Fourth-order elastic moduli of polycrystals

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The investigation of higher-order elastic moduli of polycrystalline solids is a challenging task. For this purpose the decomposition of the polycrystal Gibbs free energy at hydrostatic pressure in terms of the finite strain tensor components, taking into account the fourth-order contributions, is given. We give the definition of the fourth-order elastic moduli for the polycrystal (the fourth-order Lamé coefficients) at an arbitrary pressure. We obtain the relationships between the Lamé coefficients of the fourth order at pressure P with the corresponding constants of the single-crystal grains constituting the polycrystal. The case of the arbitrary grain symmetry and, in particular, when the grains have a cubic lattice, is considered. The calculation results for the second-, third-, and fourth-order Lamé coefficients of the series metals with cubic structure grains at $P = 0$ are analyzed. For polycrystalline tungsten, the dependence of the fourth-order elastic constants on pressure in the range of 0–600 GPa is presented.

I. INTRODUCTION

The higher-order elastic constants are important in solid-state physics, because they characterize the anharmonicity of the crystal lattice. First of all, it concerns the third- and fourth-order elastic constants (TOECs and FOECs, respectively). The second-order elastic constants (SOECs) define the linear response. TOECs and FOECs define the nonlinear response of single crystals on finite deformations. The dependence of sound velocity from the applied load [1,2], the wave-form distortion of ultrasonic finite-amplitude waves passing through a solid, and the amplitude of the second and third harmonic [3–6] allow to estimate the ideal strength and ductility of metals [7], and so on.

The polycrystalline materials are more important from a practical point of view. Modern engineering and functional materials usually have a complex and often disordered/amorphous structure. The most convenient way to describe the elasticity of these materials is to use the isotropic media description. The elastic moduli of polycrystals (Lamé coefficients) can be obtained by averaging the single-crystal different-order elastic constants over all the orientations of grains [8–11]. The relations between the second-order Lamé coefficients (SOLCs), the third-order Lamé coefficients (TOLCs), and the elastic constants of single crystals at normal pressure are given in Refs. [9–13]. Generalization of these relations for polycrystals at arbitrary hydrostatic pressure P is given in Ref. [14]. Note that the corresponding relations for the fourth-order Lamé coefficients (FOLCs) are absent in the literature.

The experimental definition of the higher-order elastic constants of single crystals and polycrystals is a difficult problem even at ambient pressure. Therefore, theoretical modeling is important for the calculations of the nonlinear elastic constants of loaded materials. Density functional theory (DFT) straightforwardly allows us to perform the "first-principles" calculations of crystal energy for the different volumes of unit cell (at the different pressures). This gives us the possibility to calculate the different-order elastic constants of single crystals at a given pressure [15–17]. The relations between the Lamé coefficients and the different-order elastic constants of a single crystal also allow estimation of the nonlinear elastic properties of a polycrystal at a given P, which is important for technical applications.

In the present work the relations between the FOLCs and FOECs are obtained. The cases when single-crystal grains have arbitrary symmetry and, in particular, cubic symmetry are considered.

II. LAMÉ COEFFICIENTS OF ISOTROPIC SOLID

Consider the isotropic solid that is in the equilibrium state at given pressure P and temperature T, and it experiences the small but finite deformation η_{ij}. We call "loaded" the initial state under hydrostatic pressure and the final state "strained," corresponding to the deformation η_{ij}. To describe the strained state we use the Lagrangian finite strain tensor [1]:

$$\eta_{ij} = \tfrac{1}{2}(\alpha_{ki}\alpha_{kj} - \delta_{ij}), \tag{1}$$

where $\alpha_{kj} = \partial r_k / \partial R_j$ is the deformation gradient, r_k and R_j are the Cartesian coordinates of an arbitrary point in the solid in the deformed and initial states, respectively, and δ_{ij} is the Kronecker symbol. Hereafter, the summation over the repeated indices is performed from 1 to 3.

The Gibbs free energy G is used for the description of the deformed isotropic solid at given P and T. G does not depend on the choice of coordinate system. It is invariant at the rotation and the translation of solid, as a whole. It is possible only when the Gibbs energy is a function of the strain tensor invariants. The strain tensor has the three invariants of

the first, second, and third order over η_{ij} [1]:

$$I_1 = \eta_{11} + \eta_{22} + \eta_{33}, \tag{2a}$$

$$I_2 = \left(\eta_{11}\eta_{22} - \eta_{12}^2\right) + \left(\eta_{11}\eta_{33} - \eta_{13}^2\right) + \left(\eta_{22}\eta_{33} - \eta_{23}^2\right), \tag{2b}$$

$$I_3 = \eta_{11}\eta_{22}\eta_{33} + 2\eta_{23}\eta_{13}\eta_{12} - \eta_{11}\eta_{23}^2 - \eta_{22}\eta_{13}^2 - \eta_{33}\eta_{12}^2. \tag{2c}$$

