

# Elastic properties of solids at high pressure

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**Abstract.** This review examines the elastic response of solids under load. The definitions of isothermal and adiabatic elastic constants of  $n$ th order ( $n \geq 2$ ) for a loaded crystal are given. For the case of hydrostatic pressure, two techniques are proposed for calculating the second-, third-, and fourth-order elastic constants from the energy–strain and stress–strain relations. As an example, using the proposed approach within the framework of the density functional theory, the second- to fourth-order elastic constants of bcc tungsten are calculated for the pressure range of 0–600 GPa.

**Keywords:** high pressure, metals, second- and higher-order elastic constants, equation of state, elastic phase transitions

## 1. Introduction

The behavior of materials under high pressure (on the order of the bulk modulus) has seen increasing interest in recent years [1–4] for two reasons. First, advances in high-pressure technology—in particular, the adoption of the diamond anvil cell—have extended the accessible pressure range to about 600 GPa [5]. Second, current computational methods based on the density functional theory provide information on the energy and other properties of any crystal structures for different unit cell volumes, i.e., for different pressure values. This is particularly true of the research field for structural transformations caused by the loss of stability of a crystal lattice under the influence of uniform strains. Such a loss is due to the ‘softening’ of the corresponding second-order elastic constants of a loaded crystal (elastic phase transitions). Importantly, the stability of the high-pressure phase during a transition depends on the nonlinear elasticity

of the material, i.e., the higher (third, fourth, etc.)-order elastic constants, because it is these which ensure the minimum of the thermodynamic potential for the strain corresponding to the structural transformation [6]. The transition pressure and character (whether the transition is first or second order) are determined by relations between the second-, third-, and fourth-order elastic constants. In turn, the jump in the order parameter and the potential barrier height at the transition are directly related to the third- and fourth-order elastic constants [6].

Because the elastic constants of solids at high pressure are very difficult to study experimentally (which is especially true of higher-order constants), the definition of various-order elastic constants of loaded solids and how to calculate them have become a focus of recent attention [4, 6–9]. While it was as far back as the mid-20th century that the elastic constants of crystalline solids under pressure first came to attention, their definition is still the subject of discussion (see, for example, Refs [4, 7, 10, 11]).

Among the first publications on the definition of the elastic constants of a loaded crystal should be mentioned paper [12], which considers the second-order constants of a cubic crystal under hydrostatic pressure. It is shown that, when under pressure, the elastic properties of a crystal, in particular the relation between stress and infinitesimal strain, are determined by elastic constants that depend on the applied pressure. These elastic constants were given the name ‘effective’ to stress the fact that they not only are determined by the interatomic interaction (the second derivative of the free energy with respect to the strain tensor components) but also depend on the external load directly.

In Ref. [13], it was shown for an arbitrary symmetry that, if a crystal is taken to be initially in equilibrium at pressure  $P$ , then an additional term, proportional to pressure, arises in the formulas for the adiabatic and isothermal second-order elastic constants, for example:

$$\tilde{C}_{ijkl} = \frac{1}{V_0} \left( \frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}} \right)_0 - P(\delta_{ij}\delta_{ik} + \delta_{ij}\delta_{jk} - \delta_{ij}\delta_{kl}). \quad (1)$$

Here,  $\tilde{C}_{ijkl}$  are the (effective) isothermal second-order elastic constants of a loaded crystal. The derivative of the free energy

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$F$  with respect to the components of the Lagrangian finite strain tensor  $\eta_{ij}$  is calculated for the equilibrium state at a given  $P$ ,  $V_0$  is the volume of the nonstrained state, and  $\delta_{ik}$  is the Kronecker symbol.

The definition issue was further addressed in Ref. [14], which derived an expression for the second-order constants for an arbitrary (not only hydrostatic compression) load and also showed that these constants fully determine the elastic properties of the crystal, i.e., the stress–strain relation and the small-amplitude vibration equation. For the special case of hydrostatic pressure, relations identical to those found in Ref. [13] [see Eqn (1)] were obtained.

It also follows from Ref. [14] that if the strained state is chosen such that the unit cell volume is constant to within terms of order  $\varepsilon^2$  (where  $\varepsilon$  is an infinitesimal strain), then the additional term proportional to  $P$  disappears. As a result, the second-order shear constants under hydrostatic pressure are simply equal to the second derivative of the free (internal) energy with respect to  $\varepsilon$  [10]. There is much in the literature [15–20] on the application of this method to calculating the second-order constants of cubic and hexagonal lattice metals under hydrostatic pressure.

Among the drawbacks of the method is its inability to determine all independent elastic constants simultaneously (only shear constants allow direct determination), so that the bulk modulus, for example, has to be calculated from the equation of state. For low-symmetry crystals, it is quite difficult to choose a strained state which retains its volume up to a second order in strain. And, of course, this methodology is not suitable for finding the higher (third and fourth)-order elastic constants.

The concept of effective elastic constants at hydrostatic pressure was extended to higher (third and fourth) orders in paper [21]. This is accomplished by taking into account that during the small adiabatic (isothermal) strain of a loaded crystal not only does the free (internal) energy undergo a change but also some amount of work is put out against the external pressure. Reference [21] presents general relations for the second-, third-, and fourth-order effective elastic constants of a cubic crystal under hydrostatic pressure, relations which link the effective constants to the respective-order derivatives of the energy with respect to the components of the Lagrangian finite strain tensor, as well as to pressure. For the second-order constants, the expressions obtained are identical to those presented in formula (1).

Review [22] argues, when discussing crystal elastic properties under load, that the experimental relations between infinitesimal strains and their inducing stresses, on the one hand, and the measured sound speeds, on the other, not only involve the derivatives of the thermodynamic potentials with respect to strain components but also contain certain combinations of the components of the applied external load. This is especially important to bear in mind when the load is comparable in magnitude to the material's elastic constants. The obtained stress–infinitesimal strain relations and the expressions for the second-order elastic constants and for the sound propagation coefficients (which determine the velocity of elastic waves in the crystal) are identical to the relations given in Ref. [14].

Thus, for a crystal strained isothermally under hydrostatic pressure, one has

$$\sigma_{ij} = -P\delta_{ij} + \tilde{C}_{ijkl} \varepsilon_{kl}, \quad (2)$$

where  $\sigma_{ij}$  are mechanical stresses,  $\varepsilon_{kl}$  are the components of the infinitesimal strain tensor, and the crystal constants  $\tilde{C}_{ijkl}$  under hydrostatic pressure are given by Eqn (1). Here and henceforth, summation over the twice repeating indices from 1 to 3 is assumed. The tensor of sound propagation coefficients  $A_{ijkl}$  has the form

$$A_{ijkl} = -P\delta_{jl}\delta_{ik} + C_{ijkl}. \quad (3)$$

Here,

$$C_{ijkl} = \frac{1}{V_0} \left( \frac{\partial^2 U}{\partial \eta_{ij} \partial \eta_{kl}} \right)_0$$

are the second-order adiabatic Brugger type elastic constants (strains in this case are adiabatic), and  $U$  is the internal energy at pressure  $P$ .

