frac{D}{D_1 + D_2 + D_3}. \tag{28}$$

For hexagonal, tetragonal, and trigonal crystals, this relation can be simplified by using the symmetry properties $C_{11} = C_{22}$ and $C_{13}=C_{23}$, which hold in this case. We obtain

$$B = \frac{C_{33}(C_{11} + C_{12}) - 2C_{13}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}}, \tag{29}$$

which coincides with Eq. (11) used in Refs. 5 and 7. For cubic crystals whose elastic constants additionally satisfy the relations $C_{33}=C_{11}$ and $C_{13}=C_{12}$, Eq. (29) becomes yet simpler, giving the well-known relation

$$B = \frac{C_{11} + 2C_{12}}{3}.$$

To derive one more relation, let us write the strain matrix for the hydrostatic compression of cubic, tetragonal, hexagonal, trigonal, and orthorhombic crystals in the form

$$\hat{\varepsilon}_0(\gamma)=\begin{pmatrix}\gamma & 0 & 0\\ 0 & \alpha(\gamma) & 0\\ 0 & 0 & \beta(\gamma)\end{pmatrix}, \tag{30}$$

where

$$\lim_{\gamma\to 0}\alpha(\gamma)=\lim_{\gamma\to 0}\beta(\gamma)=0. \tag{31}$$

Here, γ is the magnitude of strain. For tetragonal, hexagonal, and trigonal lattices, $\alpha(\gamma)=\gamma$ for cubic, $\beta(\gamma)=\gamma$. Equation (4) for the strain matrix [Eq. (30)] is

$$C_{11}+2\alpha'(0)C_{12}+2\beta'(0)C_{13}+[\alpha'(0)]^2C_{22}+2\alpha'(0)\beta'(0)C_{23}+[\beta'(0)]^2C_{33}=P[\alpha''(0)+\beta''(0)+2\alpha'(0)+2\beta'(0)+2\alpha'(0)\beta'(0)]+\left.\frac{d^2E[V_1,\hat{\varepsilon}_0(\gamma)]}{d\gamma^2}\right|_{\gamma=0}. \tag{32}$$

In this notation, Eq. (22) for the specific volume V_1' of the deformed crystal takes the form

$$V_1'=V_1(1+\gamma)[1+\alpha(\gamma)][1+\beta(\gamma)]. \tag{33}$$

Let us calculate $\frac{1}{V_1}\frac{\partial^2E[V_1,\hat{\varepsilon}_0(\gamma)]}{\partial\gamma^2}|_{\gamma=0}$ in the case of hydrostatic compression. Provided that energy only depends on volume in this case, we can write

$$\frac{1}{V_1}\left.\frac{\partial^2E[V_1,\hat{\varepsilon}_0(\gamma)]}{\partial\gamma^2}\right|_{\gamma=0}=\frac{1}{V_1}\left.\frac{\partial^2E[V_1'(\gamma)]}{\partial\gamma^2}\right|_{\gamma=0}=\frac{1}{V_1}\left.\frac{dE(V)}{dV}\right|_{V=V_1}\cdot\left.\frac{d^2V_1'}{d\gamma^2}\right|_{\gamma=0}+\frac{1}{V_1}\left.\frac{d^2E(V)}{dV^2}\right|_{V=V_1}\cdot\left(\left.\frac{dV_1'}{d\gamma}\right|_{\gamma=0}\right)^2.$$

Since

$$\left.\frac{dE(V)}{dV}\right|_{V=V_1}=-P(V_1),\qquad \left.\frac{d^2E(V)}{dV^2}\right|_{V=V_1}=\frac{B(V_1)}{V_1}, \tag{34}$$

we obtain

$$\frac{1}{V_1}\left.\frac{\partial^2E[V_1,\hat{\varepsilon}_0(\gamma)]}{\partial\gamma^2}\right|_{\gamma=0}=-\frac{P(V_1)}{V_1}\cdot\left.\frac{d^2V_1'}{d\gamma^2}\right|_{\gamma=0}+\frac{B(V_1)}{V_1^2}\cdot\left(\left.\frac{dV_1'}{d\gamma}\right|_{\gamma=0}\right)^2. \tag{35}$$