It is possible to decompose G over η_{ij} near the undeformed state because the deformations are although finite but small. The Gibbs free energy has a minimum in the equilibrium state, so $\partial G/\partial I_1|_0 = 0$, and the decomposition begins from quadratic contributions over the deformation. We take into account only the fourth-order contributions. From the invariants of Eqs. (2), it is possible to create the two quadratic scalars (I_1^2, I_2), the three cubic $(I_1^3, I_1 I_2, I_3)$, and the four of the fourth degree $(I_1^4, I_1^2 I_2, I_1 I_3, I_2^2)$.

$$\frac{\Delta G}{V_0} = \frac{\lambda + 2\mu}{2} I_1^2 - 2\mu I_2 + \frac{\nu_1 + 6\nu_2 + 8\nu_3}{6} I_1^3 - 2(\nu_2 + 2\nu_3) I_1 I_2 + 4\nu_3 I_3$$

$$+ \frac{1}{24}\xi_1 I_1^4 - \left(\frac{\xi_1 - \xi_2}{8} + \frac{\xi_4}{3}\right) I_1^2 I_2 + \left(\frac{\xi_1 - \xi_2}{8} + \frac{\xi_4}{3} - \xi_3\right) I_1 I_3 + \frac{2}{3}\xi_4 I_2^2. \tag{4}$$

Here $\Delta G = G(P, T, \eta) - G(P, T, 0)$, λ and μ – SOLCs, ν_i – TOLCs, ξ_i – FOLCs.

At such definitions of the second-, third-, and fourth-order Lamé coefficients, they coincide with the elastic constants of isotropic solid [9–14,19]:

$$\lambda = C_{12}^*, \quad \mu = C_{44}^*, \tag{5a}$$

$$\nu_1 = C_{123}^*, \quad \nu_2 = C_{144}^*, \quad \nu_3 = C_{456}^*. \tag{5b}$$

For the definition of FOLCs we have [see below, Eqs. (18)]

$$\xi_1 = C_{1111}^*, \quad \xi_2 = C_{1122}^*, \quad \xi_3 = C_{1144}^*, \quad \xi_4 = C_{4444}^*. \tag{6}$$

Here the elastic constants of the isotropic solid $C_{\alpha\beta}^*$ are given in Voigt notation ($11 - 1$, $22 - 2$, $33 - 3$, $23 - 4$, $13 - 5$, $12 - 6$). The decomposition of the elastic energy deformation, including the fourth-order contribution (η^4), is given in [6,21], where the sound propagation in nonlinear isotropic solids was considered and in Refs. [22] and [23] for the estimation of the fourth-order shear moduli in the metallic glasses. But the definition of FOLCs in these papers is not the same as in Eq. (4).

The polycrystalline material can be considered as the isotropic aggregate of single-crystal grains. These crystallites are negligible in size compared with the specimen itself but large enough to exhibit bulk elastic properties and oriented in a completely random manner. To evaluate the isotropic elastic constants (accordingly, Lamé coefficients) for such systems the averaging methods, proposed by Voigt and Reuss [10,11], are used. In the first case, when a polycrystal is deformed the deformation distribution is uniform and is not changed. Then the microscopic deformation in the single-crystal grains is equal to the macroscopic or average deformation and, according to Voigt, the elastic constants of a polycrystal (Lamé coefficients) are equal to the elastic

The third-order decomposition of energy over deformation was considered in many papers [1,4,8,18–20]. In these papers, various definitions of TOLCs were used. We give the three most common definitions: Murnaghan (l, m, and n), Toupin and Bernstein (ν_1, ν_2, and ν_3), and Landau and Lifshits (A, B, and C). The definition of TOLCs by Toupin and Bernstein is more convenient (ν_i coincides with the independent elastic constants of the isotropic solid), so we give the relations connected with other definitions of TOLCs [19,20]:

$$\nu_1 = 2(l - m) + n = 2C,$$

$$\nu_2 = m - \frac{1}{2}n = B,$$

$$\nu_3 = n/4 = A/4. \tag{3}$$

It is possible to present the expression for the Gibbs free energy at given P and T on the unit of volume V_0 in the initial (undeformed) state, including the fourth-order contributions over η_{ij}, as

constant tensor, averaged over the all directions:

$$C_{ijkl..}^V = (C_{ijkl..})_{Av}. \tag{7}$$

Usually this procedure is called "homogenization." In the second case (Reuss approximation), the distribution of stresses is uniform and constant, and the elastic compliances of polycrystal are equal to the homogenized values of single-crystal elastic compliances:

$$S_{ijkl..}^R = (S_{ijkl..})_{Av}. \tag{8}$$

In papers [9–14] the relations are given which connect SOLCs and TOLCs with SOECs and TOECs of cubic and hexagonal crystals at ambient and arbitrary pressure P.