The specific cases addressed in Ref. [22] include a cubic crystal under hydrostatic loading and a uniaxially compressed tetragonal crystal.

Marcus and coworkers [23] proposed that the second-order effective elastic constants under hydrostatic pressure be defined in terms of the derivatives of the Gibbs (rather than Helmholtz) energy with respect to the components of the Euler finite strain tensor. Using the Gibbs potential, correct relations involving the external pressure are derived for these constants. The proposal came under criticism, though [10, 11], to which Marcus and coworkers responded by first clarifying the points made [24] and then in papers [25, 26] presenting the justification for their idea with a Gibbs potential.

The effective  $n$ -order ( $n \geq 2$ ) isothermal and adiabatic elastic constants of a loaded crystal were constructed in Ref. [27] as the corresponding derivatives of the Gibbs potential and enthalpy with respects to the components of the Lagrangian finite strain tensor. For a cubic crystal under hydrostatic pressure, relations linking the effective second-, third-, and fourth-order constants with conventional (Brugger) elastic constants of respective orders and pressure were made up and found to agree with their counterparts obtained in Ref. [21]. Example calculations using the obtained relations were performed within the framework of the density functional theory for the second- and third-order constants of body-centered cubic (bcc) tantalum at  $T = 0$  K over a wide pressure range (0–600 GPa). The results for the second-order elastic constants are found to be consistent with existing experimental data and with the results obtained by other workers [16, 18] using the constant volume method (see above). Data of other authors on the third-order elastic constants are lacking in the literature.

Similarly, the second- and third-order elastic constants of bcc molybdenum and hexagonal close-packed (hcp) ruthenium were calculated in Refs [28, 29] over a wide range of pressures (0–1400 GPa and 0–600 GPa for the former and the latter, respectively). In each of these cases, there is good agreement between the experimental and calculated values of second-order elastic constants (at ambient pressure) and of their pressure derivatives. For ruthenium, the experimental behavior of the effective elastic constant  $\tilde{C}_{44}$  is also known for the pressure range of 0–60 GPa, which is found to be virtually identically fitted by the calculations.

The  $n$ th-order ( $n \geq 2$ ) elastic constants in the absence of an external load are thermodynamically defined in Ref. [30],

and this definition is widely used in research on the elastic properties of an unloaded solid. This work gives a detailed analysis on the basis of which  $n$ th-order elastic constants of a loaded crystal can be given similar definitions, and methods for calculating such constants for the case of hydrostatic pressure can be developed.

## 2. Basic definitions and relations

Let us consider a crystal with arbitrary symmetry initially in equilibrium at a fixed temperature  $T$  and under a given external load. The stressed state is described by the stress tensor  $\sigma_{ij}$ . The second- and higher-order effective constants of the loaded crystal describe its elastic properties at a finite strain which is imposed on the initial state ( $\sigma_{ij}$ ). A convenient tool with which to describe such a strained state is the Lagrangian finite strain tensor of the form [22]

$$\eta_{ij} = \frac{1}{2}(\alpha_{ki}\alpha_{kj} - \delta_{ij}). \quad (4)$$

Here,  $\alpha_{kj} = \partial r_k / \partial R_j$  is the strain gradient, and  $r_k$  and  $R_j$  are the Cartesian coordinates of a chosen point in the body in the strained and initial states, respectively. The tensor  $\eta_{ij}$  can be expressed in terms of the displacement gradients  $u_{ij} = \partial u_i / \partial R_j$  ( $u_i = r_i - R_i$ ) because

$$\alpha_{ij} = \delta_{ij} + u_{ij}, \quad (5a)$$

$$\eta_{ij} = \frac{1}{2}(u_{ij} + u_{ji} + u_{ki}u_{kj}). \quad (5b)$$

Neglecting the quadratic terms in Eqn (5b) yields the infinitesimal strain tensor

$$\varepsilon_{ij} = \frac{1}{2}(u_{ij} + u_{ji}). \quad (6)$$

The standard definition of the  $n$ th-order elastic constants (external forces are absent) is as follows [30]

$$C_{ijkl\dots}^T = \frac{1}{V_0} \left( \frac{\partial^n F}{\partial \eta_{ij} \partial \eta_{kl} \dots} \right)_T, \quad (7)$$

$$C_{ijkl\dots}^S = \frac{1}{V_0} \left( \frac{\partial^n U}{\partial \eta_{ij} \partial \eta_{kl} \dots} \right)_S.$$

Here,  $C_{ijkl\dots}^T$  and  $C_{ijkl\dots}^S$  are, respectively, the isothermal and adiabatic  $n$ th-order ( $n \geq 2$ ) Brugger elastic constants,  $F$  and  $U$  are the crystal free and internal energies, and  $V_0$  is the volume in the nonstrained state. The derivatives are taken at constant temperature  $T$  and constant entropy  $S$ .

The elastic constants (7) determine the elastic behavior of an unloaded crystal. In the case of a loaded state, these constants do not take into account the work which should be done against the external load by the forces due to the additional small strain  $\eta_{ij}$ . Therefore, the constants (7) cannot fully characterize the elastic properties of a material under load [21, 22].

Extending the results of the studies cited in Section 1, the isothermal and adiabatic elastic constants of various orders can be defined at a given external load as the corresponding derivatives of the thermodynamic Gibbs potential  $G$  and the enthalpy  $H$  with respect to the components of the finite strain

tensor  $\eta_{ij}$ :

$$\tilde{C}_{ijkl\dots}^T = \frac{1}{V_0} \left( \frac{\partial^n G}{\partial \eta_{ij} \partial \eta_{kl} \dots} \right)_T, \quad (8)$$

$$\tilde{C}_{ijkl\dots}^S = \frac{1}{V_0} \left( \frac{\partial^n H}{\partial \eta_{ij} \partial \eta_{kl} \dots} \right)_S.$$

If the assumed initial state is stressed, with  $\sigma_{ij}$  as an external parameter,  $G$  and  $H$  are the most convenient to use. If a system changes isothermally (adiabatically) at fixed  $\sigma_{ij}$ ,  $G(H)$  has a minimum at equilibrium. The elastic constants can be found in a unique way from Eqn (8) despite the fact that the strain  $\eta_{ij}$  (volume  $V$ ) is not a natural variable for these thermodynamic potentials [31].

