Ideal Strength and Intrinsic Ductility in Metals and Alloys From Second and Third Order Elastic Constants

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I. STRAIN ENERGY DENSITY: FORAMLISM AND RESULTS

A. General expressions

Consider the mapping between the reference and current configuration of a continuum solid. In the reference configuration, a particle occupies a point $\boldsymbol{p}$ with spatial coordinates $\boldsymbol{X} = X_1\boldsymbol{e}_1 + X_2\boldsymbol{e}_2 + X_3\boldsymbol{e}_3$, where e_1, e_2, e_3 is a Cartesian reference triad and X_1, X_2, X_3 are the reference coordinates. Upon deformation of the body, the point originally at $\boldsymbol{X}$ is translated by the displacement vector $\boldsymbol{u}\left(X_1, X_2, X_3\right)$ to its final coordinates $\boldsymbol{x}\left(X_1, X_2, X_3\right)$, see Eq. 1 .

$$\boldsymbol{x}\left(X_1, X_2, X_3\right) = \boldsymbol{u}\left(X_1, X_2, X_3\right) + \boldsymbol{X}\left(X_1, X_2, X_3\right) \tag{1}$$

Based on this description, a deformation gradient is formulated as in Eq. 2. The Green-Lagrange strain tensor $\boldsymbol{\eta}$ then follows from $\boldsymbol{F}$ as shown in Eq. 3, where $\boldsymbol{I}$ denotes the identity matrix.

$$\boldsymbol{F} = \frac{\partial x_i}{\partial X_j} \tag{2}$$

$$\boldsymbol{\eta} = \frac{1}{2}\left(\boldsymbol{F}^T\boldsymbol{F} - \boldsymbol{I}\right) \tag{3}$$

With the notation now established, the strain energy density E (per unit mass) can be expanded in terms of the second-order elastic constants (SOEC's), C_{ij}, third-order elastic constants (TOEC's), C_{ijk}, and the Green-Lagrange strain, $\boldsymbol{\eta}$, as in Eq. 4, where ρ_0 represents the mass density in the undeformed state and the terms η_i represent the components of the tensor defined in Eq. 3. The symmetry of the SOEC's and TOEC's will be applied in the expansions, which simplifies the resulting expressions considerably. Note that in Eq. 4, the Voigt notation $\eta_{11} \mapsto \eta_1$, $\eta_{22} \mapsto \eta_2$, $\eta_{33} \mapsto \eta_3$, $\eta_{23} \mapsto \eta_4/2$, $\eta_{13} \mapsto \eta_5/2$, $\eta_{12} \mapsto \eta_6/2$ has been applied.

$$\rho_0 E\left(\boldsymbol{\eta}\right) = \frac{1}{2!}\sum_{i,j=1}^{6} C_{ij}\eta_i\eta_j + \frac{1}{3!}\sum_{i,j,k=1}^{6} C_{ijk}\eta_i\eta_j\eta_k + \dots \tag{4}$$

In this work, strain control is assumed and the crystals are loaded uniaxially along the c-axis. All other degrees of freedom are allowed to relax to zero stress by means of Poisson contraction. The imposed strain components along c is denoted by ξ in this work and the resulting equilibrium strain along the a and b directions is $\eta_1 = \eta_2 = \bar{\eta}$. The deformation gradient $\boldsymbol{F}$ and the corresponding Green Lagrange strain tensor $\boldsymbol{E}$ that pertain to this loading situation are presented in Eqs. 5 and 6.

$$\boldsymbol{F} = \begin{bmatrix} \sqrt{2\bar{\eta}+1} & 0 & 0 \\ 0 & \sqrt{2\bar{\eta}+1} & 0 \\ 0 & 0 & \sqrt{2\xi+1} \end{bmatrix} \tag{5}$$

$$\boldsymbol{E} = \begin{bmatrix} \bar{\eta} & 0 & 0 \\ 0 & \bar{\eta} & 0 \\ 0 & 0 & \xi \end{bmatrix} \tag{6}$$

Further, we introduce the different measured of stress that are used throughout this work. First, the second Piola-Kirchoff stress tensor $\mathbf{S}$ is defined in Eq. 7 as a derivative of the strain energy density w.r.t. to Green Lagrange strains.