III. LINEAR INVARIANTS OF THE FOEC TENSOR

To calculate the Voigt average (uniform strain approximation) of the fourth-order elastic constants, the single-crystalline FOECs must be averaged over the all orientations of individual grains according to Eq. (7). With the rotation of the Cartesian coordinate system, the components of the eighth-rank tensor $C_{ijklmnpq}$ are transformed according to the following law [24]:

$$C_{ijklmnop}' = a_{iq}a_{jr}a_{ks}a_{lt}a_{mu}a_{nv}a_{ow}a_{px}C_{qrstuvwx}, \tag{9}$$

where $a_{iq}, \ldots$ are the directional cosines between the coordinate axes. The values of $C_{ijklmnop}'$ averaged over all angles are defined by the mean product of rotation matrices $a_{iq}, \ldots$. For the small rank tensors (second, fourth) these values can be defined easily by integrating over the Euler angles. However, for the higher rank tensors this procedure becomes tedious due to calculations of the large number of integrals with the trigonometric functions. In the case of higher rank tensors, it is convenient to use the method proposed in [25] for calculation

of the Voigt average of the TOECs for cubic symmetry. This method was used later in Refs. [10,26,27] for the definition of the averaged TOECs

For random orientation, such a linear average can be calculated from the condition that the linear invariants of the two tensors representing the single crystal and the polycrystal must be equal. The tensor of FOECs has four linear invariants which are not changed at any orthogonal transformation of the vector basis. To get these invariants, the rotation matrices in Eq. (9) should be taken in pairs and their indices changed in such a way that the product of each of these pairs becomes a Kronecker δ [24]. For example, if one chooses $i = j, k = l$, $m = n$, and $o = p$, it follows that

$$L_1 = C'_{iikkmmpp} = (a_{iq}a_{ir})(a_{ks}a_{kt})(a_{mu}a_{mv})(a_{pw}a_{px})C_{qrstuvwx}$$

$$= \delta_{qr}\delta_{st}\delta_{uv}\delta_{wx}C_{qrstuvwx}. \qquad (10a)$$

Taking $i = m, j = n, k = o$, and $l = p$, we get the second invariant:

$$L_2 = C'_{ijklijkl} = \delta_{qu}\delta_{rv}\delta_{sw}\delta_{tx}C_{qrstuvwx}. \qquad (10b)$$

Then, taking $i = k, j = m, l = o$, and $n = p$ we get

$$L_3 = C'_{ijiljnln} = \delta_{qs}\delta_{ru}\delta_{tw}\delta_{vx}C_{qrstuvwx}, \qquad (10c)$$

and with $i = l, j = n, k = m$, and $0 = p$ we get

$$L_4 = C'_{ijkikjoo} = \delta_{qt}\delta_{rv}\delta_{su}\delta_{wx}C_{qrstuvwx}. \qquad (10d)$$

As usual, the summation over the repeated indices from 1 to 3 takes place. In the general case (the triclinic symmetry), the expressions for L_i are given in Appendix A [Eqs. (A1)].

In the case of cubic symmetry (point groups $\bar{4}\,32, 432, \frac{4}{m}\bar{3}\frac{2}{m}$, the 11 FOECs [1]), the expressions for the linear invariants [Eqs. (10)] are

$$L_1^c = 3C_{1111} + 24C_{1112} + 18C_{1122} + 36C_{1123}, \qquad (11a)$$

$$L_2^c = 3C_{1111} + 6C_{1122} + 12C_{1144} + 24C_{1155}$$
$$+ 12C_{4444} + 24C_{4455}, \qquad (11b)$$

$$L_3^c = 3C_{1111} + 24C_{1155} + 12C_{1266} + 24C_{1456}$$
$$+ 6C_{4444} + 12C_{4455}, \qquad (11c)$$

$$L_4^c = 3C_{1111} + 6C_{1112} + 18(C_{1155} + C_{1255} + C_{1266}$$
$$+ C_{1456}). \qquad (11d)$$

Here $C_{\alpha\beta\gamma\delta}$ are the fourth-order isothermal elastic constants of a single crystal in Voigt notation at given P and T.

For Reuss averaging (the uniform stress approximation) the linear invariants in the case of compliances are defined by the same relations, Eqs. (11) where only the FOECs are replaced by compliances $S_{\alpha\beta\gamma\delta}$ with the same indexes (taking

into account the rules of recording the components of the tensor $S_{\alpha\beta\gamma\delta}$ in Voigt notation [28]).

IV. ELASTIC CONSTANTS OF LOADED CRYSTAL

The elastic constants in Eqs. (11) are defined by the relation [14]

$$C_{ijkl..} = \frac{1}{V_0}\left(\frac{\partial^n G}{\partial\eta_{ij}\partial\eta_{kl}...}\right)_T, \qquad (12)$$

where $n = 4$. Since

$$\frac{\Delta G}{V_0} = \frac{\Delta F}{V_0} + P\frac{\Delta V}{V_0}, \qquad (13)$$

where $\Delta F = F(P, T, \eta) - F(P, T, 0)$, $\Delta V = V - V_0$ are the change of the Helmholtz free energy and volume, respectively, due to the deformation given by the η_{ij} components, and $C_{ijklmnpq}$ are defined not only by the interatomic interaction but also by the work of the external load due to the additional small strain η_{ij}. Thus, $C_{ijklmnpq}$ defines the elastic response of the crystal at pressure P on a small deformation and fully describes the elastic properties under hydrostatic compression.