The quantities  $\tilde{C}_{ijkl\dots}$  are determined not only by the interatomic interaction but also directly by the applied load and, unlike the elastic constants (7), have full Voigt index permutation symmetry only for hydrostatic pressure (and not otherwise) [14, 22]. Also, because these constants include the external load, they cannot obey the Cauchy relations. When using second-order elastic constants  $\tilde{C}_{ijkl}$ , the equations determining the velocity of sound waves in the crystal under load have the same form as in the unloaded state; the same is true for stability conditions and for the stress–strain relation (see Refs [14, 22]).

Thus, relations (7) and (8) represent a unified approach to defining elastic constants: elastic constants are the  $n$ th-order ( $n \geq 2$ ) derivatives of the characteristic functions which, under given conditions, are thermodynamic potentials. The use of formulas (8) in the definition of the elastic constants of a loaded crystal results in the elasticity theory relations having the same form for both hydrostatic pressure and  $P = 0$ . As a result, while pressure does feature in the elasticity theory formulation for arbitrary hydrostatic pressure as a parameter of the state, it is not present in itself, unlike, for example, Eqns (1) and (3). For the same reason, the elastic constants (8) are essentially not effective but ordinary elastic constants that fully characterize the properties of a loaded crystal under given conditions.

We will now use formulas (8) to derive an expression for the second-to-fourth-order isothermal elastic constants under loading conditions. Of practical interest is the case of hydrostatic pressure when the strain of a crystal lattice remains elastic for any degree of compression. In this case, the change in the Gibbs potential produced by the additional strain  $\eta_{ij}$  (pressure  $P$ , temperature  $T$ ) per unit volume in a nonstrained state takes the form

$$\frac{\Delta G}{V_0} = \frac{\Delta F}{V_0} + P \frac{\Delta V}{V_0}. \quad (9)$$

Here,  $\Delta G = G(P, T, \eta) - G(P, T, 0)$ ,  $\Delta F = F(P, T, \eta) - F(P, T, 0)$ , and  $\Delta V = V - V_0$  is the change in volume due to strain determined by the components of the tensor  $\eta_{ij}$ . The volume in a strained state is given by the relation  $V = JV_0$ , where  $J = \det |\alpha_{ij}|$ , and then  $\Delta V / V_0 = J - 1$  [22]. Because we consider the case of pure strain (the crystal as a whole does not rotate,  $u_{ij} = u_{ji}$ ), Eqn (5b) takes the form

$$\eta_{ij} = u_{ij} + \frac{1}{2} u_{ki} u_{kj}.$$

Using Eqn (5a) and the relation

$$u_{ij} = \eta_{ij} - \frac{1}{2} u_{ki} u_{kj},$$

**Table 1.** Relations between  $\tilde{C}_{\alpha\beta\dots}$  and  $C_{\alpha\beta\dots}$ .

$\tilde{C}_{\alpha\beta}$	$\tilde{C}_{\alpha\beta\gamma}$	$\tilde{C}_{\alpha\beta\gamma\delta}$	
$\tilde{C}_{11} = C_{11} - P$	$\tilde{C}_{111} = C_{111} + 3P$	$\tilde{C}_{1111} = C_{1111} - 15P$	$\tilde{C}_{1255} = C_{1255} + P$
	$\tilde{C}_{112} = C_{112} - P$	$\tilde{C}_{1112} = C_{1112} + 3P$	$\tilde{C}_{1266} = C_{1266} - P$
$\tilde{C}_{12} = C_{12} + P$	$\tilde{C}_{123} = C_{123} + P$	$\tilde{C}_{1122} = C_{1122} + P$	$\tilde{C}_{1456} = C_{1456} - P$
	$\tilde{C}_{144} = C_{144} - P$	$\tilde{C}_{1123} = C_{1123} - P$	$\tilde{C}_{4444} = C_{4444} - 3P$
$\tilde{C}_{44} = C_{44} - P$	$\tilde{C}_{155} = C_{155} + P$	$\tilde{C}_{1144} = C_{1144} + P$	$\tilde{C}_{4455} = C_{4455} - P$
	$\tilde{C}_{456} = C_{456} + P$	$\tilde{C}_{1155} = C_{1155} - 3P$	

we can express  $\alpha_{ij}$  in terms of  $\eta_{kl}$ . As a result, keeping terms to fourth-order in  $\eta$ , we obtain

$$\alpha_{ij} = \delta_{ij} + \eta_{ij} - \frac{1}{2} \eta_{ki} \eta_{kj} + \frac{1}{2} \eta_{rk} \eta_{ri} \eta_{kj} - \frac{5}{8} \eta_{kj} \eta_{mk} \eta_{mn} \eta_{ni}. \quad (10)$$

Using relation (10), we find an expression for  $J$  [given in Appendix A as a sum of terms in powers of  $\eta_{kl}$ ; see formulas (A1)–(A5)].

Expanding  $\Delta F/V_0$  at pressure  $P$  up to fourth-order in the components of the finite strain tensor  $\eta_{kl}$ , we get

$$\frac{\Delta F}{V_0} = \frac{\Delta F_1}{V_0} + \frac{\Delta F_2}{V_0} + \frac{\Delta F_3}{V_0} + \frac{\Delta F_4}{V_0}. \quad (11)$$

The expressions for the terms  $\Delta F_{1-4}/V_0$  are presented in Appendix B, formulas (B1)–(B4).

Using formulas (8), (9), (11), (B1)–(B4), and the relations for  $\Delta V/V_0$  [see expressions (A1)–(A5)], we find relations between the effective elastic constants  $\tilde{C}_{\alpha\beta\dots}$  and  $C_{\alpha\beta\dots}$  by grouping in Eqn (9) the terms containing similar combinations of the strain components. The results are presented in Table 1.

The relations presented in Table 1 are consistent with the results obtained by a different approach in Ref. [21].

Thus, to calculate the elastic constants  $\tilde{C}_{\alpha\beta\dots}$ , it is necessary to find the quantities  $C_{\alpha\beta\dots}$  and the pressure  $P$  by expanding the free energy in a power series of the components of the finite strain tensor  $\eta_{\alpha}$  [see Eqns (B1)–(B4)]. Then, one can find respective quantities  $\tilde{C}_{\alpha\beta\dots}$  using relations listed in Table 1.

