Pergamon

PII: S0022-5096(96)00113-5

NEW ESTIMATES OF THE THIRD-ORDER ELASTIC CONSTANTS FOR ISOTROPIC AGGREGATES OF CUBIC CRYSTALS

V. A. LUBARDA

Department of Mechanical and Aerospace Engineering, Arizona State University, Tempe, AZ 85287-6106, U.S.A.

ABSTRACT

An improved method, based on an extension of the self-consistent method from the linear theory, is proposed to evaluate the effective third-order elastic constants for isotropic aggregates of cubic crystals. The calculated constants are compared with the Voigt and Reuss-type estimates, which are currently the only other analytical estimates available for these constants. The agreement between calculations and experimental data is then discussed. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: A. nonlinear elasticity, B. elastic constants, B. polycrystalline material, C. self-consistent method.

1. INTRODUCTION

At the level of continuum elasticity, the third-order elastic constants (TOEC) appear in the cubic representation of an introduced potential function, such as the strain or complementary energy. These constants are also important in the solid state physics, because their knowledge allows the evaluation of anharmonic properties of crystals, e.g. thermal expansion, Grüneisen parameters, specific heats, interaction of thermal and acoustic phonons, wave mixing and attenuation, defect properties of crystals, determination of general equation of state, and phase transition. For example, certain ferromagnetic alloys show strong Invar effects in a certain temperature range, including a negative pressure derivative of the bulk modulus, and a negative thermal expansion. This unusual behavior requires a study of the TOEC, which quantify the first-order anharmonic terms in the interatomic potential (Saunders *et al.*, 1993). Many examples can be given regarding a nonlinear behavior on the atomic scale near dislocations or other imperfections in crystals. For instance, a solid spherical inclusion forced into a spherical hole of a matrix material has been considered as a simple elastic model of a substitutional or interstitial atom. If the size of the hole is only slightly different from that of the inclusion, linear elasticity can be employed to calculate relevant features of the stress and deformation behavior. For large differences in size, nonlinear effects become important, and thus the use of higher-order elastic constants.

An early application of the TOEC was in modeling the material response under high pressures. The development of ultrasonic techniques increased the interest for the TOEC. A theoretical basis for their determination was developed by Toupin and Bernstein (1961), and Thurston and Brugger (1964). The experimental technique involves measuring the speed of small amplitude sound waves in statically stressed specimens. The speeds and propagation modes are different from those in unstressed specimens, and the difference can be expressed in terms of the TOEC. An alternative procedure is to measure the variation of the second-order elastic constants (SOEC) with applied pressure in the loading test, and relate this to the TOEC (Seeger and Buck, 1960). However, the calculated values often differed considerably from those obtained from the sound velocity measurements. This discrepancy was partly attributed to experimental accuracy, and to the fact that the TOEC are far more structure sensitive than the SOEC.

At the present time, there are reported measurements of the TOEC for only a few polycrystalline materials, and these are given with large margins of error (Wasserbäch, 1990). More experimentation has been done with single crystals of various materials, as evidenced by the Landolt–Börnstein (1979) compilations. These results are also reported with large error margins. For certain materials, only combinations or incomplete sets of the TOEC are listed. This situation increases the importance of the theoretical models for the calculation of the TOEC, particularly for materials for which experiments have not been performed, or cannot be easily or accurately performed.

The analytical determination of the TOEC within a continuum elasticity approach was mainly devoted to isotropic aggregates of cubic crystals (Bross, 1963; Chang, 1967; Barsch, 1968; Hamilton and Parrott, 1968). The Voigt- and Reuss-type averages were applied, within a finite strain formulation, to calculate the effective TOEC. Except for an application of the Voigt scheme to transversely isotropic aggregates of cubic crystals (Johnson, 1982), no further analytical results were reported. This is in contrast to the situation with the SOEC, where additional methods were constructed to calculate the effective constants, and appropriate theorems were formulated to derive the bounds for these constants.

There has been related work to determine the average moduli for various nonlinear isotropic composites. Ogden (1974) considered the overall moduli for a non linear isotropic elastic composite, consisting of a dilute suspension of initially spherical inclusions, which were embedded in a different matrix. Chen and Jiang (1993) developed a method for computing the effective elastic moduli for isotropic nonlinear particulate composites by using a perturbation scheme and solutions from linear elasticity only. Most recently, Imam et al. (1995) reported a study of the overall elastic moduli for a biphase material consisting of a nonlinear isotropic and incompressible matrix, and a dilute concentration of spherical inhomogeneities.

In this paper, the new estimates of the effective TOEC for isotropic aggregates of cubic crystals are derived. This is accomplished by introducing a method which is based on an extension of the self-consistent method from the linear theory. The suggested method is self-consistent with respect to the SOEC, but not the TOEC. It is thus referred to as a semi-consistent method. The TOEC are calculated for selected materials, and the results are compared with the Voigt- and Reuss-type estimates,

which are the only other analytical estimates presently available for these constants. Agreement between the calculations and experimental data is then discussed.

2. THE STRAIN AND COMPLEMENTARY ENERGY REPRESENTATIONS

The strain energy per unit initial volume of an elastic solid can be expanded in a Taylor series about the state of zero strain and stress as

$$\Phi = \frac{1}{2!} C_{ijkl} E_{ij} E_{kl} + \frac{1}{3!} C_{ijklmn} E_{jk} E_{kl} E_{mn} + \dots, \tag{2.1}$$

where E_{ij} are the components of the Lagrangian strain, and $C_{ijklmn\dots}$ are the elastic stiffness constants or the elastic moduli. The elastic constants of the nth order are the components of the tensor of the order $2n$. Since they are appropriate strain gradients of Φ evaluated at zero strain, they possess the obvious basic symmetries. For example, the TOEC satisfy $C_{ijklmn} = C_{jiklmn}$, and $C_{ijklmn} = C_{klijmn} = C_{mnklij}$. Following the Voigt notation: $11 \sim 1$, $22 \sim 2$, $33 \sim 3$, $23 \sim 4$, $13 \sim 5$, $12 \sim 6$, and the recipe $E_{ij} = (1 + \delta_{ij}) \eta_{\vartheta}/2$ ($\vartheta = 1, 2, \dots, 6$), (2.1) can be rewritten as (Brugger, 1964)

$$\Phi = \frac{1}{2} \sum_i c_{ii} \eta_i^2 + \sum_{i<j} c_{ij} \eta_i \eta_j + \frac{1}{6} \sum_i c_{iii} \eta_i^3 + \frac{1}{2} \sum_{i \neq j} c_{iij} \eta_i^2 \eta_j + \sum_{i<j<k} c_{ijk} \eta_i \eta_j \eta_k + \dots \quad . \tag{2.2}$$

For a material whose symmetry group consists solely of the identify transformation, there are $\binom{5+n}{n}$ independent nth order elastic constants (i.e. there are at most 21 independent SOEC, and at most 56 independent TOEC). In the presence of material symmetry, fewer independent constants are involved, since they must be invariant under the symmetry group of transformations. Tables for the independent TOEC in crystals for all crystallographic groups are well known (Brugger, 1965). For a cubic crystal belonging to the Laue group CI (point groups O, O_h and T_d), there are at most three independent SOEC and six independent TOEC. Written with respect to the principal cubic axes, the corresponding strain energy is

$$\Phi = \frac{1}{2} c_{11} (\eta_1^2 + \eta_2^2 + \eta_3^2) + \frac{1}{2} c_{44} (\eta_4^2 + \eta_5^2 + \eta_6^2) + c_{12} (\eta_1 \eta_2 + \eta_2 \eta_3 + \eta_3 \eta_1)$$

$$+ \frac{1}{6} c_{111} (\eta_1^3 + \eta_2^3 + \eta_3^3) + \frac{1}{2} c_{112} [\eta_1^2 (\eta_2 + \eta_3) + \eta_2^2 (\eta_3 + \eta_1) + \eta_3^2 (\eta_1 + \eta_2)]$$