The decomposition of $\frac{\Delta F}{V_0}$ is as follows:

$$\frac{\Delta F}{V_0} = -P\eta_{ij}\delta_{ij} + \frac{1}{2}c_{ijkl}\eta_{ij}\eta_{kl} + \frac{1}{6}c_{ijklmn}\eta_{ij}\eta_{kl}\eta_{mn}$$
$$+ \frac{1}{24}c_{ijklmnpq}\eta_{ij}\eta_{kl}\eta_{mn}\eta_{pq} + \dots , \qquad (14)$$

where

$$c_{ijkl..} = \frac{1}{V_0}\left(\frac{\partial^n F}{\partial\eta_{ij}\partial\eta_{kl}...}\right)_T. \qquad (15)$$

The elastic constants $c_{ijkl...}$ [Eq. (15)], calculated at the same volume, in contrast to $C_{ijkl...}$ are defined only by the interatomic interaction and so do not give the full picture of the elastic behavior of the material. Note that under the hydrostatic pressure the elastic constants $C_{ijkl...}$ have the Voigt symmetry relative to the index permutations [1]. The definition of the elastic constants $c_{ijkl...}$ for the unloaded crystal is given in [29].

The relation between $C_{ijkl...}$ and $c_{ijkl...}$ can be found using Eqs. (12)–(15). The volume of the deformed crystal is expressed [1] by $V = JV_0$, where $J = \det(\alpha_{ij})$. In the case of pure deformation (no crystal rotation), the inversion of Eq. (1) gives [16]

$$\alpha_{ij} = \delta_{ij} + \eta_{ij} - \frac{1}{2}\eta_{ki}\eta_{kj} + \frac{1}{2}\eta_{rk}\eta_{ri}\eta_{kj} - \frac{5}{8}\eta_{kj}\eta_{mk}\eta_{mn}\eta_{ni}. \qquad (16)$$

The substitution of $\Delta F/V_0$ and $\Delta V/V_0$ in Eq. (13) allows one to express $C_{\alpha\beta\gamma\delta}$ via the elastic constant $c_{\alpha\beta\gamma\delta}$ and pressure P. For crystals with cubic symmetry, the obtained results are given in Table I [16].

TABLE I. The relations between $C_{\alpha\beta\gamma\delta}$ and $c_{\alpha\beta\gamma\delta}$ for cubic crystal.

$C_{1111} = c_{1111} - 15P$	$C_{1123} = c_{1123} - P$	$C_{1255} = c_{1255} + P$	$C_{4444} = c_{4444} - 3P$
$C_{1112} = c_{1112} + 3P$	$C_{1144} = c_{1144} + P$	$C_{1266} = c_{1266} - P$	$C_{4455} = c_{4455} - P$
$C_{1122} = c_{1122} + P$	$C_{1155} = c_{1155} - 3P$	$C_{1456} = c_{1456} - P$	

V. RELATIONS BETWEEN THE FOLCs AND CUBIC FOECs

Now we express the fourth-order contribution in Eq. (4) via the strain tensor components using the connection I_1, I_2, and I_3 with η_{ij}:

$$
\begin{aligned}
\left(\frac{\Delta G}{V_0}\right)_4 &= \frac{1}{24}\xi_1\left(\eta_{11}^4 + \eta_{22}^4 + \eta_{33}^4\right) + \left(\frac{\xi_1}{24} + \frac{\xi_2}{8} - \frac{\xi_4}{3}\right)\left[\eta_{11}^3(\eta_{22} + \eta_{33})\right. \\
&\quad \left. + \eta_{22}^3(\eta_{11} + \eta_{33}) + \eta_{33}^3(\eta_{11} + \eta_{22})\right] + \frac{\xi_2}{4}\left(\eta_{11}^2\eta_{22}^2 + \eta_{11}^2\eta_{33}^2 + \eta_{22}^2\eta_{33}^2\right) \\
&\quad + \left(\frac{\xi_2}{2} - \xi_3\right)\eta_{11}\eta_{22}\eta_{33}(\eta_{11} + \eta_{22} + \eta_{33}) + \xi_3\left(\eta_{11}^2\eta_{23}^2 + \eta_{22}^2\eta_{13}^2 + \eta_{33}^2\eta_{12}^2\right) \\
&\quad + \left(\frac{\xi_1 - \xi_2}{8} + \frac{\xi_4}{3}\right)\left[\eta_{11}^2\left(\eta_{12}^2 + \eta_{13}^2\right) + \eta_{22}^2\left(\eta_{12}^2 + \eta_{23}^2\right) + \eta_{33}^2\left(\eta_{13}^2 + \eta_{23}^2\right)\right] \\
&\quad + \left(\frac{\xi_1 - \xi_2}{8} + \xi_3 - \xi_4\right)\left[\eta_{11}\eta_{22}\left(\eta_{13}^2 + \eta_{23}^2\right) + \eta_{22}\eta_{33}\left(\eta_{13}^2 + \eta_{12}^2\right) + \eta_{11}\eta_{33}\left(\eta_{12}^2 + \eta_{23}^2\right)\right] \\
&\quad + \left(\frac{\xi_1 - \xi_2}{4} - \frac{2\xi_4}{3}\right)\left(\eta_{11}\eta_{22}\eta_{12}^2 + \eta_{11}\eta_{33}\eta_{13}^2 + \eta_{22}\eta_{33}\eta_{23}^2\right) + \left(\frac{\xi_1 - \xi_2}{4} - 2\xi_3 + \frac{2\xi_4}{3}\right) \\
&\quad \times \eta_{23}\eta_{13}\eta_{12}(\eta_{11} + \eta_{22} + \eta_{33}) + \frac{2\xi_4}{3}\left(\eta_{23}^4 + \eta_{13}^4 + \eta_{12}^4\right) + \frac{4\xi_4}{3}\left(\eta_{23}^2\eta_{12}^2 + \eta_{23}^2\eta_{13}^2 + \eta_{13}^2\eta_{12}^2\right).
\end{aligned} \tag{17}
$$