Another possible approach to calculating the effective elastic constants of different orders is based on the results of Refs [32–34], whose authors use the stress–strain relations rather than the energy–strain relation in calculating the second-, third-, and fourth-order elastic constants at  $P = 0$ . Because the strain is defined with respect to the initial, nonstrained state of the body ( $\eta_{ij} = 0$ ), and because the stress is calculated per unit area of the strained body, finite strain and stress are related in a complex way. Note here that the differential of the work done by stress is not equal to the product of the stress components  $\sigma_{ij}$  by the corresponding strain components. The way to remedy the situation is to introduce the quantities  $t_{ij}$  (‘thermodynamic stresses’ [35]), defined such that the sum  $t_{ij} d\eta_{ij}$  [35] is equal to the differential of the work done by stress per unit of the initial (nonstrained) volume. According to Ref. [35], one finds

$$t_{ij} = \frac{1}{V_0} \left( \frac{\partial F}{\partial \eta_{ij}} \right), \quad (12)$$

i.e., they are related to strains through the corresponding number of elastic constants  $C_{\alpha\beta\dots}$ . The quantities  $t_{ij}$ , in turn, are related to the total stress components  $\sigma_{kl}$  by the relation [35]

$$t_{ij} = J \sigma_{kl} \gamma_{ik} \gamma_{jl}, \quad (13)$$

where the matrix  $\gamma_{ik}$  is the inverse of  $\alpha_{jl}$ . In the theory of finite strains, the quantities  $t_{ij}$  correspond, according to relation (13), to the components of the second Piola–Kirchhoff stress tensor, which determine the stress related to the nonstrained configuration.

The authors of Ref. [33], using the density functional theory, obtained an analytical expression for  $\sigma_{kl}$  [formula (2)], making it possible to calculate the stress components  $\sigma_{ij}$  directly without the necessity of calculating the total energy. Following this, the thermodynamic stresses  $t_{ij}$  can be obtained from relation (13), which should then be used to calculate the corresponding combinations of elastic constants  $C_{\alpha\beta\dots}$  using relations (12) and (B1)–(B4). Then, using the known  $C_{\alpha\beta\dots}$ , the effective elastic constants  $\tilde{C}_{\alpha\beta\dots}$  at pressure  $P$  can be calculated from the relations given in Table 1.

The advantage of this methodology is that the calculation of higher-order elastic constants from the stress–strain relation requires an expansion to third (rather than fourth) order in  $\eta$ . References [32, 33] demonstrate the application of this methodology to the calculation (at  $P = 0$ ) of a number of Brugger elastic constants [see Eqn (7)] of the second, third, and fourth order for Si, Ge, and GaAs. In Ref. [36], illustrative calculations are made for the second- and third-order constants ( $P = 0$ ) in Si, GaAs, AlN, GaN, and InN.

### 3. Methodology and details of calculations

To illustrate the use of the relations obtained, we calculated the elastic constants of second, third, and fourth order of bcc tungsten in the pressure range of 0–600 GPa at  $T = 0$  K (no difference between the isothermal and adiabatic constants). The initial stressed state was specified by the magnitude of the atomic volume  $V_0$ . For each such state, a number of variants of unit cell deformation were considered, which are presented in Appendix B (Table 4). The lattice vectors in the strained state are determined by the relation  $r_i = \alpha_{ij} R_j$ , in which the strain gradient  $\alpha_{ij}$  is expressed, using Eqn (10), in terms of the components of the Lagrangian finite strain tensor.

The total energy of bcc tungsten and mechanical stresses  $\sigma_{ij}$  at different values of  $V_0$  and strain  $\eta_{ij}$  were calculated using the implemented in VASP [37], density functional theory, where VASP stands for the Vienna *Ab initio* Simulation Package. The exchange–correlation contribution was included in the generalized gradient approximation with

**Table 2.** Second order elastic constants and their pressure derivatives at  $P = 0$ .

Quantity	$C_{11}$	$C_{12}$	$C'$	$C_{44}$	$B$	Source
$C_{\alpha\beta}$ , GPa	519.4	200.4	161.0	144.2	306.8	Present work (energy–strain)
	519.7	200.5	159.6	146.0	306.9	Present work (stress–strain)
	512.6	205.8		152.7		Experiment [45]
	523	203		160		Experiment [46]
	532.6	205.0		163.1		Experiment [47]
	502.6	213.6	144.5	145.9	309.9	Calculation [48]
			166.8	170.5	306.5	Calculation [15]
	513	199		140		Calculation [19]
$\frac{1}{C_{\alpha\beta}} \frac{dC_{\alpha\beta}}{dP} \times 10^3$ , GPa $^{-1}$	10.8	16.2		10.4		Present work
	11.8	16.4		10.0		Experiment [46]

**Table 3.** Third- and fourth-order elastic constants (in GPa) of bcc tungsten at  $P = 0$  ( $T = 0$  K).

	$-C_{111} \times 10^{-1}$	$-C_{112} \times 10^{-1}$	$-C_{123} \times 10^{-1}$	$-C_{144} \times 10^{-1}$	$-C_{155} \times 10^{-1}$	$-C_{456} \times 10^{-1}$	$C_{1111} \times 10^{-2}$	$C_{1112} \times 10^{-2}$	$C_{4444} \times 10^{-2}$
1	523.0	93.23	74.21	78.64	92.46	93.47	407.5	115.7	52.47
2	528.3	93.88	66.71	83.02	96.88	100.4	411.2	122.7	59.73

the Purdue–Wang parameterization PW91 [38]. To describe the ion–electron interaction, the method of projector-augmented waves was employed [39]. The integration over the Brillouin zone was performed by the tetrahedron method using a  $28 \times 28 \times 28$  array of points obtained by the Monkhorst–Pack method [40]. The plane wave cutoff energy was 700 eV. The reason why the calculation parameters are chosen so large is due to the small magnitude of the third- and fourth-order effects in  $\eta$ .

The pressure and the elastic constants of different orders were obtained by the least-square method (21 points in the interval  $\pm 0.08$  with a step of 0.008) from the polynomial dependences  $\Delta F(\eta)/V_0$  and  $t_{ij}(\eta)$  (see Table 4).

#### 4. Calculated results and discussion

The tungsten equation of state calculated in the present work is shown in Fig. 1 together with available experimental  $P(V)$  data. The equation of state was studied in sufficient detail at pressures up to 300 GPa using the shock wave technique [41] and static measurements [42–44]. The data shown in Fig. 1 suggest that the variation of  $P$  with  $V$  calculated in the present work agrees well with the experimental data (at  $V/V_0 = 0.664$ , the difference in pressure values does not exceed 3%).