$$+ \frac{1}{2} c_{144} (\eta_4^2 \eta_1 + \eta_5^2 \eta_2 + \eta_6^2 \eta_3) + \frac{1}{2} c_{244} [\eta_4^2 (\eta_2 + \eta_3) + \eta_5^2 (\eta_3 + \eta_1)$$

$$+ \eta_6^2 (\eta_1 + \eta_2)] + c_{123} \eta_1 \eta_2 \eta_3 + c_{456} \eta_4 \eta_5 \eta_6, \tag{2.3}$$

to the third-order terms in strain. Equation (2.3) can be rewritten with respect to an arbitrary coordinate system as

$$\Phi = \alpha_1 J_1^2 + \alpha_2 J_2 + \alpha_3 K_2 + \beta_1 J_1^3 + \beta_2 J_1 J_2 + \beta_3 J_3 + \beta_4 J_1 K_2 + \beta_5 K_3 + \beta_6 L_3, \quad (2.4)$$

where $\alpha_1 = c_{11}/2$, $\alpha_2 = -2c_{44}$, $\alpha_3 = 2c_{44} + c_{12} - c_{11}$, and

$$\beta_1 = \frac{1}{6}c_{111}, \quad \beta_2 = -2c_{244}, \quad \beta_3 = 2(c_{244} - c_{144}), \quad \beta_4 = \frac{1}{2}(c_{112} - c_{111} + 4c_{244}),$$

$$\beta_5 = \frac{1}{2}(c_{111} - 3c_{112} + 2c_{123} + 4c_{144} - 4c_{244}), \quad \beta_6 = 4(c_{144} - c_{244} + 2c_{456}). \quad (2.5)$$

The invariants incorporated in (2.4) are

$$J_1 = \mathbf{E} : \mathbf{1}, \quad J_2 = \frac{1}{2}(J_1^2 - \mathbf{E} : \mathbf{E}), \quad J_3 = \frac{1}{3}(-J_1^3 + 3J_1 J_2 + \mathbf{E}^2 : \mathbf{E}), \quad (2.6)$$

$$K_2 = (\mathbf{a} \cdot \mathbf{E} \cdot \mathbf{a})(\mathbf{b} \cdot \mathbf{E} \cdot \mathbf{b}) + (\mathbf{b} \cdot \mathbf{E} \cdot \mathbf{b})(\mathbf{c} \cdot \mathbf{E} \cdot \mathbf{c}) + (\mathbf{c} \cdot \mathbf{E} \cdot \mathbf{c})(\mathbf{a} \cdot \mathbf{E} \cdot \mathbf{a}), \quad (2.7)$$

$$K_3 = (\mathbf{a} \cdot \mathbf{E} \cdot \mathbf{a})(\mathbf{b} \cdot \mathbf{E} \cdot \mathbf{b})(\mathbf{c} \cdot \mathbf{E} \cdot \mathbf{c}), \quad L_3 = (\mathbf{a} \cdot \mathbf{E} \cdot \mathbf{b})(\mathbf{b} \cdot \mathbf{E} \cdot \mathbf{c})(\mathbf{c} \cdot \mathbf{E} \cdot \mathbf{a}). \quad (2.8)$$

Here, $\mathbf{1}$ denotes the second-order unit tensor, and the vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ are the orthogonal unit vectors along the principal cubic axes. The tensors obtained by a dyadic products of these vectors are sometimes referred to as the structural tensors. The function Φ in (2.4) is an isotropic function of all its arguments (strain and structural tensors), thus satisfying the requirement of the frame indifference.

The symmetric Piola–Kirchhoff stress is the gradient of the strain energy with respect to the Lagrangian strain

$$S_{ij} = \frac{\partial \Phi}{\partial E_{ij}} = C_{ijkl} E_{kl} + \frac{1}{2} C_{ijklmn} E_{kl} E_{mn} + \dots \quad . \quad (2.9)$$

If this is an invertible stress–strain relationship, then

$$E_{ij} = \frac{\partial \Psi}{\partial S_{ij}} = D_{ijkl} S_{kl} + \frac{1}{2} D_{ijklmn} S_{kl} S_{mn} + \dots \quad , \quad (2.10)$$

where

$$\Psi(S_{ij}) = S_{kl} E_{kl} - \Phi(E_{ij}) = \frac{1}{2!} D_{ijkl} S_{ij} S_{kl} + \frac{1}{3!} D_{ijklmn} S_{ij} S_{kl} S_{mn} + \dots \quad (2.11)$$

is the complementary strain energy, the Legendre transform of Φ. The elastic constants $D_{ijkl...}$ are the elastic compliances.

Since $\partial S_{ij}/\partial S_{kl} = I_{ijkl}$ (fourth-order unit tensor), and $\partial^2 S_{ij}/\partial S_{kl} \partial S_{mn} = 0$, it follows that the second- and third-order elastic moduli and compliances are related by $D_{ijkl} = C_{ijkl}^{-1}$, and

$$D_{ijklmn} = -D_{ijpq} C_{pqrsuv} D_{rskl} D_{uvmn} \quad (2.12)$$

For a cubic crystal, the complementary energy can be written as

$$\Psi = \frac{1}{2}d_{11}(\tau_1^2 + \tau_2^2 + \tau_3^2) + 2d_{44}(\tau_4^2 + \tau_5^2 + \tau_6^2) + d_{12}(\tau_1\tau_2 + \tau_2\tau_3 + \tau_3\tau_1)$$

$$+ \frac{1}{6}d_{111}(\tau_1^3 + \tau_2^3 + \tau_3^3) + \frac{1}{2}d_{112}[\tau_1^2(\tau_2 + \tau_3) + \tau_2^2(\tau_3 + \tau_1) + \tau_3^2(\tau_1 + \tau_2)]$$

$$+ 2d_{144}(\tau_4^2\tau_1 + \tau_5^2\tau_2 + \tau_6^2\tau_3) + 2d_{244}[\tau_4^2(\tau_2 + \tau_3) + \tau_5^2(\tau_3 + \tau_1)$$

$$+ \tau_6^2(\tau_1 + \tau_2)] + d_{123}\tau_1\tau_2\tau_3 + 8d_{456}\tau_4\tau_5\tau_6, \tag{2.13}$$

to the third-order terms in stress. Note that the coefficients in front of the constants d_{44}, d_{144}, d_{244} and d_{456} are appropriately adjusted, since in the Voigt notation, the recipe $\tau_9 = S_{ij}$ ($9 = 1, 2, \ldots, 6$) is used for the stress components. Consequently, an invariant form of Ψ is exactly equal to that given by (2.4) with the constants c_{ijk} replaced by d_{ijk} in the expressions defining the constants αs and βs, and with the tensor $\mathbf{E}$ replaced by $\mathbf{S}$ in (2.6)–(2.8).

3. SECOND- AND THIRD-ORDER ELASTIC CONSTANTS OF CUBIC CRYSTALS

The components of the fourth-order tensor C_{ijkl} of the second-order elastic moduli with respect to an arbitrary rectangular basis, can be identified by comparing (2.1) and (2.4). This gives

$$C_{ijkl} = c_{12}\delta_{ij}\delta_{kl} + 2c_{44}I_{ijkl} + (c_{11} - c_{12} + 2c_{44})A_{ijkl}, \tag{3.1}$$

where $A_{ijkl} = a_ia_ja_ka_l + b_ib_jb_kb_l + c_ic_jc_kc_l$. The non-dimensional anisotropy factor

$$f_0 = 1 - \frac{c_{11} - c_{12}}{2c_{44}} \tag{3.2}$$

is usually introduced as a measure of the degree of anisotropy at the second-order level, so that in the case of isotropy $f_0 = 0$.