$$\mathbf{S}_{ij} = \rho_0 \frac{E}{\eta_{ij}} \tag{7}$$

Nanson's equation is used to convert between $\mathbf{S}$ and the Cauchy stress tensor σ according to Eq. 8, where $|\mathbf{F}|$ denotes the determinant of $\mathbf{F}$.

$$\mathbf{S} = |\mathbf{F}|\,\mathbf{F}^{-1}\sigma\mathbf{F}^{-T} \leftrightarrow \sigma = \frac{1}{|\mathbf{F}|}\mathbf{F}\mathbf{S}\mathbf{F}^{T} \tag{8}$$

For a loading direction where only σ_{33} (and S_{33}) are nonzero, and $\mathbf{F}$ given by Eq. 5, the relation between σ_{33} and S_{33} is particularly simple, see Eq. 9.

$$\sigma_{33} = \frac{\sqrt{2\xi+1}}{2\bar{\eta}+1}S_{33} \tag{9}$$

In the next sections, we derive explicit relations between strain, stress and elastic constants for cubic and hexagonal crystals under a uniaxial stress along c.

B. Cubic crystal system

We consider a cubic material that is loaded along the c-axis by a Green Lagrangian strain denoted by ξ. Initially, we allow for additional strains denoted by $\eta_1, \eta_2, \eta_4, \eta_5, \eta_6$. Consider an expansion of the strain energy density up to and including SOEC's. When the symmetry of the SOEC's is invoked, the expression in Eq. 10 is obtained.

$$\rho_0 E(\boldsymbol{\eta}) = C_{11}\frac{\eta_1^2}{2} + C_{11}\frac{\eta_2^2}{2} + C_{33}\frac{\xi^2}{2} + C_{44}\frac{\eta_4^2}{2} + C_{44}\frac{\eta_5^2}{2} + C_{44}\frac{\eta_6^2}{2} + C_{12}\eta_1\eta_2 + C_{12}\xi\eta_2 + C_{12}\eta_1\xi \tag{10}$$

Eq. 10 generally suffices for small strains. For larger strains, a higher-order expansion of the strain energy density involving TOEC's is required, as shown in Eq. 11, where the terms P_i are given in Eqs. 12.

$$\rho_0 E(\boldsymbol{\eta}) = C_{11}P_{1c} + C_{44}P_{2c} + C_{12}P_{3c} + C_{111}P_{4c} + C_{112}P_{5c} + C_{123}P_{6c} + C_{144}P_{7c} + C_{155}P_{8c} + C_{456}P_{9c} \tag{11}$$

$$P_{1c} = \frac{\eta_1^2}{2} + \frac{\eta_2^2}{2} + \frac{\xi^2}{2}, \tag{12a}$$

$$P_{2c} = \frac{\eta_4^2}{2} + \frac{\eta_5^2}{2} + \frac{\eta_6^2}{2}, \tag{12b}$$

$$P_{3c} = \eta_1\eta_2 + \eta_2\xi + \eta_1\xi, \tag{12c}$$

$$P_{4c} = \frac{1}{6}\left(\eta_1^3 + \eta_2^3 + \xi^3\right), \tag{12d}$$

$$P_{5c} = \frac{1}{2}\left(\eta_2\eta_1^2 + \xi\eta_1^2 + \eta_2^2\eta_1 + \xi^2\eta_1 + \eta_2\xi^2 + \eta_2^2\xi\right), \tag{12e}$$

$$P_{6c} = \eta_1\eta_2\xi, \tag{12f}$$

$$P_{7c} = \frac{1}{2}\left(\eta_1\eta_4^2 + \eta_2\eta_5^2 + \xi\eta_6^2\right), \tag{12g}$$

$$P_{8c} = \frac{1}{2}\left(\eta_2\eta_4^2 + \xi\eta_4^2 + \eta_1\eta_5^2 + \xi\eta_5^2 + \eta_1\eta_6^2 + \eta_2\eta_6^2\right), \tag{12h}$$

$$P_{9c} = \eta_4\eta_5\eta_6 \tag{12i}$$

In this work, we consider deformations of the type shown in Eq. 5, resulting in a strain tensor as shown in Eq. 6. This implies that $\eta_4 = \eta_5 = \eta_6 = 0$ and also $\eta_1 = \eta_2$. If we further invoke that $\eta_1 = \eta_2 = \bar{\eta}$ and $\eta_3 = \xi$, Eq. 13 is obtained.