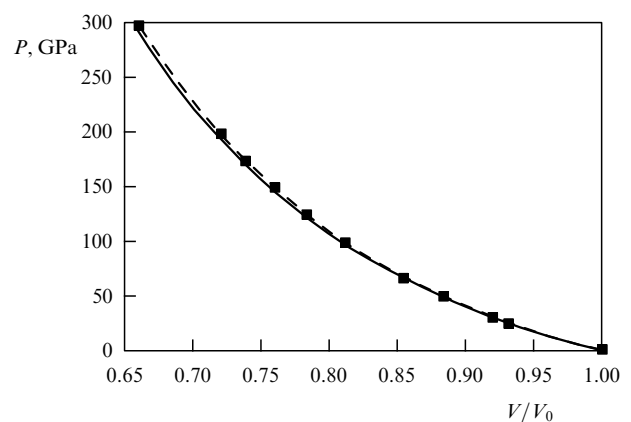
Experimental data on tungsten elastic constants are available only for those of second order at atmospheric pressure. Tables 2 and 3 and Figs 2–4 present our calculated second-, third-, and fourth-order elastic constants of bcc tungsten at pressures up to 600 GPa. The calculations were performed using the energy–finite strain and stress–finite strain relations.

In Table 2, the calculated second-order constants and their pressure derivatives at  $P = 0$  are compared with the experimental and theoretical results of other researchers. The calculated results correspond to  $T = 0$  K; the experimental data were obtained at room temperature. It is seen that both

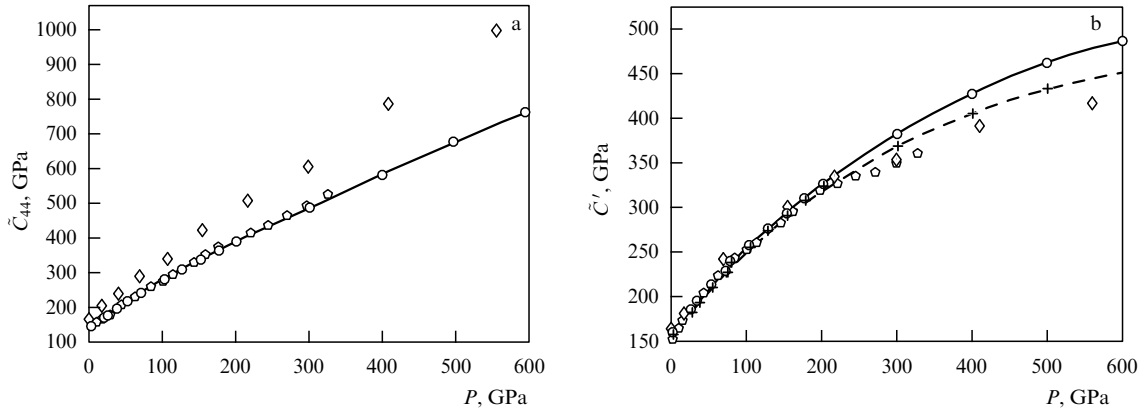
methods used give virtually the same values for  $C_{\alpha\beta}$ . Because both the energy and mechanical stresses  $\sigma_{ij}$  are calculated with VASP independently, the good agreement between the results obtained by the two methods implies a high calculation precision.

The obtained values of  $C_{11}$  and  $C_{12}$  agree well (to within 2.5%) with the experimental data. For  $C_{44}$ , the agreement is worse: the calculation underestimates the data by about 8%.

In some studies [15, 19, 48] (see also Table 2), the elastic constants were calculated from first principles using infinitesimal strains  $\varepsilon_{ij}$  and keeping the unit cell volume fixed to first and second order in  $\varepsilon_{ij}$ . The predicted value of  $C_{44}$  is again much different from the experimental value. In Ref. [19], a similar difference between the calculated and experimental  $C_{44}$  was observed for vanadium and niobium.



**Figure 1.** Pressure versus volume for bcc tungsten. Dashed line is calculated from the regression by the Birch–Murnaghan equation of state of the  $P(V)$  dependence obtained in the present paper (data are shown by squares), and solid line is the experimental  $P(V)$  curve obtained from the results of Refs [41–44]).



**Figure 2.** Variation with pressure of the elastic constants  $\tilde{C}_{44}$  (a) and  $\tilde{C}'$  (b) of bcc tungsten. The results of this work are shown by circles and connected by a solid line for viewing convenience; data from elsewhere are shown by diamonds [15] and pentagons [19]. The data of our work obtained using volume-conserving infinitesimal strains are shown by crosses and connected by a dashed line.

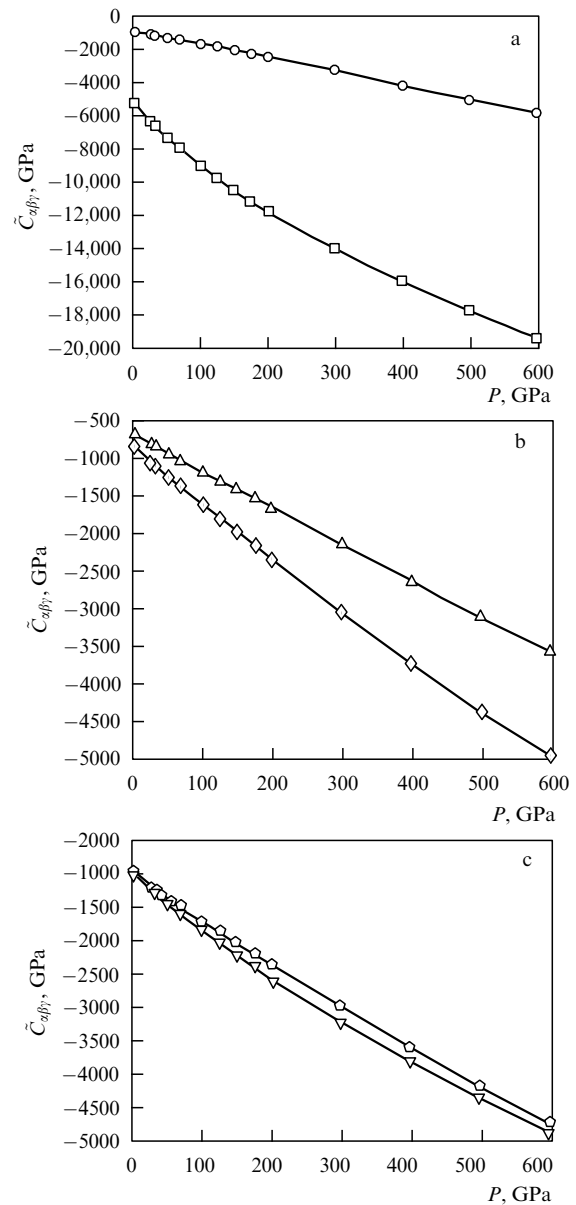
Given in the last two rows of Table 2 are our calculated results and available experimental data on the pressure derivatives of the second-order constants corresponding to  $P$  close to atmospheric pressure. It is seen that our results agree perfectly with the data.