The fourth-order tensor of the second-order elastic compliances has the components

$$D_{ijkl} = d_{12}\delta_{ij}\delta_{kl} + 2d_{44}I_{ijkl} + (d_{11} - d_{12} - 2d_{44})A_{ijkl}, \tag{3.3}$$

with the connections

$$d_{11} = \frac{c_{11} + c_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})}, \quad d_{12} = -\frac{c_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})}, \quad d_{44} = \frac{1}{4c_{44}}. \tag{3.4}$$

If the symbols c and d are interchanged in (3.4), the relationship expressing the second-order moduli c_{ij} in terms of the second-order compliances d_{ij} are obtained. Other base tensors for the fourth-order tensors with cubic symmetry can be used in (3.1) and (3.3). A particularly convenient choice, which enables easy determination of the inverse tensors, has been utilized by Walpole (1984).

Further comparing (2.1) and (2.4), it is found that the components of the sixth-order tensor C_{ijklmn} are

$$C_{ijklmn} = \gamma_1 \delta_{ij}\delta_{kl}\delta_{mn} + \gamma_2 \delta_{(ij}I_{klmn)} + \gamma_3 \delta_{(ik}\delta_{lm}\delta_{nj)} + \gamma_4 \delta_{(ij}A_{klmn)}$$
$$+ \gamma_5 a_{(i}a_j b_k b_l c_m c_{n)} + \gamma_6 a_{(i}b_j c_k a_l b_m c_{n)}, \quad (3.5)$$

where

$$\gamma_1 = c_{123} - \beta_5, \gamma_2 = 6c_{144}, \gamma_3 = 2\beta_3, \gamma_4 = -3\beta_4, \gamma_5 = 6\beta_5, \gamma_6 = 6\beta_6. \quad (3.6)$$

The coefficients β_1 through β_6 are defined by (2.5). The tensors appearing on the right-hand side of (3.5) are the base tensors for the sixth-order elastic stiffness tensor with cubic symmetry. The notation such as $a_{(i}a_j b_k b_l c_m c_{n)}$ designates the symmetrization with respect to i and j, k and l, m and n, and ij, kl and mn. For example

$$\delta_{(ik}\delta_{lm}\delta_{nj)} = \frac{1}{4}(\delta_{ik}I_{jlmn} + \delta_{il}I_{jkmn} + \delta_{im}J_{klnj} + \delta_{in}I_{klmj}). \quad (3.7)$$

Other base tensors could be selected, such as those used by Toupin and Rivlin (1960).

For isotropic material $\beta_4 = \beta_5 = \beta_6 = 0$, i.e. $c_{111} = c_{123} + 6c_{144} + 8a_{456}$, $c_{112} = c_{123} + 2c_{144}$, and $c_{244} = c_{144} + 2c_{456}$. The components C_{ijklmn} are then the components of an isotropic sixth-order tensor

$$C_{ijklmn} = c_{123}\delta_{ij}\delta_{kl}\delta_{mn} + 6c_{144}\delta_{(ij}I_{klmn)} + 8c_{456}\delta_{(ik}\delta_{lm}\delta_{nj)}. \quad (3.8)$$

The tensors $\delta_{ij}\delta_{kl}\delta_{mn}$, $\delta_{(ij}I_{klmn)}$ and $\delta_{(ik}\delta_{lm}\delta_{nj)}$ constitute an integrity basis for the sixth-order isotropic tensors. If a Cauchy-type or Milder symmetry $C_{ijklmn} = C_{ikjlmn}$ would apply, then $c_{123} = c_{144} = c_{456}$.

The anisotropy factors for the TOEC of a cubic crystal can be introduced in various ways. One convenient definition is

$$f_1 = 1 - \frac{\gamma_1}{c_{123}}, \quad f_2 = 1 - \frac{\gamma_2 + \gamma_4}{6c_{144}}, \quad f_3 = 1 - \frac{\gamma_3}{8c_{456}}, \quad (3.9)$$

so that in the case of isotropy $f_1 = f_2 = f_3 = 0$.

The components of the sixth-order elastic compliance tensor D_{ijklmn} are given by the right-hand side of (3.5), with the constants c_{ijk} replaced by d_{ijk} in (2.5) and (3.6).

Having in mind (2.12), rewritten for convenience in the Voigt notation as $d_{ikm} = -d_{ip}c_{pru}d_{rk}d_{um}$, and in view of tables for independent SOEC and TOEC (Brugger, 1965), the relationships between the third-order elastic moduli and compliances are (Barsch, 1968)

$$d_{111} = (d_{11}^3 + 2d_{12}^3)c_{111} - 6d_{12}(d_{11}^2 + d_{11}d_{12} + d_{12}^2)c_{112} - 6d_{11}d_{12}^2 c_{123}, \quad (3.10)$$

$$d_{112} = -d_{12}(d_{11}^2 + d_{11}d_{12} + d_{12}^2)(c_{111} + 2c_{123})$$
$$- (d_{11}^3 + 3d_{11}^2 d_{12} + 9d_{11}d_{12}^2 + 5d_{12}^3)c_{112}, \quad (3.11)$$

$$d_{123} = -3d_{11}d_{12}^2 c_{111} - 6d_{12}(d_{11}^2 + d_{11}d_{12} + d_{12}^2)c_{112}$$
$$- (d_{11}^3 + 3d_{11}d_{12}^2 + 2d_{12}^3)c_{123}, \quad (3.12)$$

$$d_{144} = -4d_{44}^2(d_{11}c_{144} + 2d_{12}c_{244}), \quad (3.13)$$

$$d_{244} = -4d_{44}^2[d_{12}c_{144} + (d_{11} + d_{12})c_{244}], \quad (3.14)$$

$$d_{456} = -8d_{44}^3 c_{456}. \quad (3.15)$$

If the symbols c and d are interchanged in (3.10)–(3.15), we have the inverse relationships expressing c_{ijk} in terms of d_{ijk}.

Cousins (1968) observed that certain linear combinations of the third-order elastic moduli and compliances are proportional to each other. For example, for isotropic material it can be shown that

$$9d_{123} + 18d_{144} + 8d_{456} = -(3d_{12} + 2d_{44})^3 (9c_{123} + 18c_{144} + 8c_{456}), \qquad (3.16)$$

$$3d_{144} + 4d_{456} = -4d_{44}^2 (3d_{12} + 2d_{44})(3c_{144} + 4c_{456}). \qquad (3.17)$$

These equations will be conveniently used to compare the Voigt- and Reuss-type estimates of the TOEC in the subsequent section.

4. VOIGT- AND REUSS-TYPE ESTIMATES OF THE ELASTIC CONSTANTS OF AN ISOTROPIC AGGREGATE OF CUBIC CRYSTALS

For the sake of comparison with the results presented in Section 5, we list in this section relevant results for the Voigt- and Reuss-type estimates of the SOEC and TOEC. According to the Voigt assumption, when a polycrystalline aggregate is subjected to the overall uniform strain, the individual crystals will all be in the same state of applied strain. It follows that the effective elastic moduli of a polycrystalline aggregate are directional averages of the single crystal moduli

$$C_{ijkl}^* = \frac{1}{8\pi^2} \int_\Omega C_{ijkl} d\Omega, \qquad (4.1)$$

$$C_{ijklmn}^* = \frac{1}{8\pi^2} \int_\Omega C_{ijklmn} d\Omega. \qquad (4.2)$$

Equation (4.1) gives, upon integration

$$C_{ijkl}^* = \frac{1}{5}(c_{11} + 4c_{12} - 2c_{44})\delta_{ij}\delta_{kl} + \frac{2}{5}(c_{11} - c_{12} + 3c_{44})I_{ijkl}. \qquad (4.3)$$

The well-known Voigt estimates of the effective second-order elastic moduli for a polycrystalline aggregate are thus

$$c_{12}^* = \frac{1}{5}(c_{11} + 4c_{12} - 2c_{44}), \quad c_{44}^* = \frac{1}{5}(c_{11} - c_{12} + 3c_{44}). \qquad (4.4)$$

Similarly, Equation (4.2) yields

$$C_{ijklmn}^* = \left(6\beta_1 + 3\beta_2 + \beta_3 + \frac{12}{5}\beta_4 + \frac{16}{35}\beta_5 + \frac{2}{35}\beta_6\right)\delta_{ij}\delta_{kl}\delta_{mn}$$

$$- \left(3\beta_2 + 3\beta_3 + \frac{6}{5}\beta_4 + \frac{6}{7}\beta_5 + \frac{9}{35}\beta_6\right)\delta_{(ij}I_{klmn)} + \left(2\beta_3 + \frac{16}{35}\beta_5 + \frac{9}{35}\beta_6\right)\delta_{(ik}\delta_{lm}\delta_{nj)}. \qquad (4.5)$$