$$\rho_0 E(\boldsymbol{\eta}) = \left(\frac{C_{111}}{3} + C_{112}\right)\bar{\eta}^3 + \left(C_{11} + C_{12} + C_{112}\xi + C_{123}\xi\right)\bar{\eta}^2 + \left(C_{112}\xi^2 + 2C_{12}\xi\right)\bar{\eta} + \frac{C_{111}\xi^3}{6} + \frac{C_{11}\xi^2}{2} \tag{13}$$

The strains $\bar{\eta}$ and ξ are clearly not independent and in fact, we can write $\bar{\eta} = \bar{\eta}(\xi)$.The value of $\bar{\eta}$ can be obtained by differentiating Eq. 13 with respect to $\bar{\eta}$ and setting the resulting expression equal to zero. The governing quadratic equation in $\bar{\eta}$ is shown in Eq. 14. The resulting expression for $\bar{\eta}$ is rather long and is not shown here.

$$3\left(\frac{C_{111}}{3}+C_{112}\right)\bar{\eta}^2+2\left(C_{11}+C_{12}+C_{112}\xi+C_{123}\xi\right)\bar{\eta}+2C_{12}\xi+C_{112}\xi^2=0\Rightarrow\bar{\eta}=\bar{\eta}\left(\xi\right) \tag{14}$$

The component S_{33} of the second Piola-Kirchoff stress tensor can be obtained from Eq. 7 (upon the insertion of $\bar{\eta}$ and ξ) and is shown in Eq. 15. All other components in $\mathbf{S}$ are zero and the same is true for σ.

$$S_{33}=\left(2C_{12}+2C_{112}\xi\right)\bar{\eta}+C_{11}\xi+\left(C_{112}+C_{123}\xi\right)\bar{\eta}^2+\frac{C_{111}\xi^2}{2} \tag{15}$$

The Cauchy stress component σ_{33} can now be obtained for every strain ξ as follows.

1. Consider an applied strain ξ
2. Compute the resulting strain (Poisson contraction) $\bar{\eta}$ from Eq. 14
3. Compute S_{33} from Eq. 15
4. Compute σ_{33} from Eq. 9

C. Hexagonal crystal system

For the hexagonal crystal system, the formalism follows a similar path as for the cubic crystal system. The various expressions are longer however, due to the lower amount of symmetry present.

Consider an imposed strain ξ along the c-axis of a hexagonal material, in addition to strains denoted by $\eta_1, \eta_2, \eta_4, \eta_5, \eta_6$. Consider first the expansion of Eq. 4, retaining only terms up to and including the SOEC's (hence, ignoring the TOEC's for now). This gives the energy expression in Eq. 16, in which the symmetry of the SOEC's has been applied.

$$\rho_0 E\left(\boldsymbol{\eta}\right)=C_{11}\frac{\eta_1^2}{2}+C_{11}\frac{\eta_2^2}{2}+C_{33}\frac{\xi^2}{2}+C_{44}\frac{\eta_4^2}{2}+C_{44}\frac{\eta_5^2}{2}+\frac{1}{2}\left(C_{11}-C_{12}\right)\frac{\eta_6^2}{2}+C_{12}\eta_1\eta_2+C_{13}\eta_1\xi+C_{13}\eta_2\xi \tag{16}$$

For large strains, the expansion in Eq. 16 is not sufficient and instead, TOEC's have to be included as well. The expansion of the strain energy up to the third order in strain is given in Eq. 17, in which the terms P are given in Eq. 18. Note that in Eq. 17, the symmetry of the SOEC's and TOEC's has been incorporated to simplify the resulting expression.

$$\begin{aligned}\rho_0 E\left(\boldsymbol{\eta}\right)=\ & C_{11}P_1+C_{12}P_2+C_{13}P_3+C_{33}P_4+C_{44}P_5+C_{111}P_6+C_{222}P_7+C_{333}P_8+\\ & C_{133}P_9+C_{113}P_{10}+C_{112}P_{11}+C_{123}P_{12}+C_{144}P_{13}+C_{155}P_{14}+C_{344}P_{15}\end{aligned} \tag{17}$$

$$P_1 = \frac{\eta_1^2}{2} + \frac{\eta_2^2}{2} + \frac{\eta_6^2}{4}, \tag{18a}$$