Figure 2 presents our calculated shear constants  $\tilde{C}_{44}$  and  $\tilde{C}'$  as a function of pressure in the pressure range of 0–600 GPa. Both calculation methods used in this work yield the same dependences (to within 0.5% for  $\tilde{C}_{44}$ , and 2% for  $\tilde{C}'$  for each specific value of  $P$ ). It is seen that for the elastic constant  $\tilde{C}_{44}$  our results compare well with another calculation using the first-principles pseudopotential of Ref. [19], but strongly disagree with full potential calculations performed in Ref. [15]. In the case of  $\tilde{C}'$ , our results and those of Refs [15, 19] are virtually the same up to  $\approx 200$  GPa. At higher pressures, however, considerable differences are observed among the results of all the three papers.

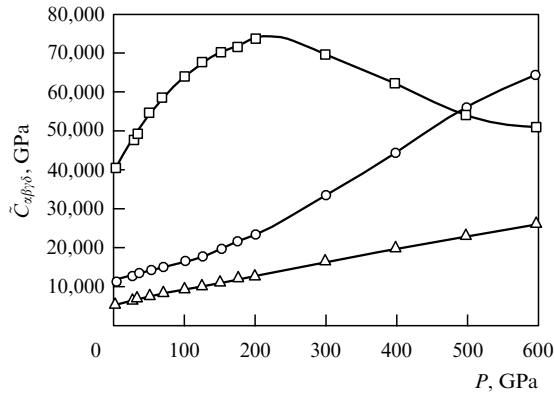
It should be noted that the FP-LMTO (full potential muffin-tin orbitals) method is (as the name suggests) a full-potential one and is bound to be more accurate than a combination of the PAW (projector augmented wave) and GGA (generalized gradient approximation) methods used in the present work. At the same time, Refs [15, 19] calculated second-order elastic constants using the energy–infinitesimal strain relation (when volume is conserved to second order in  $\varepsilon$ ). The resulting values of  $\tilde{C}_{44}$  and  $\tilde{C}'$  implicitly contain contributions from the higher-order expansion terms. Similar calculations by the present authors using a relation between energy and volume–conserving infinitesimal strain (dashed line in Fig. 2b) agree much better with those of Refs [15, 19].

The calculated values of the third- and fourth-order elastic constants at  $P = 0$  are presented in Table 3. The first and second rows represent the elastic constants obtained from the energy–finite strain and stress–finite strain relations, respectively. Shown are all six of the  $C_{\alpha\beta\gamma}$ 's and the three most characteristic of  $C_{\alpha\beta\gamma\delta}$ . As seen from Table 3, both methodologies produce similar results, although the difference between the corresponding constants is somewhat larger than in the case of  $C_{\alpha\beta}$ .

Figure 3 presents a plot of  $\tilde{C}_{\alpha\beta\gamma}$  as a function of pressure in the range of 0–600 GPa obtained from the stress–finite strain relation (the other method yields essentially the same behavior). It is seen that, over the entire pressure range studied, the third-order elastic constants are negative and



**Figure 3.** Third-order elastic constants obtained from the small finite strain–stress relation. Squares:  $\tilde{C}_{111}$ , circles:  $\tilde{C}_{112}$  (a), triangles:  $\tilde{C}_{123}$ , diamonds:  $\tilde{C}_{144}$  (b), pentagons:  $\tilde{C}_{155}$ , and triangles:  $\tilde{C}_{456}$  (c).



**Figure 4.** Variation with pressure of the fourth-order elastic constants for bcc tungsten ( $T = 0$  K). Squares:  $\tilde{C}_{1111}$ , circles:  $\tilde{C}_{1122}$ , and triangles:  $\tilde{C}_{4444}$ .

their absolute value increases monotonically with increasing pressure.

The variation of the fourth-order constants with pressure is shown in Fig. 4. It is seen that in the pressure range of 0–600 GPa, the constants  $\tilde{C}_{\alpha\beta\gamma\delta}$  are positive. The constant  $\tilde{C}_{1111}$  reaches a maximum at  $P \approx 200$  GPa and then decreases monotonically. The elastic constants  $\tilde{C}_{1112}$  and  $\tilde{C}_{4444}$  increase nearly linearly with increasing pressure.

Because the literature offers no data on the third- and fourth-order elastic constants of bcc tungsten and their variation with pressure, the results obtained here are of undoubted interest.

In our earlier work, similar calculations of second- and higher-order elastic constants were performed over a wide range of pressures for bcc vanadium [9], bcc tantalum [27], bcc molybdenum [28] and hcp ruthenium [29]. To summarize the results, we have found that in the megabar pressure range the term containing  $P$  in the expression for elastic constants (see Table 1) has a significant effect on the magnitude of the constants. This is especially true of second-order constants, leading sometimes to the ‘softening’ of  $\tilde{C}_{\alpha\beta}$  with pressure: vanadium,  $\tilde{C}_{44}$  [9], molybdenum,  $\tilde{C}'$  [28], and, to a lesser degree, tungsten,  $\tilde{C}'$  (present work). This softening is a precursor of the elastic phase transition [6].

## 5. Conclusion

This paper has given definitions for the isothermal and adiabatic elastic constants of  $n$ th order ( $n \geq 2$ ) for a loaded crystal. These constants fully characterize the elastic behavior of a solid in a loaded state and are determined not only by the interatomic interactions but also by the external load. For the case of hydrostatic pressure, two methodologies are presented for calculating second-, third-, and fourth-order elastic constants in the framework of nonlinear elasticity theory, one of which uses the energy–finite strain relation, while the other works with the stress–finite strain relation. Both methodologies were used to calculate the second-, third-, and fourth-order elastic constants of bcc tungsten over the pressure range of 0–600 GPa ( $T = 0$  K). Energy and mechanical stress calculations for different deformations of a loaded crystal are performed within the framework of the density-functional theory using the VASP code.

Both methods yield similar values for the respective elastic constants of different orders, the difference not exceeding a few percent. As pressure increases, the second-, third-, and

fourth-order elastic constants of bcc tungsten increase monotonically in absolute value. The results obtained agree well with available experimental and calculated results on the second-order elastic constants at  $P = 0$ , as well as with the calculations on the pressure dependence of second-order constants performed by others using the method of infinitesimal volume-conserving strains. No literature data are available on the values and pressure derivatives of the third- and fourth-order elastic constants of tungsten.