Comparing (4.5) with the general isotropic structure of (3.8), the effective third-order elastic moduli for a polycrystalline aggregate are found to be

$$c_{123}^* = \frac{1}{35}(c_{111} + 18c_{112} + 16c_{123} - 30c_{144} - 12c_{244} + 16c_{456}), \qquad (4.6)$$

$$c_{144}^* = \frac{1}{35}(c_{111} + 4c_{112} - 5c_{123} + 19c_{144} + 2c_{244} - 12c_{456}), \qquad (4.7)$$

$$c_{456}^* = \frac{1}{35}(c_{111} - 3c_{112} + 2c_{123} - 9c_{144} + 9c_{244} + 9c_{456}). \qquad (4.8)$$

These relationships can also be obtained without the involved integration (see Appendix), from the system of three algebraic equations for three unknowns c_{123}^*, c_{144}^* and c_{456}^*, obtained by equating the linear invariants of the sixth-order tensor of a single cubic crystal, with the corresponding invariants of the isotropic sixth-order tensor of a polycrystalline aggregate (Bross, 1963; Barsch, 1968). Johnson (1982) has extended the Voigt-type averaging to derive expressions for the nine TOEC of transversely isotropic aggregates of cubic crystals.

When a polycrystalline aggregate is subjected to the overall uniform stress, Reuss assumed that the individual crystals are also in the same state of applied stress. The effective elastic compliances of a polycrystalline aggregate are then directional averages of the single crystal compliances

$$D_{ijkl}^* = \frac{1}{8\pi^2} \int_\Omega D_{ijkl} d\Omega, \qquad (4.9)$$

$$D_{ijklmn}^* = \frac{1}{8\pi^2} \int_\Omega D_{ijklmn} d\Omega \qquad (4.10)$$

From (4.9), the Reuss estimates of the second-order elastic compliances are

$$d_{12}^* = \frac{1}{5}(d_{11} + 4d_{12} - 2d_{44}), \quad d_{44}^* = \frac{1}{5}(d_{11} - d_{12} + 3d_{44}). \qquad (4.11)$$

From (4.10) we obtain the third-order elastic compliances c_{ijk}^* in terms of d_{ijk}. The resulting equations are (4.6)–(4.8), with the constants c_{ijk} replaced by the constants d_{ijk}. The corresponding elastic moduli are

$$c_{123}^* = -(3c_{12}^* + 2c_{44}^*)^3 d_{123}^* - 6c_{12}^*(3c_{12}^* + 2c_{44}^*)(3c_{12}^* + 4c_{44}^*)d_{144}^*$$
$$-24(c_{12}^* + 2c_{44}^*)c_{12}^{*2} d_{456}^*, \qquad (4.12)$$

$$c_{144}^* = -4c_{44}^{*2}[(3c_{12}^* + 2c_{44}^*)d_{144}^* + 4c_{12}^* d_{456}^*], \qquad (4.13)$$

$$c_{456}^* = -8c_{44}^{*3} d_{456}^*. \qquad (4.14)$$

To compare the Voigt- and Reuss-type estimates, it is helpful to use (3.16) and (3.17). The linear combination $9c_{123}^* + 18c_{144}^* + 8c_{456}^*$ is associated with a pure hydrostatic response, and is the same for both, Voigt- and Reus-type estimates. However

$$(3c_{144}^* + 4c_{456}^*)^V = \frac{1}{5}[(c_{111} - c_{123}) + 3(c_{144} + 2c_{244})], \qquad (4.15)$$

$$(3c_{44}^* + 4c_{456}^*)^R = \frac{1}{5 - 3f_0}[(c_{111} - c_{123}) + 3(1 - f_0)(c_{144} + 2c_{244})], \qquad (4.16)$$

and

$$(c_{456}^*)^V = \frac{1}{35}[(c_{111} - 3c_{112} + 2c_{123}) - 9(c_{144} - c_{244}) + 9c_{456}], \qquad (4.17)$$

$$(c_{456}^*)^R = \frac{1}{35}\left(\frac{5}{5 - 3f_0}\right)^3 [(c_{111} - 3c_{112} + 2c_{123}) - 9(1 - f_0)^2(c_{144} - c_{244})$$

$$+ 9(1 - f_0)^3 c_{456}]. \qquad (4.18)$$

Thus, the smaller the magnitude of anisotropy factor f_0 for the SOEC, the smaller the difference between the Voigt and Reuss estimates of the TOEC. If $f_0 = 0$, the two estimates coincide. They can also coincide, or can be close to each other, for certain crystals with large magnitude of f_0, such as niobium (see Section 6). There are materials that are nearly isotropic in their SOEC, but strongly anisotropic in their TOEC (Chang and Graham, 1968). For example, aluminum is nearly isotropic at the second-order level, but strongly anisotropic at the third-order level. As discussed by Johnson (1986), the degree of anisotropy found among the SOEC does not give any information on the degree of anisotropy to be expected at the third-order level. Furthermore, the coincidence of the Voigt- and Reuss-type estimates does not imply that they represent the exact values of the TOEC (as would be the case with the SOEC), because there is no proof that some, or any, of the Voigt and Reuss estimates of the third-order elastic moduli are the upper or lower bounds for these constants.

5.   SEMI-CONSISTENT ESTIMATES OF THE ELASTIC CONSTANTS FOR AN ISOTROPIC AGGREGATE OF CUBIC CRYSTALS

An improved method to determine the effective TOEC for an isotropic aggregate of anisotropic cubic crystals is presented. This method is an extension of the well-known self-consistent method used to calculate the effective SOEC in linear theory. In the first approach, we assume that the Lagrangian strain within a single crystal, embedded in an isotropic effective matrix, is proportional to the corresponding far-field strain in the matrix. This is adopted from the linear theory, where the infinitesimal strain within a crystal is exactly proportional to the far-field applied strain. In the second approach, we assume that the symmetric Piola–Kirchhoff stress within a crystal is proportional to the corresponding far-field stress in the matrix. When applied to calculate the effective elastic properties, the two approaches are self-consistent with respect to the SOEC, but not the TOEC. The method is thus referred to as a semi-consistent method.

5.1. *Elastic moduli approach*

Denote the symmetric Piola–Kirchhoff stress in an arbitrary cubic crystal of a polycrystalline aggregate by S_{ij}^0. This is a gradient of the strain energy with respect to the corresponding Lagrangian strain E_{kl}^0, i.e. to within the second-order terms in strain

$$S_{ij}^0 = C_{ijkl}E_{kl}^0 + \frac{1}{2}C_{ijklmn}E_{kl}^0E_{mn}^0 \tag{5.1}$$

The constants C_{ijkl} are defined by (3.1), and C_{ijklmn} by (3.5). The average stress in a polycrystal is

$$S_{ij} = \frac{1}{8\pi^2}\int_\Omega S_{ij}^0 d\Omega. \tag{5.2}$$

where $d\Omega = \sin\theta\, d\varphi\, d\theta\, d\psi$, and φ, θ and ψ are the Euler angles. Denoting by C_{ijkl}^* and C_{ijklmn}^* the effective elastic constants of a polycrystalline aggregate, we have

$$S_{ij} = C_{ijkl}^*E_{kl} + \frac{1}{2}C_{ijklmn}^*E_{kl}E_{mn}. \tag{5.3}$$

In his well-known paper, Eshelby (1957) has shown, through an equivalent inclusion method, that the strain in an ellipsoidal inhomogeneity within a matrix subjected to far field uniform strain is also uniform. Linear elasticity and small deformations were assumed. Since an ellipsoidal inclusion under uniform deformation remains an ellipsoidal inclusion, the result also applies in the case of nonlinear elasticity and finite deformations. This can be considered as a sequence of infinitesimal increments. For each increment of applied strain there is a uniform increment of strain within the inhomogeneity, and thus the total strain in the inhomogeneity is also uniform. The relationship between this strain and the applied strain is, however, difficult to find due to mathematical complexities in handling the corresponding nonlinear boundary value problem. We shall accordingly assume that the Lagrangian strain in a single crystal of a polycrystalline aggregate is proportional to applied strain, i.e.