The connection between the isotropic elastic constants $C^*_{\alpha\beta\gamma\delta}$ and FOLCs is obtained by comparing (17) with the same decomposition for the cubic crystal [see Eq. (B3)]:

$$
C^*_{1111} = \xi_1; \quad C^*_{1122} = \xi_2; \quad C^*_{1144} = \xi_3; \quad C^*_{4444} = \xi_4; \quad C^*_{1112} = \frac{\xi_1 + 3\xi_2 - 8\xi_4}{4};
$$

$$
C^*_{1123} = \xi_2 - 2\xi_3; \quad C^*_{1155} = \frac{3(\xi_1 - \xi_2) + 8\xi_4}{24}; \quad C^*_{1255} = \frac{\xi_1 - \xi_2 + 8(\xi_3 - \xi_4)}{16};
$$

$$
C^*_{1266} = \frac{3(\xi_1 - \xi_2) - 8\xi_4}{24}; \quad C^*_{1456} = \frac{3(\xi_1 - \xi_2 - 8\xi_3) + 8\xi_4}{96}; \quad C^*_{4455} = \frac{\xi_4}{3}. \tag{18}
$$

The linear invariants of polycrystalline solid, corresponding to the Voigt average and expressed via the Lamé coefficients, can be obtained from Eqs. (11) and Eqs. (18). As a result,

$$
L_1^{is} = 3(3\xi_1 + 24\xi_2 - 24\xi_3 - 16\xi_4), \tag{19a}
$$

$$
L_2^{is} = 6\xi_1 + 3\xi_2 + 12\xi_3 + 28\xi_4, \tag{19b}
$$

$$
L_3^{is} = (33\xi_1 - 21\xi_2 - 24\xi_3 + 64\xi_4)/4, \tag{19c}
$$

$$
L_4^{is} = 3(57\xi_1 - 9\xi_2 + 24\xi_3 - 104\xi_4)/16. \tag{19d}
$$

TABLE II. Calculation results for Lamé coefficients of metals. All values are given in GPa ($P = 0$, $T = 0$ K).

Constant	Cu	Al	Au	Ag	W
$\lambda = C^*_{12}$	94.56	53.16	164.6	104.3	206.7 [14]
$\mu = C^*_{44}$	55.56	29.96	28.32	43.28	150.1 [14]
$C^*_{11} = \lambda + 2\mu$	205.7	113.1	221.3	190.8	506.9
$\nu_1 = C^*_{123}$	−236.3	−15.2	−431.6	−240.4	−405.1 [14]
$\nu_2 = C^*_{144}$	−213.9	−133.8	−270.8	−181.6	−305.7 [14]
$\nu_3 = C^*_{456}$	−182.7	−119.6	−173.4	−138.2	−395.0 [14]
$C^*_{111} = \nu_1 + 6\nu_2 + 8\nu_3$	−2981	−1775	−3443	−2436	−5399
$\xi_1 = C^*_{1111}$	31857	20565	44560	31704	52698
$\xi_2 = C^*_{1122}$	3407	480	4353	2787	6012
$\xi_3 = C^*_{1144}$	1176	238.2	1216	912.4	1275
$\xi_4 = C^*_{4444}$	2754	1631	3875	2139	2392

Equating the invariants of Eqs. (11) and Eqs. (19) and solving the system of obtained equations relative to ξ_i, we get the relations between FOLCs of polycrystal and the elastic constants of single-crystal grains for the cubic symmetry (Voigt approximation):

$$\xi_1 = C_{1111}^V = \frac{1}{105}(35C_{1111} + 40C_{1112} + 18C_{1122} + 12C_{1123} + 24C_{1144} + 240C_{1155}$$

$$+ 96C_{1255} + 144C_{1266} + 192C_{1456} + 48C_{4444} + 96C_{4455}), \tag{20a}$$

$$\xi_2 = C_{1122}^V = \frac{1}{35}(C_{1111} + 8C_{1112} + 14C_{1122} + 12C_{1123} + 16C_{1144} - 16C_{1266} - 32C_{1456} + 8C_{4444} + 16C_{4455}), \tag{20b}$$

$$\xi_3 = C_{1144}^V = \frac{1}{105}(C_{1111} + 2C_{1112} + 12C_{1122} - 15C_{1123} + 39C_{1144} + 6C_{1155}$$

$$- 18C_{1266} + 36C_{1255} - 72C_{1456} + 12C_{4444} + 24C_{4455}), \tag{20c}$$

$$\xi_4 = C_{4444}^V = \frac{1}{35}(C_{1111} - 4C_{1112} + 3C_{1122} + 6C_{1144} + 12C_{1155} - 12C_{1255} - 6C_{1266} + 9C_{4444} + 18C_{4455}). \tag{20d}$$

The expressions for ξ_i in the case of arbitrary symmetry of single-crystal grains are given in Appendix A [Eqs. (A3)].