Here, $P(V_1)$ and $B(V_1)$ are pressure and bulk moduli for the undeformed crystal at $V=V_1$ and $T=0$, respectively. By using Eq. (33), we obtain

$$\frac{1}{V_1}\frac{dV_1'}{d\gamma}=[1+\alpha(\gamma)][1+\beta(\gamma)]+(1+\gamma)[1+\beta(\gamma)]\alpha'(\gamma)+(1+\gamma)[1+\alpha(\gamma)]\beta'(\gamma).$$

$$\frac{1}{V_1}\frac{d^2V_1'}{d\gamma^2}=(1+\gamma)\{[1+\beta(\gamma)]\alpha''(\gamma)+[1+\alpha(\gamma)]\beta''(\gamma)\}+(1+\gamma)[1+\beta(\gamma)]\alpha'(\gamma)+(1+\gamma)[1+\alpha(\gamma)]\beta'(\gamma).$$

By passing the limit as $\gamma\to 0$ and by using Eq. (31), we obtain

$$\frac{1}{V_1}\left.\frac{dV_1'}{d\gamma}\right|_{\gamma=0}=1+\alpha'(0)+\beta'(0), \tag{36}$$

$$\frac{1}{V_1}\left.\frac{d^2V_1'}{d\gamma^2}\right|_{\gamma=0}=\alpha''(0)+\beta''(0)+2[\alpha'(0)+\beta'(0)+\alpha'(0)\beta'(0)]. \tag{37}$$

With Eqs. (36) and (37), Eq. (35) takes the form

$$\frac{1}{V_1}\left.\frac{\partial^2E[V_1,\hat{\varepsilon}_0(\gamma)]}{\partial\gamma^2}\right|_{\gamma=0}=-P(V_1)\{\alpha''(0)+\beta''(0)+2[\alpha'(0)+\beta'(0)+\alpha'(0)\beta'(0)]\}+B[1+\alpha'(0)+\beta'(0)]^2. \tag{38}$$

Substituting Eq. (38) into Eq. (32) gives

$$C_{11}+2\alpha'(0)C_{12}+2\beta'(0)C_{13}+[\alpha'(0)]^2C_{22}+2\alpha'(0)\beta'(0)C_{23}+[\beta'(0)]^2C_{33}=B[1+\alpha'(0)+\beta'(0)]^2. \tag{39}$$

Now, we will derive a relation between $\alpha'(0)$, $\beta'(0)$, and the volume derivatives of lattice parameters for hydrostatic pressure and use it in Eq. (39) to obtain the second of the sought relations. It is easy to see that the strain described by Eq. (30) only changes the lengths, not the directions, of the primitive lattice vectors of the Bravais lattice in the crystals under consideration. The relations that connect the new lattice parameters with the old ones take the form

$$\frac{a'}{a} = 1+\gamma, \quad \frac{b'}{a'} = \frac{1+\alpha(\gamma)}{1+\gamma}\frac{b}{a}, \quad \frac{c'}{a'} = \frac{1+\beta(\gamma)}{1+\gamma}\frac{c}{a}.$$

To be accurate to the γ-order-of-magnitude terms, these can be rewritten as

$$\frac{b'}{a'} \approx \frac{b}{a}(1+[\alpha'(0)-1]\gamma),$$

$$\frac{c'}{a'} \approx \frac{c}{a}(1+[\beta'(0)-1]\gamma). \tag{40}$$

By limiting them to the same accuracy for hydrostatic compression, we can write

$$\frac{b'}{a'} \approx \frac{b}{a} + \left.\frac{d(b/a)}{dV}\right|_{V=V_1} \cdot (V_1'-V_1)$$

$$\approx \frac{b}{a}(1+\nu[1+\alpha'(0)+\beta'(0)]\gamma), \tag{41}$$

Similarly,

$$\frac{c'}{a'} \approx \frac{c}{a}(1+\mu[1+\alpha'(0)+\beta'(0)]\gamma), \tag{42}$$

Here,

$$\nu = \frac{V_1}{b/a}\left.\frac{d(b/a)}{dV}\right|_{V=V_1}, \quad \mu = \frac{V_1}{c/a}\left.\frac{d(c/a)}{dV}\right|_{V=V_1},$$

and we have shown that Eq. (33) can be written accurate to the γ-order-of-magnitude terms as

$$\frac{V_1'-V_1}{V_1} \approx [1+\alpha'(0)+\beta'(0)]\gamma.$$

Comparing Eq. (40) and Eqs. (41) and (42), we obtain a system of equations relating $\alpha'(0)$ and $\beta'(0)$ to ν and μ, which are the volume derivatives of lattice parameters, in the case of isotropic compression,