$$E_{ij}^0 = \mathscr{H}_{ijkl}E_{kl}, \tag{5.4}$$

where $\mathscr{H}_{ijkl}$ is the same tensor as in the corresponding linear elasticity problem. This is an improvement relative to the Voigt-type assumption $E_{ij}^0 = E_{ij}$, although it is still a simplification, since a nonlinear relationship between E_{ij}^0 and E_{ij} should hold in the nonlinear elastic domain. (Addition of the quadratic terms $\mathscr{H}_{ijklmn}E_{kl}E_{mn}$ to the right-hand side of (5.4) would be the next order of approximation, provided that the sixth-order tensor $\mathscr{H}_{ijklmn}$ can be appropriately constructed.) Adopting (5.4), the tensor $\mathscr{H}_{ijkl}$ can be obtained by a self-consistent method originally introduced by Hershey (1954) and Kröner (1958). If an individual cubic crystal of a spherical shape is considered to be an anisotropic inhomogeneity surrounded by an effective isotropic matrix of the polycrystalline aggregate, it can be shown that

$$\mathcal{H}_{ijkl} = I_{ijkl} + h(\delta_{ij}\delta_{kl} + 2I_{ijkl} - 5A_{ijkl}), \tag{5.5}$$

where

$$h = \frac{(c_{11} + 2c_{12} + 6c_{44}^*)(c_{11} - c_{12} - 2c_{44}^*)}{3[8c_{44}^{*\,2} + 9c_{11}c_{44}^* + (c_{11} - c_{12})(c_{11} + 2c_{12})]}. \tag{5.6}$$

The tensor components A_{ijkl} are given by the expression following (3.1). Substituting (5.4) into (5.1), we obtain

$$S_{ij}^0 = \hat{C}_{ijkl}E_{kl} + \frac{1}{2}\hat{C}_{ijklmn}E_{kl}E_{mn}, \tag{5.7}$$

where

$$\hat{C}_{ijkl} = C_{ijpq}\mathcal{H}_{pqkl}, \quad \hat{C}_{ijklmn} = C_{ijpqrs}\mathcal{H}_{pqkl}\mathcal{H}_{rsmn}. \tag{5.8}$$

For example, in an expanded form

$$\hat{C}_{ijkl} = C_{ijkl} + h\{(c_{11} - c_{12})\delta_{ij}\delta_{kl} + 4c_{44}I_{ijkl} - [3(c_{11} - c_{12}) + 4c_{44}]A_{ijkl}\}. \tag{5.9}$$

Thus, in view of (5.2) and (5.3), it follows that

$$C_{ijkl}^* = \frac{1}{8\pi^2}\int_\Omega \hat{C}_{ijkl}d\Omega, \tag{5.10}$$

$$C_{ijklmn}^* = \frac{1}{8\pi^2}\int_\Omega \hat{C}_{ijklmn}d\Omega. \tag{5.11}$$

By equating the linear invariants of C_{ijkl}^* and $\hat{C}_{ijkl}(C_{iijj}^* = \hat{C}_{iijj}, C_{ijij}^* = \hat{C}_{ijij})$, we obtain $3c_{12}^* + 2c_{44}^* = c_{11} + 2c_{12}$, and

$$8c_{44}^{*\,3} + (5c_{11} + 4c_{12})c_{44}^{*\,2} - c_{44}(7c_{11} - 4c_{12})c_{44}^*$$
$$- c_{44}(c_{11} - c_{12})(c_{11} + 2c_{12}) = 0. \tag{5.12}$$

This cubic equation for c_{44}^* was originally derived by Kröner (1958).

In view of (3.5), (5.5) and (5.8), the three linear invariants of the sixth-order tensor $\hat{C}_{ijklmn}$ are

$$\hat{C}_{iijjkk} = 3(c_{111} + 6c_{112} + 2c_{123}), \tag{5.13}$$

$$\hat{C}_{iiklkl} = 3(c_{111} + 2c_{112} + 2c_{144} + 4c_{244}) + 12h(-c_{111} + c_{123} + 2c_{144} + 4c_{244})$$
$$+ 6h^2(3c_{111} - 3c_{123} + 4c_{144} + 8c_{244}), \tag{5.14}$$

$$\hat{C}_{ijjkki} = 3(c_{111} + 6c_{244} + 2c_{456}) + 12h(-c_{111} + c_{112} + c_{144} + 3c_{244} + 2c_{456})$$
$$+ 6h^2(2c_{111} - 3c_{112} + c_{123} + 4c_{144} + 4c_{456}). \tag{5.15}$$

Making these equal to the corresponding invariants of the isotropic sixth-order tensor of a polycrystalline aggregate

$$C_{iijjkk}^* = 3(9c_{123}^* + 18c_{144}^* + 8c_{456}^*), \tag{5.16}$$

$$C_{iiklkl}^* = 3(3c_{123}^* + 16c_{144}^* + 16c_{456}^*), \tag{5.17}$$

$$C^*_{ijjkki} = 3(c^*_{123} + 12c^*_{144} + 22c^*_{456}), \tag{5.18}$$

and solving for the three unknowns, we obtain

$$c^*_{123} = \frac{1}{70}(16j_1 - 30j_2 + 16j_3), \tag{5.19}$$

$$c^*_{144} = \frac{1}{70}(-5j_1 + 19j_2 - 12j_3), \tag{5.20}$$

$$c^*_{456} = \frac{1}{70}(2j_1 - 9j_2 + 9j_3). \tag{5.21}$$

In (5.19)–(5.21), the abbreviations used were $j_1 = \hat{C}_{iijjkk}/3, j_2 = \hat{C}_{iiklkl}/3$ and $j_3 = \hat{C}_{ijjkki}/3$.

5.2. *Elastic compliances approach*

The stress state in an ellipsoidal inhomogeneity within a matrix subjected to the far field uniform stress is also uniform. In a dual formulation to that presented in the previous subsection, we assume that

$$S^0_{ij} = \mathscr{G}_{ijkl}S_{kl}, \tag{5.22}$$

where $\mathscr{G}_{ijkl}$ is the same tensor as in the corresponding linear elasticity problem. The tensor components $\mathscr{G}_{ijkl}$ are

$$\mathscr{G}_{ijkl} = g_1\delta_{ij}\delta_{kl} + g_2 I_{ijkl} + g_3 A_{ijkl}, \tag{5.23}$$

where

$$g_1 = \frac{1}{3}\left[1 + 2(3g-1)\frac{d^*_{44}}{d_{11}-d_{12}}\right], \quad g_2 = (1+2g)\frac{d^*_{44}}{d_{44}}, \quad g_3 = 1 - 3g_1 - g_2 \tag{5.24}$$

and

$$g = \frac{[2d^*_{44} + 3(d_{11}+2d_{12})][2d^*_{44} - (d_{11}-d_{12})]}{3[4d^{*2}_{44} + 9(d_{11}+d_{12})d^*_{44} + 2(d_{11}-d_{12})(d_{11}+2d_{12})]}. \tag{5.25}$$

Consequently,

$$E^0_{ij} = \hat{D}_{ijkl}S_{kl} + \frac{1}{2}\hat{D}_{ijklmn}S_{kl}S_{mn}, \tag{5.26}$$

with

$$\hat{D}_{ijkl} = D_{ijpq}\mathscr{G}_{pqkl}, \quad \hat{D}_{ijklmn} = D_{ijpqrs}\mathscr{G}_{pqkl}\mathscr{G}_{rsmn}. \tag{5.27}$$