VI. NUMERICAL RESULTS AND DISCUSSION

We analyze the second-, third-, and fourth-order homogenized moduli (Lamé coefficients) of metals with a cubic lattice, for which the full set of elastic constants exists. In paper [30] the results of DFT calculations for all FOECs ($P = 0, T = 0$ K) of fcc metals (Cu, Al, Ag, and Au) are given. The values of SOECs and TOECs are also given there. Using these data, we have estimated the values of the second-, third-, and fourth-order Lamé coefficients of these metals at $P = 0$. The relations for calculating SOLCs and TOLCs were taken from [11]. FOLCs for tungsten were calculated using the full set of FOECs in the pressure interval 0–600 GPa ($T = 0$ K) [16]. For tungsten, the values of SOLCs and TOLCs were taken from [14].

The results of our calculations, using the data for elastic constants from [30,16], are given in Table II and in Figs. 1 and 2. As follows from Table II, the elastic moduli of polycrystals $C_{\alpha\beta..}^*$ (Lamé coefficients) are increased by absolute value at

the transition from the second to the fourth order. It is seen in Figs. 1 and 2 that with the pressure increasing, FOLCs for W (for $\xi_2 = C_{1122}^*$ and $\xi_3 = C_{1144}^*$ at $P > 100$ GPa) are increased. The same behavior is demonstrated for the SOLCs and TOLCs of tungsten [14].

VII. CONCLUSION

The definition of the fourth-order elastic moduli of polycrystals (the fourth-order Lamé coefficients) at arbitrary pressure is given. The relations are obtained which define these constants via the fourth-order elastic constants of the single-crystal grains, which form the polycrystal. We have calculated the second-, third-, and fourth-order Lamé coefficients of some metals (fcc – Cu, Al, Au, Ag; and bcc – W) using the available data of DFT calculations for elastic constants at normal pressure and T = 0 K. Additionally, we calculated the fourth-order Lamé coefficients in the pressure range 0–600 GPa for tungsten using the existing data on fourth-order elastic constants. The Lamé coefficients are increased by about an order of magnitude at the transition from the second to the third and fourth order. It is seen on the example of
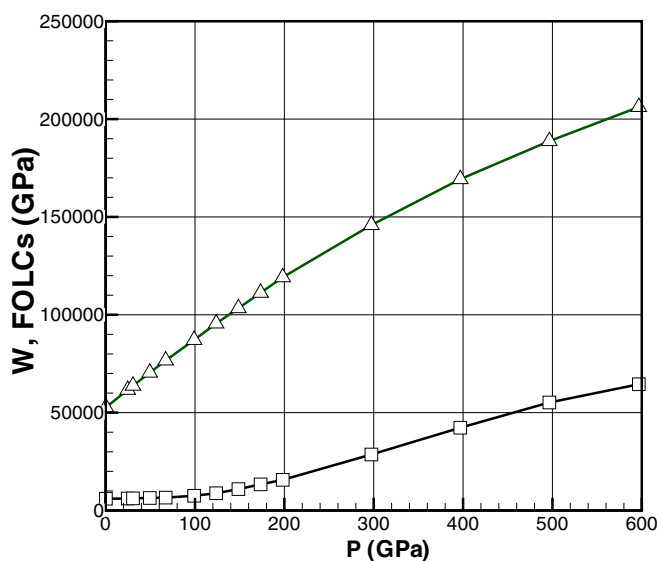

FIG. 1. The pressure dependence of FOLCs C_{1111}^* (triangles) and C_{1122}^* (squares).
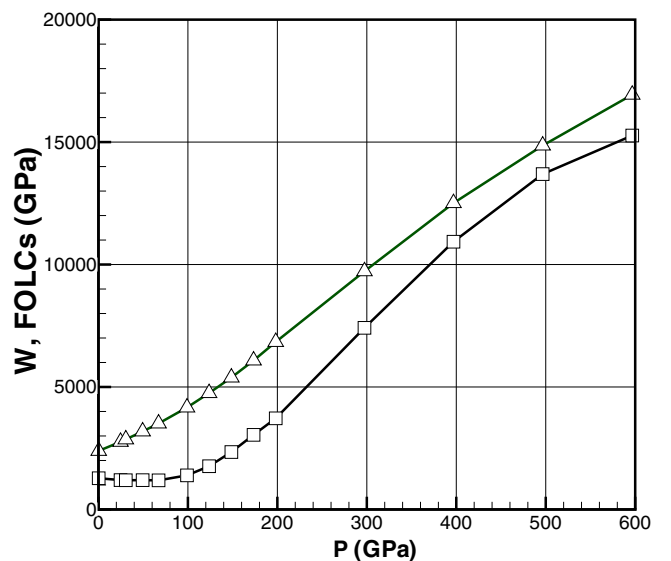

FIG. 2. The pressure dependence of FOLCs C_{1144}^* (squares) and C_{4444}^* (triangles).

tungsten that the Lamé coefficients of any order are increased in absolute value with increasing pressure.