$$\alpha'(0)-1 = \nu[1+\alpha'(0)+\beta'(0)],$$

$$\beta'(0)-1 = \mu[1+\alpha'(0)+\beta'(0)].$$

Solving the system, we find that

$$\alpha'(0) = \frac{1+2\nu-\mu}{1-(\nu+\mu)}, \tag{43}$$

$$\beta'(0) = \frac{1+2\mu-\nu}{1-(\nu+\mu)}, \tag{44}$$

whence

$$\alpha'(0)\beta'(0) = \frac{1+\mu+\nu+5\nu\mu-2\mu^2-2\nu^2}{[1-(\nu+\mu)]^2},$$

$$1+\alpha'(0)+\beta'(0) = \frac{3}{1-(\nu+\mu)}, \tag{45}$$

By substituting Eqs. (43)–(45) into Eq. (39), we obtain the sought relation connecting the elastic constants to the bulk modulus and the quantities that characterize the dependence of lattice parameters on volume for hydrostatic compression,

$$\begin{aligned} &C_{11} + 2\frac{1+2\nu-\mu}{1-(\nu+\mu)}C_{12} + 2\frac{1+2\mu-\nu}{1-(\nu+\mu)}C_{13} \\ &\quad + \left[\frac{1+2\nu-\mu}{1-(\nu+\mu)}\right]^2 C_{22} + \left[\frac{1+2\mu-\nu}{1-(\nu+\mu)}\right]^2 C_{33} \\ &\quad + 2\frac{1+\mu+\nu+5\nu\mu-2\nu^2-2\mu^2}{[1-(\nu+\mu)]^2}C_{23} = \frac{9B}{[1-(\nu+\mu)]^2}. \end{aligned} \tag{46}$$

This relation is valid for cubic, tetragonal, hexagonal, trigonal, and orthorhombic crystals.

For hexagonal, tetragonal, and trigonal crystals, it can be simplified by using the symmetry properties $C_{11}=C_{22}$ and $C_{13}=C_{23}$, which hold in this case, and the equality $\nu=0$, which follows from the equality of the parameters a and b for the lattices of these crystal classes,

$$2C_{11} + 2C_{12} + 4\frac{1+2\mu}{1-\mu}C_{13} + \left[\frac{1+2\mu}{1-\mu}\right]^2 C_{33} = \frac{9B}{(1-\mu)^2}. \tag{47}$$

This equality was earlier derived in Ref. 2. If we substitute into it equality (29), which relates the bulk modulus to the elastic constants for hexagonal, tetragonal, and trigonal crystals, and solve the resulted quadratic equation for μ, we obtain

$$\mu = \frac{C_{11}+C_{12}-C_{33}-C_{13}}{C_{11}+C_{12}+2C_{33}-4C_{13}}, \tag{48}$$

which coincides with Eq. (12) used in Refs. 5 and 7.

For cubic crystals whose elastic constants additionally satisfy the relations $C_{33}=C_{11}$ and $C_{13}=C_{12}$ and for which $\mu=0$, Eq. (47) becomes yet simpler and we again obtain the well-known relation

$$C_{11} + 2C_{12} = 3B.$$

As an example, let us apply formulas (28) and (46) to experimental data obtained for some orthorhombic crystals. Reference 23 presents experimentally determined elastic constants for orthorhombic single-crystal forsterite Mg_2SiO_4 at room temperature and different pressures. It also provides a third-order Birch–Murnaghan equation fit to static compression data ($K_0=125$ GPa, $K_0'=4$), which can be used to

TABLE I. Orthorhombic single-crystal forsterite Mg_2SiO_4: experimental elastic constants C_{ij} (GPa) and bulk modulus B (GPa) (Ref. 23) and the value of the bulk modulus B_1 from Eq. (28) and its estimate B_0 from Eq. (49).

P (GPa)	0	3.1	6.1	9.6	10.5	12.2	15.1	16.2
C_{11}	328.4	341.93	363.27	376.59	390.54	391.56	443.15	437.18
C_{22}	199.8	215.69	227.84	251.16	256.18	261.67	277.74	279.11
C_{33}	235.3	248.46	261.37	284.48	283.18	286.02	310.93	319.47
C_{12}	63.9	77.23	89.42	105.34	104.17	107.53	123.55	125.40
C_{13}	68.8	78.50	86.62	95.12	102.96	102.96	126.42	128.19
C_{23}	73.8	83.73	93.69	104.09	107.28	112.77	128.28	130.52
B	125	137.26	148.88	162.20	165.59	171.94	182.67	186.71
B_1	126.5	138.73	150.17	165.33	168.77	172.38	192.32	194.63
$\frac{B_1-B}{B}$	1.2%	1.1%	0.9%	1.9%	1.9%	0.3%	5.3%	4.2%
B_0	130.7	142.78	154.66	169.04	173.19	176.20	198.70	200.44
$\frac{B_0-B}{B}$	4.6%	4.0%	3.9%	4.4%	4.6%	2.5%	8.8%	7.4%