Thus, the results of the present work make it possible to foresee the high-pressure properties of metals. In particular, information on the behavior of the second-to-fourth-order elastic constants of solids is necessary when analyzing the possibility of diffusionless phase transformations (martensite or elastic phase transitions) under pressure. Also, because  $\tilde{C}_{\alpha\beta\gamma}$  and  $\tilde{C}_{\alpha\beta\gamma\delta}$  are determined by the third- and fourth-order effects, their calculation provides a test for *ab initio* computer codes based on the density functional approximation.

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## 6. Appendices

### Appendix A

The further analysis of relation (9) can be facilitated by using formula (10) to represent the Jacobian  $J$  of the variables  $r_i$  with respect to the variables  $R_j$  as a sum of terms up to the fourth power of  $\eta_{ij}$ , giving

$$J - 1 = J_1 + J_2 + J_3 + J_4, \quad (\text{A1})$$

$$J_1 = \eta_1 + \eta_2 + \eta_3, \quad (\text{A2})$$

$$J_2 = \eta_1\eta_2 + \eta_1\eta_3 + \eta_2\eta_3 - \frac{1}{2}(\eta_1^2 + \eta_2^2 + \eta_3^2 + \eta_4^2 + \eta_5^2 + \eta_6^2), \quad (\text{A3})$$

$$J_3 = \eta_1\eta_2\eta_3 + \eta_4\eta_5\eta_6 + \frac{1}{2}(\eta_1^3 + \eta_2^3 + \eta_3^3 + \eta_3\eta_5^2 - \eta_1\eta_2^2 - \eta_1\eta_3^2 - \eta_1\eta_4^2 + \eta_1\eta_5^2 + \eta_1\eta_6^2 - \eta_2\eta_3^2 + \eta_2\eta_4^2 - \eta_1^2\eta_2 - \eta_1^2\eta_3 - \eta_2^2\eta_3 - \eta_2\eta_5^2 + \eta_2\eta_6^2 + \eta_3\eta_4^2 - \eta_3\eta_6^2), \quad (\text{A4})$$

$$J_4 = -\eta_1\eta_4\eta_5\eta_6 - \eta_2\eta_4\eta_5\eta_6 - \eta_3\eta_4\eta_5\eta_6 - \frac{1}{8}(5\eta_1^4 + 5\eta_2^4 + 5\eta_3^4 + \eta_4^4 + \eta_5^4 + \eta_6^4) + \frac{1}{4}(\eta_1^2\eta_4^2 - 3\eta_1^2\eta_5^2 - 3\eta_1^2\eta_6^2 - 3\eta_2^2\eta_4^2 - 3\eta_2^2\eta_6^2 - 3\eta_3^2\eta_4^2 - 3\eta_3^2\eta_5^2 + \eta_3^2\eta_6^2 - \eta_4^2\eta_5^2 - \eta_4^2\eta_6^2 - \eta_5^2\eta_6^2)$$

**Table 4.** Deformation conditions for a cubic crystal (elastic constants and the components of the finite strain tensor are presented in Voigt's notation).

Deformation	Free energy and thermodynamic stress
$\eta_1 = \eta^*$	$\frac{\Delta F}{V_0} = -P\eta + \frac{1}{2} C_{11}\eta^2 + \frac{1}{6} C_{111}\eta^3 + \frac{1}{24} C_{1111}\eta^4,$ $t_1(\eta) = -P + C_{11}\eta + \frac{1}{2} C_{111}\eta^2 + \frac{1}{6} C_{1111}\eta^3, \quad t_2(\eta) = -P + C_{12}\eta + \frac{1}{2} C_{112}\eta^2 + \frac{1}{6} C_{1112}\eta^3$
$\eta_1 = \eta_2 = \eta$	$\frac{\Delta F}{V_0} = -2P\eta + (C_{11} + C_{12})\eta^2 + \left(\frac{1}{3} C_{111} + C_{112}\right)\eta^3 + \frac{1}{12}(C_{1111} + 4C_{1112} + 3C_{1122})\eta^4,$ $t_3(\eta) = -P + 2C_{12}\eta + (C_{123} + C_{112})\eta^2 + \left(\frac{1}{3} C_{1112} + C_{1123}\right)\eta^3$
$\eta_1 = -\eta_2 = \eta$	$\frac{\Delta F}{V_0} = (C_{11} - C_{12})\eta^2 + \frac{1}{12}(C_{1111} - 4C_{1112} + 3C_{1122})\eta^4,$ $t_1(\eta) = -P + (C_{11} - C_{12})\eta + \frac{1}{2}(C_{111} - C_{112})\eta^2 + \frac{1}{6}(C_{1111} - 4C_{1112} + 3C_{1122})\eta^3$
$\eta_6 = 2\eta$	$\frac{\Delta F}{V_0} = 2C_{44}\eta^2 + \frac{2}{3} C_{4444}\eta^4,$ $t_1 = -P + 2C_{155}\eta^2, \quad t_6 = 2C_{44}\eta + \frac{4}{3} C_{4444}\eta^3$
$\eta_1 = \eta,$ $\eta_4 = 2\eta$	$\frac{\Delta F}{V_0} = -P\eta + \left(\frac{1}{2} C_{11} + 2C_{44}\right)\eta^2 + \left(\frac{1}{6} C_{111} + 2C_{144}\right)\eta^3 + \left(\frac{1}{24} C_{1111} + C_{1144} + \frac{2}{3} C_{4444}\right)\eta^4,$ $t_4 = 2C_{44}\eta + 2C_{144}\eta^2 + \left(C_{1144} + \frac{4}{3} C_{4444}\right)\eta^3$
$\eta_1 = \eta,$ $\eta_5 = 2\eta$	$\frac{\Delta F}{V_0} = -P\eta + \left(\frac{1}{2} C_{11} + 2C_{44}\right)\eta^2 + \left(\frac{1}{6} C_{111} + 2C_{155}\right)\eta^3 + \left(\frac{1}{24} C_{1111} + C_{1155} + \frac{2}{3} C_{4444}\right)\eta^4,$ $t_2 = -P + C_{12}\eta + \left(\frac{1}{2} C_{112} + 2C_{144}\right)\eta^2 + \left(\frac{1}{6} C_{1112} + 2C_{1255}\right)\eta^3,$ $t_3 = -P + C_{12}\eta + \left(\frac{1}{2} C_{112} + 2C_{155}\right)\eta^2 + \left(\frac{1}{6} C_{1112} + 2C_{1266}\right)\eta^3,$ $t_5 = 2C_{44}\eta + 2C_{155}\eta^2 + \left(C_{1155} + \frac{4}{3} C_{4444}\right)\eta^3$
$\eta_4 = \eta_5 = \eta_6 = 2\eta$	$t_1 = -P + 2(C_{144} + C_{155})\eta^2 + 8C_{1456}\eta^3,$ $t_6 = 2C_{44}\eta + 4C_{456}\eta^2 + \frac{4}{3}(C_{4444} + 6C_{4455})\eta^3$