APPENDIX A: LINEAR INVARIANTS AND LAMÉ COEFFICIENTS IN THE CASE OF ARBITRARY SYMMETRY

Using Eqs. (10), we will express the linear invariants L_i via FOECs in the general case (the triclinic symmetry). After summation over the repeated indices we get

$$
\begin{aligned}
L_1 = {} & C_{1111} + C_{2222} + C_{3333} + 4C_{1112} + 4C_{1113} + 6C_{1122} + 6C_{1133} + 12C_{1123} \\
& + 4C_{1222} + 12C_{1223} + 12C_{1233} + 4C_{1333} + 4C_{2333} + 4C_{3222} + 6C_{2233},
\end{aligned} \tag{A1a}
$$

$$
\begin{aligned}
L_2 = {} & C_{1111} + C_{2222} + C_{3333} + 4C_{4444} + 4C_{5555} + 4C_{6666} + 2C_{1122} + 2C_{1133} \\
& + 4C_{1144} + 4C_{1155} + 4C_{1166} + 4C_{2244} + 2C_{2233} + 4C_{2255} + 4C_{2266} + 4C_{3366} + 8C_{4466} \\
& + 8C_{4455} + 8C_{5566} + 4C_{3355} + 4C_{3344},
\end{aligned} \tag{A1b}
$$

$$
\begin{aligned}
L_3 = {} & C_{1111} + C_{2222} + C_{3333} + 2C_{4444} + 2C_{5555} + 2C_{6666} + 8C_{1456} + 8C_{2456} + 8C_{3456} \\
& + 4C_{1155} + 4C_{1166} + 4C_{2244} + 4C_{3344} + 4C_{3355} + 4C_{4455} + 4C_{4466} + 4C_{2266} \\
& + 4C_{5566} + 4C_{1266} + 4C_{1355} + 4C_{2344},
\end{aligned} \tag{A1c}
$$

$$
\begin{aligned}
L_4 = {} & C_{1111} + C_{2222} + C_{3333} + C_{1112} + C_{1113} + 3C_{1155} + 3C_{1166} + 3C_{1244} + 3C_{1255} \\
& + 6C_{1266} + 3C_{1344} + 6C_{1355} + 3C_{1366} + C_{1222} + C_{1333} + C_{2223} + C_{2333} + 6C_{1456} \\
& + 6C_{2456} + 6C_{3456} + 3C_{2266} + 3C_{3355} + 3C_{3344} + 3C_{2244} + 6C_{2344} + 3C_{2355} + 3C_{2366}.
\end{aligned} \tag{A1d}
$$

$C_{\alpha\beta\gamma\delta}$ are given in Voigt notations and are defined according to Eq. (12).

Now we will obtain the expressions for the Lamé coefficients ξ_i via FOECs of single crystal for the case of arbitrary symmetry. We get the system of linear equations relative to ξ_i by equating the invariants L_i [Eqs. (A1)] and L_i^{is} [Eqs. (19)]:

$$3\xi_1 + 24\xi_2 - 24\xi_3 - 16\xi_4 = L_1/3, \tag{A2a}$$

$$6\xi_1 + 3\xi_2 + 12\xi_3 + 28\xi_4 = L_2, \tag{A2b}$$

$$33\xi_1 - 21\xi_2 - 24\xi_3 + 64\xi_4 = 4L_3, \tag{A2c}$$

$$57\xi_1 - 9\xi_2 + 24\xi_3 - 104\xi_4 = 16L_4/3. \tag{A2d}$$

The solution of this system is

$$\xi_1 = \tfrac{1}{105}(a + 6b + 12c + 16d), \tag{A3a}$$

$$\xi_2 = \tfrac{1}{35}(a + 4b - 4c), \tag{A3b}$$

$$\xi_3 = \tfrac{1}{420}(-5a + 39b - 54c + 24d), \tag{A3c}$$

$$\xi_4 = \tfrac{1}{70}(3b + 3c - 4d), \tag{A3d}$$

where $a = L_1/3$, $b = L_2/3$, $c = L_3/3$, $d = L_4/3$.

The relations of Eqs. (20) are the particular case of Eqs. (A3) when the polycrystal contains the arbitrary-oriented grains with cubic symmetry.

APPENDIX B: DERIVATION OF (20a) BY INTEGRATION OVER THE ANGLES

To verify the relations (20), defining FOLCs of polycrystal with the randomly oriented grains with the cubic symmetry, we will obtain Eq. (20a) by integration over the Euler angles

in the process of calculating the elastic constant C^*_{1111} of polycrystal. For this we use the suggestion given in [9] in the process of deriving the equation for TOLCs.