determine the experimental values of the bulk modulus at different pressures. By using these data, we can, with formula (28), find out how the measured elastic constants and bulk modulus agree with each other at different pressures. Unfortunately, Zha *et al.*[23] did not provide the dependence of lattice parameters on pressure, but it is nevertheless possible to use formula (46) if we notice that it can be rewritten as

$$B = B_0 + \Delta B_1 + \Delta B_2,$$

where

$$B_0 = (C_{11} + 2C_{12} + 2C_{13} + 2C_{23} + C_{22} + C_{33})/9, \qquad (49)$$

and ΔB_1 and ΔB_2 contain only terms that are linear and quadratic with respect to ν and μ, respectively,

$$\Delta B_1 = 2[(\mu+\nu)(C_{23}-C_{11}) + (\nu-2\mu)(C_{12}-C_{33}) + (\mu-2\nu)(C_{13}-C_{22})]/9,$$

$$\Delta B_2 = 2[(\mu+\nu)^2 C_{11} + 2(\mu^2-\nu\mu-2\nu^2)C_{12} + (\mu-2\nu)^2 C_{22} - 2(2\mu^2-5\nu\mu+2\nu^2)C_{23} + (\nu-2\mu)^2 C_{33} + 2(\nu^2-\nu\mu-2\mu^2)C_{13}]/9.$$

Since for similar crystals, ν and μ are usually small, $\frac{(\Delta B_1+\Delta B_2)}{\Delta B_0}$ is also small. Hence, one can expect that B_0 will be a good estimate of the bulk modulus B. It should be noted that B_0 was earlier used to estimate the bulk modulus in Ref. 24. Table I provides values for some elastic constants and bulk modulus of single-crystal forsterite Mg_2SiO_4, obtained in the experiment in Ref. 23 at different pressures, and the corresponding values of B_1 and B_0 calculated from Eqs. (28) and (49), respectively. Since Ref. 23 does not provide elastic constants at $P=0$, Table I contains experimental data from Ref. 25. $B(P=0)$ was calculated from the third-order Birch–Murnaghan formula with parameters provided in Ref. 23. Table I shows that the elastic constants at 15.1 and 16.2 GPa are determined with the biggest errors.

References 26 and 27 provide the experimental elastic constants, bulk modulus, and linear compressibilities β_a, β_b, and β_c of a $MgSiO_3$ perovskite. With these data, we can evaluate the consistency of the experimental elastic constants and bulk modulus by using both Eqs. (28) and (46) with ν and μ calculated as

$$\nu = B(\beta_b - \beta_a), \quad \mu = B(\beta_c - \beta_a). \qquad (50)$$

The results of this evaluation are presented in Table II. The

TABLE II. Orthorhombic single-crystal $MgSiO_3$ perovskite: experimental elastic constants C_{ij} (GPa) and bulk modulus B (GPa) (Refs. 26 and 27), and the bulk modulus B_1 from Eq. (28), the bulk modulus B_2 from Eq. (46), and the estimate B_0 from Eq. (49).

	Ref. 26	Ref. 27
C_{11}	515	482
C_{22}	525	537
C_{33}	435	485
C_{12}	117	144
C_{13}	117	147
C_{23}	139	146
B	246.4[a]	264
B_1	245.3903	263.6940
$\frac{B_1-B}{B}$	−0.4%	−0.1%
B_2	245.3907	263.6948
$\frac{B_2-B}{B}$	−0.4%	−0.1%
B_0	246.78	264.22
$\frac{B_0-B}{B}$	+0.15%	+0.08%

[a] Isotropic aggregate (VRH) adiabatic bulk module.

TABLE III. Experimental linear compressibilities of $MgSiO_3$ perovskite and ν and μ calculated from Eq. (50).

	β_a (GPa^{-1})	β_b (GPa^{-1})	β_c (GPa^{-1})	ν	μ
Ref. 26	0.00131	0.00120	0.00156	−0.0271	0.0616
Ref. 27	0.00133	0.00114	0.00131	−0.0502	−0.00528

linear compressibilities from Refs. 26 and 27, as well as ν and μ calculated from Eq. (50), are provided in Table III. It is interesting to note that B_1 and B_2 are almost identical in experiments both in Refs. 26 and 27 though the values of ν and μ markedly differ. In both cases, B_0 is a very good estimate to the bulk modulus.