\* The remaining components of the finite strain components are zero.

$$\begin{aligned}
& + \eta_1^2\eta_2^2 + \eta_1^2\eta_3^2 + \eta_2^2\eta_3^2 + \eta_2^2\eta_5^2 + \frac{1}{2}(\eta_1\eta_2^3 + \eta_1\eta_3^3) \\
& + \eta_2\eta_3^3 + \eta_1^3\eta_2 + \eta_1^3\eta_3 + \eta_2^3\eta_3 + \eta_2\eta_3\eta_6^2 + \eta_1\eta_3\eta_6^2 \\
& - \eta_1\eta_2\eta_6^2 + \eta_2\eta_3\eta_5^2 - \eta_1\eta_3\eta_5^2 + \eta_1\eta_2\eta_5^2 - \eta_2\eta_3\eta_4^2 \\
& + \eta_1\eta_3\eta_4^2 + \eta_1\eta_2\eta_4^2 - \eta_1\eta_2\eta_3^2 - \eta_1\eta_2^2\eta_3 - \eta_1^2\eta_2\eta_3. \quad (\text{A5})
\end{aligned}$$

Here, we used Voigt's notation for the Lagrangian finite strain tensor components: 11  $\rightarrow$  1, 22  $\rightarrow$  2, 33  $\rightarrow$  3, 23  $\rightarrow$  4, 13  $\rightarrow$  5, 12  $\rightarrow$  6.

## Appendix B

$\Delta F/V_0$  is directly found to be

$$\frac{\Delta F_1}{V_0} = -P(\eta_1 + \eta_2 + \eta_3). \quad (\text{B1})$$

Expressions for the remaining terms in formula (11) depend on the crystal symmetry. Crystals with cubic symmetry [point groups (432), (432), (4/m $\bar{3}$ 2/m)] have three independent

second order elastic constants  $C_{\alpha\beta}$ , six third-order constants  $C_{\alpha\beta\gamma}$ , and eleven fourth-order constants  $C_{\alpha\beta\gamma\delta}$  [22]. The elastic constants are presented in Voigt notation. As a result, using relations from Ref. [49], the expressions for  $\Delta F_{2-4}/V_0$  for a cubic crystal can be written out in the form

$$\begin{aligned}
\frac{\Delta F_2}{V_0} &= \frac{1}{2} C_{11}(\eta_1^2 + \eta_2^2 + \eta_3^2) + C_{12}(\eta_1\eta_2 + \eta_2\eta_3 + \eta_1\eta_3) \\
&+ \frac{1}{2} C_{44}(\eta_4^2 + \eta_5^2 + \eta_6^2), \quad (\text{B2})
\end{aligned}$$

$$\begin{aligned}
\frac{\Delta F_3}{V_0} &= \frac{1}{6} C_{111}(\eta_1^3 + \eta_2^3 + \eta_3^3) + \frac{1}{2} C_{112}[\eta_1^2(\eta_2 + \eta_3) \\
&+ \eta_2^2(\eta_1 + \eta_3) + \eta_3^2(\eta_1 + \eta_2)] + C_{123}\eta_1\eta_2\eta_3 \\
&+ C_{456}\eta_4\eta_5\eta_6 + \frac{1}{2} C_{144}(\eta_1\eta_4^2 + \eta_2\eta_5^2 + \eta_3\eta_6^2) \\
&+ \frac{1}{2} C_{155}[\eta_4^2(\eta_2 + \eta_3) + \eta_5^2(\eta_1 + \eta_3) + \eta_6^2(\eta_1 + \eta_2)], \quad (\text{B3})
\end{aligned}$$



$$\begin{aligned}
\frac{\Delta F_4}{V_0} = & \frac{1}{24} C_{1111}(\eta_1^4 + \eta_2^4 + \eta_3^4) \\
& + \frac{1}{6} C_{1112}[\eta_1^3(\eta_2 + \eta_3) + \eta_2^3(\eta_1 + \eta_3) + \eta_3^3(\eta_1 + \eta_2)] \\
& + \frac{1}{4} C_{1122}(\eta_1^2\eta_2^2 + \eta_2^2\eta_3^2 + \eta_1^2\eta_3^2) \\
& + \frac{1}{2} C_{1123}\eta_1\eta_2\eta_3(\eta_1 + \eta_2 + \eta_3) \\
& + \frac{1}{4} C_{1144}(\eta_1^2\eta_4^2 + \eta_2^2\eta_5^2 + \eta_3^2\eta_6^2) \\
& + \frac{1}{4} C_{1155}[\eta_1^2(\eta_6^2 + \eta_5^2) + \eta_2^2(\eta_6^2 + \eta_4^2) + \eta_3^2(\eta_5^2 + \eta_4^2)] \\
& + \frac{1}{2} C_{1255}[\eta_1\eta_2(\eta_4^2 + \eta_5^2) + \eta_2\eta_3(\eta_5^2 + \eta_6^2) + \eta_1\eta_3(\eta_4^2 + \eta_6^2)] \\
& + \frac{1}{2} C_{1266}(\eta_1\eta_2\eta_6^2 + \eta_2\eta_3\eta_4^2 + \eta_1\eta_3\eta_5^2) \\
& + C_{1456}\eta_4\eta_5\eta_6(\eta_1 + \eta_2 + \eta_3) + \frac{1}{24} C_{4444}(\eta_4^4 + \eta_5^4 + \eta_6^4) \\
& + \frac{1}{4} C_{4455}(\eta_4^2\eta_5^2 + \eta_5^2\eta_6^2 + \eta_4^2\eta_6^2). \tag{B4}
\end{aligned}$$

Here,  $C_{\alpha\beta\dots}$  are the Brugger type isothermal elastic constants of the corresponding order [see formula (7)] under pressure  $P$ .

### Appendix C

Using expressions (B1)–(B4) for the change in the free energy of a cubic crystal under strain and also using the thermodynamic stress relation (12), we find expressions for  $\Delta F/V_0$  and  $t_{ij}$  for different deformation conditions. Table 4 lists a number of simple strained states and their corresponding combinations of elastic constants. The relations listed in the table allow the total set of second-to-fourth-order elastic constants to be calculated for a cubic crystal at a given pressure.

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