$$P_2 = -\frac{\eta_6^2}{4} + \eta_1\eta_2, \tag{18b}$$

$$P_3 = \eta_1\xi + \eta_2\xi, \tag{18c}$$

$$P_4 = \frac{\xi^2}{2}, \tag{18d}$$

$$P_5 = \frac{\eta_4^2}{2} + \frac{\eta_5^2}{2}, \tag{18e}$$

$$P_6 = \frac{\eta_1^3}{6} + \frac{\eta_1\eta_2^2}{2} - \frac{\eta_1\eta_6^2}{4} + \frac{\eta_2\eta_6^2}{4}, \tag{18f}$$

$$P_7 = \frac{\eta_2^3}{6} - \frac{\eta_1\eta_2^2}{2} - \frac{\eta_2\eta_6^2}{8} + 3\frac{\eta_1\eta_6^2}{8}, \tag{18g}$$

$$P_8 = \frac{\xi^3}{6}, \tag{18h}$$

$$P_9 = \frac{\eta_1\xi^2}{2} + \frac{\eta_2\xi^2}{2}, \tag{18i}$$

$$P_{10} = \frac{\xi\eta_1^2}{2} + \frac{\xi\eta_2^2}{2} + \frac{\xi\eta_6^2}{4}, \tag{18j}$$

$$P_{11} = \frac{\eta_1^2\eta_2}{2} + \frac{\eta_1\eta_2^2}{2} - \frac{\eta_6^2\eta_1}{8} - \frac{\eta_6^2\eta_2}{8}, \tag{18k}$$

$$P_{12} = \eta_1\eta_2\xi - \frac{\xi\eta_6^2}{4}, \tag{18l}$$

$$P_{13} = \frac{\eta_1\eta_4^2}{2} + \frac{\eta_2\eta_5^2}{2} - \frac{\eta_4\eta_5\eta_6}{2}, \tag{18m}$$

$$P_{14} = \frac{\eta_2\eta_4^2}{2} + \frac{\eta_1\eta_5^2}{2} + \frac{\eta_4\eta_5\eta_6}{2}, \tag{18n}$$

$$P_{15} = \frac{\xi\eta_4^2}{2} + \frac{\xi\eta_5^2}{2} \tag{18o}$$

Similar to the cubic materials, we now invoke the symmetry of the material and the specifics of the loading condition to simplify the resulting expressions that relate stress, strain and elastic constants. As a hexagonal material is loaded uniaxially along c by a strain ξ, it contracts or expands in the basal plane by an amount $\eta_1 = \eta_2 = \bar{\eta}$. In addition, no shear strain can result from this type of loading, hence $\eta_4 = \eta_5 = \eta_6 = 0$. These constraints simplify Eq. 17 considerably, to the expression shown in Eq. 19.

$$\rho_0 E(\boldsymbol{\eta}) = \left(\frac{2C_{111}}{3} + C_{112} - \frac{C_{222}}{3}\right)\bar{\eta}^3 + (C_{11} + C_{12} + C_{113}\xi + C_{123}\xi)\,\bar{\eta}^2 + \left(C_{113}\xi^2 + 2C_{23}\xi\right)\bar{\eta} + \frac{C_{333}}{6}\xi^3 + \frac{C_{33}}{2}\xi^2 \tag{19}$$

The equilibrium strain in the basal plane due to the application of ξ is obtained by a strain-energy minimization of Eq. 19 with respect to $\bar{\eta}$. This equation and the resulting solution of the type $\bar{\eta} = \bar{\eta}(\xi)$ are rather long and are not shown here.

Similar to the case of a cubic crystal, the component S_{33} of the second Piola-Kirchoff stress tensor can be obtained from Eq. 7 and is shown in Eq. 20. All other components in $\mathbf{S}$ are zero and the same is true for σ.

$$S_{33} = 2C_{23}\bar{\eta} + C_{33}\xi + (C_{113} + C_{123})\,\bar{\eta}^2 + \frac{C_{333}}{2}\xi^2 + 2C_{133}\bar{\eta}\xi \tag{20}$$

The Cauchy (true) stress component σ_{33} can now be calculated for every strain ξ from Eq. 9. The detailed procedure is summarized below.