The effective elastic compliances of the polycrystalline aggregate are then

$$D^*_{ijkl} = \frac{1}{8\pi^2}\int_\Omega \hat{D}_{ijkl}\mathrm{d}\Omega, \tag{5.28}$$

$$D^*_{ijklmn} = \frac{1}{8\pi^2}\int_\Omega \hat{D}_{ijklmn}\mathrm{d}\Omega. \tag{5.29}$$

By equating the linear invariants of D_{ijkl}^* and $\hat{D}_{ijkl}(D_{iijj}^* = \hat{D}_{iijj},\ D_{ijij}^* = \hat{D}_{ijij})$, we obtain $3d_{12}^* + 2d_{44}^* = d_{11} + 2d_{12}$, and

$$4d_{44}^{*\ 3} + (7d_{11} + 11d_{12})d_{44}^{*\ 2} - d_{44}(5d_{11} + d_{12})d_{44}^*$$
$$- 2d_{44}(d_{11} - d_{12})(d_{11} + 2d_{12}) = 0. \quad (5.30)$$

This cubic equation for d_{44}^* is a dual equation to (5.12) for c_{44}^*. One equation follows from another by direct substitution of the relationships (3.4) between the elastic moduli and compliances. Hence, the SOEC c_{12}^* and c_{44}^* (or, d_{12}^* and d_{44}^*) are identical in both types of calculation, and the method is self-consistent with respect to them.

In view of (5.23) and (5.27), the three linear invariants of the sixth-order tensor $\hat{D}_{ijklmn}$ are

$$\hat{D}_{iijjkk} = 27\gamma_1 + 9\gamma_2 + 3\gamma_3 + 9\gamma_4 + \gamma_5, \quad (5.31)$$

$$\hat{D}_{iiklkl} = g_1(1 + g_3)(27\gamma_1 + 9\gamma_2 + 3\gamma_3 + 9\gamma_4 + \gamma_5) + (g_2 + g_2 g_3 + g_3^2)$$
$$\times (9\gamma_1 + 5\gamma_2 + 3\gamma_3 + 5\gamma_4) + 3g_2(g_2 - 2g_1)(\gamma_2 + \gamma_3) - g_1 g_2(6\gamma_4 - \gamma_5), \quad (5.32)$$

$$\hat{D}_{ijjkki} = g_1^2(27\gamma_1 + 9\gamma_2 + 3\gamma_3 + 9\gamma_4 + \gamma_5) + 2g_1 g_2(9\gamma_1 + 8\gamma_2 + 6\gamma_3 + 5\gamma_4)$$
$$+ 2g_1 g_3(9\gamma_1 + 5\gamma_2 + 3\gamma_3 + 5\gamma_4) + 2g_2 g_3\left(3\gamma_1 + 4\gamma_2 + \frac{9}{2}\gamma_3 + 3\gamma_4\right)$$
$$+ g_2^2\left(3\gamma_1 + 6\gamma_2 + \frac{33}{4}\gamma_3 + 3\gamma_4 + \frac{1}{8}\gamma_6\right) + 3g_3^2(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4). \quad (5.33)$$

In the above equations, the constants γ_1 to γ_6 are given by (3.6), where β_1 to β_6 are defined by (2.5), with the constants c_{ijk} replaced by the constants d_{ijk}. The first invariant $\hat{D}_{iijjkk}$ is identically equal to D_{iijjkk}. The right-hand sides of (5.32) and (5.33) can be rearranged in various ways, but for the known compliances d_{ijk} and calculated g_1, g_2 and g_3, they represent two easily determined numbers. By equating them to the corresponding invariants of the isotropic sixth-order tensor of a polycrystalline aggregate, and solving for the three unknowns, we obtain

$$d_{123}^* = \frac{1}{70}(16k_1 - 30k_2 + 16k_3), \quad (5.34)$$

$$d_{144}^* = \frac{1}{70}(-5k_1 + 19k_2 - 12k_3), \quad (5.35)$$

$$d_{456}^* = \frac{1}{70}(2k_1 - 9k_2 + 9k_3), \quad (5.36)$$

where $k_1 = \hat{D}_{iijjkk}/3$, $k_2 = \hat{D}_{iiklkl}/3$, and $k_3 = \hat{D}_{ijjkki}/3$. The corresponding elastic moduli c_{123}^*, c_{144}^* and c_{456}^* are determined from (4.12)–(4.14). The calculated values are different from those obtained in the previous subsection. Hence, while the two procedures are self-consistent with respect to the SOEC, they are not with respect to the TOEC, and we refer to the method as a semi-consistent method.

Table 1. *Experimental values for the SOEC* c_{ij} *(in GPa) of selected cubic crystals, listed in Landolt-Börnstein (1979). The parameter* f_0 *is the corresponding anisotropy factor, calculated from (3.2). The constants* c_{ij}^* *are the experimental values for isotropic polycrystalline aggregates, calculated from the data reported by Hertzberg (1976)*

Material	c_{11}	c_{12}	c_{44}	f_0	c_{12}^*	c_{44}^*
Al	108	62	28.3	0.19	58.1	26.1
Cu	169	122	75.3	0.69	105.5	48.3
Nb	245	132	28.4	−0.99	144.5	37.5
Fe	230	135	117	0.59	115.5	81.6

6. NUMERICAL RESULTS AND DISCUSSION

Experimental values for the SOEC of selected cubic crystals are listed in Table 1. The table also contains experimental data for the polycrystalline aggregates. The accuracy of the data is high at both single crystal and polycrystalline levels. Table 2 lists the Voigt, Reuss and the self-consistent estimates of these constants. The agreement between the self-consistent estimates and the experimental data are good.

The accuracy of analytical estimates of the TOEC, based on the presently available experimental data, can only be assessed to a limited extent. This is because there is substantial uncertainty about the accuracy of the measured values of the TOEC for most single crystals. An inspection of the Landolt-Börnstein (1979) compilations reveals a large margin of error for the constants c_{123}, c_{144} and c_{456}, which is in some cases in the range from 100 to 300%. This is also evident from the values for the TOEC of aluminum, copper, niobium and iron, listed in Table 3. Furthermore, while the data for the TOEC of single crystals and single-crystalline alloys are available in the literature, the data for isotropic polycrystals are rather rare. Table 4 lists the

Table 2. *Voigt, Reuss and self-consistent estimates of the second-order elastic constants for isotropic polycrystalline aggregates (in GPa). Note that* $c_{12}^{*V} < c_{12}^* < c_{12}^{*R}$ *and* $c_{44}^{*R} < c_{44}^* < c_{44}^{*V}$

Material	c_{12}^{*V}	c_{44}^{*V}	c_{12}^{*R}	c_{44}^{*R}	c_{12}^*	c_{44}^*
Al	59.88	26.18	60.06	25.91	59.96	26.06
Cu	101.28	54.58	110.99	40.02	105.58	48.13
Nb	143.24	39.64	146.03	35.45	144.61	37.58
Fe	107.20	89.20	117.46	73.80	111.90	82.15

Table 3. *Experimental values for the TOEC of single crystals (in GPa); Landolt-Börnstein (1979)*

Material	c_{111}	c_{112}	c_{123}	c_{144}	c_{244}	c_{456}
Al	-1080 ± 30	-315 ± 10	36 ± 15	-23 ± 15	-340 ± 10	-30 ± 30
Cu	-1271 ± 22	-814 ± 9	-50 ± 18	-3 ± 9	-780 ± 5	-95 ± 87
Nb	-2564 ± 25	-1140 ± 25	-467 ± 25	-343 ± 10	-168 ± 5	137 ± 5
Fe	-2705 ± 5	-626 ± 5	-575 ± 5	-836 ± 13	-531 ± 7	-721 ± 12

Table 4. *Experimental values for the TOEC (in GPa). Values for Cu and Fe are calculated from the reported values of the Murnaghan constants* l, m, n

Material	c_{123}^{*}	c_{144}^{*}	c_{456}^{*}	Reference
Al	-39 ± 17	-124 ± 4	-86 ± 1	Wasserbäch (1990)
Cu	-670 ± 180	175 ± 207	-398 ± 5	Seeger and Buck (1960)
Nb	-480 ± 120	-370 ± 20	75 ± 5	Graham *et al.* (1968)
Fe	-320 ± 110	-10 ± 15	-380 ± 3	Seeger and Buck (1960)

values of the TOEC for polycrystalline materials that we were able to find in the literature. The margin of error is small for the constant c_{456}^{*}, but rather pronounced for the remaining two constants. Smith *et al.* (1966) and Wasserbäch (1990) discussed the error in c_{123}^{*}, and pointed out that it is large because the final stage of calculating this constant from the experimental data involves the difference between approximately equal quantities.