Let us say that the polycrystal undergoes uniaxial deformation η'_{11} in the arbitrary rectangular coordinate system $(1', 2', 3')$. Then a monocrystalline grain in the own crystal axes $(1, 2, 3)$ experiences the following deformations:

$$
\begin{aligned}
& \eta_{11} = \eta'_{11} a_{11}^2, \quad \eta_{22} = \eta'_{11} a_{12}^2, \quad \eta_{33} = \eta'_{11} a_{13}^2, \\
& \eta_{23} = \eta'_{11} a_{13} a_{12}, \quad \eta_{13} = \eta'_{11} a_{11} a_{13}, \quad \eta_{12} = \eta'_{11} a_{11} a_{12}.
\end{aligned} \tag{B1}
$$

Here a_{ij} are the direction cosines between crystal axes $(1, 2, 3)$ and the prime axes $(1', 2', 3')$. If one denotes the angle between the strain direction $(1')$ and the 3 axis of the crystal as θ and the angle between the projection of the strain direction $(1')$ onto the 1–2 plane and 1 axis of the crystal as ϕ, it follows that

$$a_{11} = \sin\theta\cos\phi, \quad a_{12} = \sin\theta\sin\phi, \quad a_{13} = \cos\theta. \tag{B2}$$

The fourth-order contribution over η in the elastic deformation energy for the cubic crystal is defined by the

expression [16]

$$
\begin{aligned}
\left(\frac{\Delta G}{V_0}\right)_4 &= \frac{1}{24}C_{1111}\big(\eta_{11}^4 + \eta_{22}^4 + \eta_{33}^4\big) + \frac{1}{6}C_{1112}\big[\eta_{11}^3(\eta_{22} + \eta_{33}) \\
&\quad + \eta_{22}^3(\eta_{11} + \eta_{33}) + \eta_{33}^3(\eta_{11} + \eta_{22})\big] + \frac{1}{4}C_{1122}\big(\eta_{11}^2\eta_{22}^2 + \eta_{11}^2\eta_{33}^2 + \eta_{22}^2\eta_{33}^2\big) \\
&\quad + \frac{1}{2}C_{1123}\eta_{11}\eta_{22}\eta_{33}(\eta_{11} + \eta_{22} + \eta_{33}) + C_{1144}\big(\eta_{11}^2\eta_{23}^2 + \eta_{22}^2\eta_{13}^2 + \eta_{33}^2\eta_{12}^2\big) \\
&\quad + C_{1155}\big[\eta_{11}^2\big(\eta_{12}^2 + \eta_{13}^2\big) + \eta_{22}^2\big(\eta_{12}^2 + \eta_{23}^2\big) + \eta_{33}^2\big(\eta_{13}^2 + \eta_{23}^2\big)\big] \\
&\quad \times 2C_{1255}\big[\eta_{11}\eta_{22}\big(\eta_{13}^2 + \eta_{23}^2\big) + \eta_{22}\eta_{33}\big(\eta_{13}^2 + \eta_{12}^2\big) + \eta_{11}\eta_{33}\big(\eta_{12}^2 + \eta_{23}^2\big)\big] \\
&\quad + 2C_{1266}\big(\eta_{11}\eta_{22}\eta_{12}^2 + \eta_{11}\eta_{33}\eta_{13}^2 + \eta_{22}\eta_{33}\eta_{23}^2\big) + 8C_{1456}\eta_{23}\eta_{13}\eta_{12}(\eta_{11} + \eta_{22} + \eta_{33}) \\
&\quad + \frac{2}{3}C_{4444}\big(\eta_{23}^4 + \eta_{13}^4 + \eta_{12}^4\big) + 4C_{4455}\big(\eta_{23}^2\eta_{12}^2 + \eta_{23}^2\eta_{13}^2 + \eta_{13}^2\eta_{12}^2\big).
\end{aligned} \tag{B3}
$$

Here η_{ij} is defined in accordance with Eqs. (B1) and (B2). For all possible orientations of single-crystal grains, the homogeneous elastic energy is

$$
\left(\overline{\frac{\Delta G}{V_0}}\right)_4 = \frac{\int_0^{\pi/2} d\phi \int_0^{\pi/2} \frac{\Delta G}{V_0}(\theta, \phi)\sin\theta\, d\theta}{\int_0^{\pi/2} d\phi \int_0^{\pi/2} \sin\theta\, d\theta}. \tag{B4}
$$

The energy of polycrystals at the deformation η'_{11} equals

$$
\left(\frac{\Delta G}{V_0}\right)_4^{is} = \frac{1}{24}C_{1111}^*\eta'^4_{11}. \tag{B5}
$$

Because the contribution in the elastic energy due to grain boundary mismatch is negligible, it is possible to believe that the elastic energy of the polycrystal should be equal to the average value of the elastic energy of single-crystal grains.

We will obtain $\left(\overline{\frac{\Delta G}{V_0}}\right)_4$ after integration according to Eq. (B4) for each term in (B3). From the equality

$$
\left(\overline{\frac{\Delta G}{V_0}}\right)_4 = \left(\frac{\Delta G}{V_0}\right)_4^{is},
$$

we get the expression for C_{1111}^* exactly compatible with Eq. (20a), which was obtained through the linear invariants.

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