As another example, we apply formulas (28) and (46) to the results of *ab initio* calculations. Reference 16 provides calculated single-crystal elastic moduli and bulk modulus for orthorhombic $MgSiO_3$ perovskite at $T=298$ K and several pressures in the interval of 0–150 GPa. Unfortunately, the authors did not provide the dependence of lattice parameters on pressure. Therefore, formula (49) was used instead of Eq. (46).

Table IV contains the calculated elastic constants and bulk modulus of the orthorhombic modification of the $MgSiO_3$ perovskite[16] for different pressures, as well as B_1 and B_0 calculated from Eqs. (28) and (49) with the use of the elastic constants from Ref. 16. The data provided in Table IV suggest that the mathematical error of the elastic constants calculated in Ref. 16 is small and roughly equal for different pressures. In this case, the difference of the calculated elastic constants from experiment is mainly associated with the physical approximations that were made in the description of atomic interactions in the crystal.

It is necessary to note the following. Expressions (4), (28), and (46) were obtained for zero temperature when entropy is constant and zero. It is easy to see that the formulas are valid for any constant entropy and can be used to determine the adiabatic elastic constants. As an illustration, let us consider the results of Ref. 28, where measurements of the adiabatic elastic constants of the single-crystal Mg_2SiO_4 forsterite are reported for the temperature range of 300–1700 K at ambient pressure. The adiabatic bulk modulus of the single crystal was not measured; only the adiabatic bulk modulus of an isotropic solid was determined by the Hill averaging method.[29] Nevertheless, formula (28) allows calculating the adiabatic bulk modulus of the single-crystal forsterite for the temperature range of 300–1700 K at ambient pressure, using experimental data from Ref. 28. The results of this calculation are presented in Table V. Also, the derivation remains valid, and formulas (4), (28), and (46) do not change their forms for any nonzero temperature T_0 if we use the free energy $F[V,\hat{\varepsilon}(\gamma),T_0]$ instead of energy $E[V,\hat{\varepsilon}(\gamma)]$. In this way, one can obtain the isothermal elastic constants.

IV. CONCLUSION

To summarize, we derived an equation that relates the second-order elastic constants of an arbitrary single crystal under hydrostatic pressure to the magnitude of this pressure, the characteristics of a small homogeneous strain, and the second derivative of a specific energy with respect to the magnitude of strain. The equation is convenient for *ab initio* calculations of the elastic constants. Also, two relations were derived, which are valid for cubic, hexagonal, tetragonal, trigonal, and orthorhombic crystals and relate the elastic constants to the bulk modulus and the volume dependence of lattice parameters. They help improve the accuracy of

TABLE IV. Some calculated single-crystal elastic constants C_{ij} (GPa) and bulk modulus B (GPa) (Ref. 16) and the bulk modulus B_1 from Eq. (28) and its estimate from Eq. (49) for the orthorhombic $MgSiO_3$ perovskite.

P (GPa)	0	30	60	90	120	150
C_{11}	492	629	746	851	947	1036
C_{22}	550	727	888	1044	1196	1344
C_{33}	472	661	833	995	1150	1298
C_{12}	142	246	349	449	546	639
C_{13}	148	216	287	360	433	505
C_{23}	160	237	311	385	457	528
B	267	379	483	583	681	775
B_1	267.22	377.45	481.19	581.13	677.12	769.12
$\frac{B_1-B}{B}$	0.08%	−0.41%	−0.37%	−0.32%	−0.57%	−0.76%
B_0	268.22	379.44	484.56	586.44	685.00	780.22
$\frac{B_0-B}{B}$	0.46%	0.11%	0.32%	0.59%	0.59%	0.67%

TABLE V. The adiabatic bulk modulus K_S (GPa) of an isotropic solid (Ref. 28) and the bulk modulus B (GPa) of a single crystal calculated according to Eq. (28) from measured adiabatic elastic constants of the single crystal Mg_2SiO_4 forsterite.

T (K)	300	500	700	1000	1300	1700
K_S	128.72	125.50	122.04	116.67	111.22	103.83
B	126.51	123.33	119.89	114.56	109.20	101.90

calculated elastic constants for crystals with a lower symmetry, evaluate the accuracy of their calculated and experimental values, and also calculate the bulk modulus using the measured elastic constants.

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