The Voigt and Reuss estimates of the TOEC for isotropic polycrystalline aggregates are given in Table 5. They are calculated according to expressions of the type given by (4.6)–(4.8) (without the error margins from Table 3). The difference between these

Table 5. *Voigt and Reuss estimates of the TOEC for isotropic polycrystalline aggregates (in GPa)*

Material	c_{123}^{*V}	c_{144}^{*V}	c_{456}^{*V}	c_{123}^{*R}	c_{144}^{*R}	c_{456}^{*R}
Al	-53.83	-93.63	-91.03	-49.37	-98.32	-85.48
Cu	-251.23	-135.83	-193.63	44.95	-392.77	51.34
Nb	-458.80	-379.60	78.00	-416.22	-415.98	111.99
Fe	-93.06	-303.66	-163.46	-231.14	-213.96	-209.94

Table 6. *Two types of semi-consistent estimates of the TOEC (in GPa) for isotropic polycrystalline aggregates*

Material	$c_{123}^{*}{}^{(1)}$	$c_{144}^{*}{}^{(1)}$	$c_{456}^{*}{}^{(1)}$	$c_{123}^{*}{}^{(2)}$	$c_{144}^{*}{}^{(2)}$	$c_{456}^{*}{}^{(2)}$
Al	−55.73	−93.09	−90.11	−52.49	−95.51	−88.29
Cu	−304.33	−124.85	−158.60	−172.40	−223.79	−84.39
Nb	−464.97	−380.64	87.28	−433.52	−404.23	104.97
Fe	−144.11	−283.54	−151.29	−206.42	−236.80	−186.35

estimates is rather small for aluminum, because a single crystal of aluminum is mildly anisotropic at the level of the SOEC ($f_0 = 0.19$). The estimates are also close for niobium (columbium), although its single crystals are very anisotropic at the second-order level ($f_0 = -0.99$). This is because the TOEC of a single crystal of niobium happen to be such that the right-hand sides of (4.17) and (4.18), for example, do not differ appreciably, in spite of the large magnitude of f_0. More often, however, the difference between the Voigt and Reuss estimates is more pronounced, the higher the magnitude of the anisotropy factor f_0. For example, the Voigt estimate of the constant c_{123}^{*} for copper ($f_0 = 0.69$) is about -251 GPa, while its Reuss estimate is positive and equal to about -45 GPa.

Table 6 lists the two estimates of the TOEC, based on the proposed semi-consistent method. A common feature of these results is that for each TOEC, the two semi-consistent estimates are closer to each other, than the Voigt and Reuss estimates are. For example, the two estimates of the constant c_{123}^{*} for copper are about -304 and -172 GPa. The difference is equal to -132 GPa, i.e. about 55% of -238, which is the arithmetic mean between -304 and -172. The difference between the Voigt and Reuss estimates is more than twice that high, about -296 GPa, i.e. 287% of -103, which is the arithmetic mean between -251 and 45. A similar situation is found with constants c_{144}^{*} and c_{456}^{*}.

Since the Voigt averaging procedure assumes that the material is in the state of homogeneous strain, and the Reuss procedure assumes it to be in the state of homogeneous stress, these assumptions correspond to two extreme situations. It is reasonable to expect that a real polycrystalline aggregate will be somewhere in-between these extremes. Consequently, we give in Table 7 the values of the third-

Table 7. *Average estimates of the third-order elastic moduli based on the arithmetic mean of the Voigt and Reuss estimates, and on the arithmetic mean of the two semi-consistent estimates (in GPa)*

Material	$c_{123}^{*}{}^{VR}$	$c_{144}^{*}{}^{VR}$	$c_{456}^{*}{}^{VR}$	$c_{123}^{*}{}^{SC}$	$c_{144}^{*}{}^{SC}$	$c_{456}^{*}{}^{SC}$
Al	−51.60	−95.98	−88.26	−54.11	−94.30	−89.20
Cu	−103.14	−264.30	−71.14	−238.37	−174.32	−121.49
Nb	−437.51	−397.79	94.99	−449.25	−392.43	96.13
Fe	−162.10	−258.81	−186.70	−175.26	−260.17	−168.82

Table 8. *Average estimates of the third-order elastic moduli for five additional-polycrystalline materials, based on the arithmetic mean of the Voigt and Reuss estimates, and on the arithmetic mean of the two semi-consistent estimates (in GPa)*

Material	c_{123}^{*VR}	c_{144}^{*VR}	c_{456}^{*VR}	c_{123}^{*SC}	c_{144}^{*SC}	c_{456}^{*SC}
Ag	111.04	−242.03	−35.23	3.00	−168.69	−78.69
Au	−286.63	−249.62	−81.85	−390.82	−182.41	−115.97
Si	−210.98	−61.09	−77.07	−221.83	−53.82	81.22
Ge	−121.55	−82.09	−61.04	−134.62	−73.40	−65.90
Ni	−227.94	−314.74	−124.15	−334.76	−245.29	−160.25

order elastic moduli calculated from the arithmetic mean of the Voigt and Reuss estimates. For the second-order elastic moduli, such an estimate is sometimes referred to as the Voigt–Reuss–Hill estimate, since Hill (1952) observed that it often makes a good agreement with experimental observations. Table 7 also contains the third-order elastic moduli calculated from the arithmetic mean of the two semi-consistent estimates. Finally, we give Table 8 which lists the estimates of the TOEC for five additional polycrystals. No comparison with experimental data is given here, since all reported laboratory investigations on these materials were done in their single crystal form.

An unambiguous judgement of the accuracy for either of the presented estimates must await more accurate experimental measurements for both, single crystals and polycrystalline aggregates. For the data presented in Table 3, we find the best agreement between theoretical estimates and the experiment in the case of niobium. This is partly because niobium is a BCC refractory metal with a high yield strength, so that measurements under uniaxial stress are less effected by a possible dislocation motion. Agreement in the case of iron is far less satisfactory, particularly for the constant c_{144}^{*}, even though iron is also a BCC metal, with a high yield strength, and with dislocations usually pinned by impurities such as nitrogen and carbon. Agreement with experimental data for aluminum appears to be rather good for all analytical estimates. There is a pronounced disagreement for copper, albeit the semi-consistent estimates are closer to experimental values. Disagreements may be partly attributed to the precision of experimental techniques, and to the fact that analytical estimates are based on the assumption that grains are negligible in size compared to the specimen, and oriented in a completely random manner. Johnson (1986) indicated that ultrasonic measurements can be considerably affected when the number of grains within the acoustic beam of the transducer is not large (less than 1000). The experimental data from such tests cannot be in close agreement with theoretical estimates considered in this paper. The TOEC are also sensitive to small variations in a polycrystalline microstructure. Graham *et al.* (1968) reported large differences in the measured TOEC for two samples of polycrystalline columbium, one of which had more elongated grains than the other. In contrast, the measured values of the SOEC were only slightly influenced by this grain structure. The presence of grain boundaries and voids between grains also affects the ultrasonic measurements and resulting values for the TOEC.

7. CONCLUSION

Several extensions of the presented analysis should be undertaken. One is a derivation of the sixth-order tensors $\mathscr{H}_{ijklmn}$ or $\mathscr{G}_{ijklmn}$, which appear in (5.4) and (5.22), when the quadratic terms in strain and stress are included there. If this is accomplished, the calculation of the corresponding average TOEC proceeds with no further difficulties, in an analogous manner to that described in Section 5. However, the estimates of the TOEC based on the elastic moduli and the elastic compliances approach will still be different, because the quadratic approximations of the strain and complementary energies are not exact Legendre transforms of each other. The second effort should address the variational estimates and derivation of possible bounds for the TOEC. The existing results for nonlinear heterogeneous solids, already considered in the literature (Willis, 1990), may in that respect be of significant help. An extension of the analyses also needs to be undertaken to determine the effective TOEC for transversely isotropic and orthotropic aggregates of cubic crystals. The corresponding results for the SOEC are the well-known self-consistent calculations by Kneer (1965) and Morris (1970) and, more recently, by Walpole (1987) regarding additional estimates and the bounds for the overall moduli.

ACKNOWLEDGEMENTS

REFERENCES

Andrews, D. L. and Thirunamachandran, T. (1977) On three-dimensional rotation averages. *J. Chem. Phys.* **67**, 5026–5033.

Barsch, G. R. (1968) Relation between third-order elastic constants of single crystals and polycrystals. *J. Appl. Phys.* **39**, 3780–3793.

Bross, H. (1963) Berechnung der elastischen Konstanten dritter Ordnung der Alkalihalogenidkristalle. *Z. für Physik* **175**, 345–369.

Brugger, K. (1964) Thermodynamic definition of higher order elastic coefficients. *Phys. Rev.* **133**, A1611–A1612.

Brugger, K. (1965) Pure modes for elastic waves in crystals. *J. Appl. Phys.* **36**, 759–768.

Chang, R. (1967) Relationships between the nonlinear elastic constants of monocrystalline and polycrystalline solids of cubic symmetry. *Appl. Phys. Lett.* **11**, 305–308.

Chang, R. and Graham, L. J. (1968) On the third order elastic constants of polycrystalline media and their relationships to the single crystal constants. *Mater. Res. Bull.* **3**, 745–752.

Chen, Y. C. and Jiang, X. (1993) Nonlinear elastic properties of particulate composites. *J. Mech. Phys. Solids* **41**, 1177–1190.

Cousins, C. S. G. (1968) A note on the estimation of the third-order elastic constants of quasi-isotropic materials. *J. Phys. C* **1**, 835–838.

Eshelby, J. D. (1957) The determination of the elastic field of an ellipsoidal inclusion, and related problems. *Proc. Roy. Soc. Lond. A* **241**, 376–396.

Graham, L. J., Nadler, H. and Chang, R. (1968) Third-order elastic constants of single-crystal and polycrystalline columbium. *J. Appl. Phys.* **39**, 3025–3033.

Hamilton, R. A. H. and Parrott, J. E. (1968) The third-order elastic constants of quasi-isotropic materials. *J. Phys. C* **1**, 829–834.

Hershey, A. V. (1954) The elasticity of an isotropic aggregate of anisotropic cubic crystals. *J. Appl. Mech.* **21**, 236–240.

Hertzberg, R. W. (1976) *Deformation and Fracture Mechanics of Engineering Materials.* John Wiley & Sons, New York.

Hill, R. (1952) The elastic behavior of a crystalline aggregate. *Proc. Phys. Soc. Lond. A* **65**, 349–354.

Imam, A., Johnson, G. C. and Ferrari, M. (1995) Determination of the overall moduli in second order incompressible elasticity. *J. Mech. Phys. Solids* **43**, 1087–1104.

Johnson, G. C. (1982) Acoustoelastic response of polycrystalline aggregates exhibiting transverse isotropy. *J. Nondestr. Eval.* **3**, 1–8.

Johnson, G. C. (1986) Variations in the second- and third-order elastic constants in polycrystalline aggregates. *J. Appl. Phys.* **59**, 4057–4061.

Kneer, G. (1965) Über die Berechnung der Elastizitätsmoduln vielkristalliner Aggregate mit Textur. *Phys. Stat. Sol.* **9**, 825–838.

Kröner, E. (1958) Berechnung der elastischen Konstanten des Vielkristalls aus den Konstanten des Einkristalls. *Z. für Phys.* **151**, 504–518.

Landolt-Börnstein (1979). *Numerical Data and Functional Relationships in Science and Technology*, ed. K.-H. Hellwege and A. M. Hellwege, Group III, Vol. 11. Springer-Verlag, Berlin.

Morris, P. R. (1970) Elastic constants of polycrystals. *Int. J. Engng Sci.* **8**, 49–61.

Ogden, R. W. (1974) On the overall moduli of non-linear elastic composite materials. *J. Mech. Phys. Solids* **22**, 541–553.

Saunders, G. A., Senin, H. B., Sidek, H. A. A. and Pelzl, J. (1993) Third-order elastic constants, vibrational anharmonicity, and the Invar behavior of the $Fe_{72}Pt_{28}$ alloy. *Phys. Rev. B* **48**, 15, 801–15, 806.

Seeger, A. and Buck, O. (1960) Die experimentelle Ermittlung der elastischen Konstanten höherer Ordnung. *Z. Naturforschg.* **15a**, 1056–1067.

Smith, R. T., Stern, R. and Stephens, R. W. B. (1966) Third-order elastic moduli of polycrystalline metals from ultrasonic velocity measurements. *J. Acoust. Soc. Amer.* **40**, 1002–1008.

Thurston, R. N. and Brugger, K. (1964) Third-order constants and the velocity of small amplitude elastic waves in homogeneously stressed media. *Phys. Rev.* **133**, A1604–A1610.

Toupin, R. A. and Bernstein, B. (1961) Sound waves in deformed perfectly elastic materials. Acoustoelastic effect. *J. Acoust. Soc. Amer.* **33**, 216–225.

Toupin, R. A. and Rivlin, R. S. (1960) Dimensional changes in crystals caused by dislocations. *J. Math. Phys.* **1**, 8–15.

Walpole, L. J. (1984) Fourth rank tensors of the thirty two crystal classes. *Proc. R. Soc. Lond. A* **391**, 149–179.

Walpole, L. J. (1987) Orthotropically textured elastic aggregates of cubic crystals. *J. Mech. Phys. Solids* **35**, 497–517.

Wasserbäch, W. (1990) Third-order constants of a cubic quasi-isotropic solid. *Phys. Stat. Sol. B* **159**, 689–697.

Willis, J. R. (1990) Variational estimates for the overall behavior of a nonlinear matrix-inclusion composite. *Micromechanics and Inhomogeneities*, ed. G. J. Weng, M. Taya and H. Abe, pp. 581–597. Springer-Verlag, New York.

APPENDIX

To derive the effective third-order polycrystalline elastic constants by integration from (4.2), the following three integrals were evaluated

V. A. LUBARDA

$$\frac{1}{8\pi^2}\int_\Omega \delta_{(ij}a_k a_l a_m a_{n)}\mathrm{d}\Omega = \frac{1}{15}[\delta_{ij}\delta_{kl}\delta_{mn}+2\delta_{(ij}I_{klmn)}], \tag{A.1}$$

$$\frac{1}{8\pi^2}\int_\Omega a_{(i}a_j b_k b_l c_m c_{n)}\mathrm{d}\Omega = \frac{1}{105}[8\delta_{ij}\delta_{kl}\delta_{mn}-15\delta_{(ij}I_{klmn)}+8\delta_{(ik}\delta_{lm}\delta_{nj)}], \tag{A.2}$$

$$\frac{1}{8\pi^2}\int_\Omega a_{(i}b_j c_k a_l b_m c_{n)}\mathrm{d}\Omega = \frac{1}{210}[2\delta_{ij}\delta_{kl}\delta_{mn}-9\delta_{(ij}I_{klmn)}+9\delta_{(ik}\delta_{lm}\delta_{nj)}], \tag{A.3}$$

where $\mathrm{d}\Omega = \sin\theta\,\mathrm{d}\varphi\,\mathrm{d}\theta\,\mathrm{d}\psi$, and φ, θ and ψ are the Euler angles.

The three-dimensional averages of the type given by (A.1)–(A.3) occur in the study of many other physical and chemical processes (Andrews and Thirunamachandran, 1977).