1. Consider an applied strain ξ
2. Compute the resulting strain (Poisson contraction) $\bar{\eta}$ from Eq. 19
3. Compute S_{33} from Eq. 20
4. Compute σ_{33} from Eq. 9

II. DERIVATION OF WALLACE TENSORS

The Wallace tensor is defined in Eq. 21, where the terms C'_{ijkl} represent the elastic constants in the deformed configuration and σ_{ij} are the components of the Cauchy (true) stress tensor. Further, δ is the Kronecker delta function. The eigenvalues of the symmetrized Wallace tensor govern the mechanical stability of a solid under stress and its eigenvectors describe the type of deformation (e.g. shear or tensile deformation modes).

For the loading situations considered in this work, the Cauchy stress tensor can be written out as in Eq. 24. Note that σ_{33} can be expressed as a function of only the SOEC's, TOEC's and ξ (see Eq. 22). Similarly, C'_{ijkl} can be expressed in terms of the SOEC's, TOEC's and ξ (see Eq. 22). Hence, the formalism proposed in this work can be used to express the mechanical stability of any solid under uniaxial loading in terms of material constants and the applied strain.

$$B_{ijkl} = C'_{ijkl} + \frac{1}{2}\left(\sigma_{il}\delta_{jk} + \sigma_{jl}\delta_{ik} + \sigma_{ik}\delta_{jl} + \sigma_{jk}\delta_{il} - 2\sigma_{ij}\delta_{kl}\right) \tag{21}$$

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}\left(C_{ijkl}, C_{ijklmn}, \xi\right) \tag{22}$$

$$C'_{ijkl} = C'_{ijkl}\left(C_{ijkl}, C_{ijklmn}, \xi\right) \tag{23}$$

$$\boldsymbol{\sigma} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix} \tag{24}$$

$$\bar{B}_{ij} = \frac{1}{2}\left(B_{ij} + B_{ji}\right) \tag{25}$$

Note that the Wallace tensor as defined in Eq. 21 does not in general lead to a symmetric tensor. The stability is in fact governed by the symmetrized Wallace tensor, denoted by $\bar{B}$, and defined in Eq. 25 (in Voigt notation). The simplicity of Eq. 24 allows Eq. 21 to be written in a particularly simple form. Expressions are derived specifically for cubic and hexagonal materials. Note that the term $\frac{1}{2}\left(\sigma_{il}\delta_{jk} + \sigma_{jl}\delta_{ik} + \sigma_{ik}\delta_{jl} + \sigma_{jk}\delta_{il} - 2\sigma_{ij}\delta_{kl}\right)$ in the Wallace tensor will be identical for cubic and hexagonal materials considered in this work, and the difference comes in only in the symmetry of C'_{ijkl}. In Voigt notation, the term $\frac{1}{2}\left(\sigma_{il}\delta_{jk} + \sigma_{jl}\delta_{ik} + \sigma_{ik}\delta_{jl} + \sigma_{jk}\delta_{il} - 2\sigma_{ij}\delta_{kl}\right)$ is shown in Eq. 26.

$$\frac{1}{2}\left(\sigma_{il}\delta_{jk} + \sigma_{jl}\delta_{ik} + \sigma_{ik}\delta_{jl} + \sigma_{jk}\delta_{il} - 2\sigma_{ij}\delta_{kl}\right) = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -\sigma_{33} & -\sigma_{33} & \sigma_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{\sigma_{33}}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{\sigma_{33}}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{26}$$

A. Cubic crystal system

For cubic materials, 3 independent SOEC's exist, which are taken here to be C_{11}, C_{12} and C_{44}. Further, 6 independent TOEC's exist, chosen here as C_{111}, C_{112}, C_{123}, C_{144}, C_{155} and C_{456}. Employing Eq. 21 and subsequently symmetrizing according to Eq. 25 yields the symmetrized Wallace tensor (in Voigt notation) as shown in 27.

$$\bar{B}_{ij} = \begin{bmatrix} C'_{11} & C'_{12} & C'_{13} - \frac{\sigma_{33}}{2} & 0 & 0 & 0 \\ C'_{12} & C'_{11} & C'_{13} - \frac{\sigma_{33}}{2} & 0 & 0 & 0 \\ C'_{13} - \frac{\sigma_{33}}{2} & C'_{13} - \frac{\sigma_{33}}{2} & C'_{33} + \sigma_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C'_{44} + \frac{\sigma_{33}}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & C'_{44} + \frac{\sigma_{33}}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & C'_{66} \end{bmatrix} \tag{27}$$

B. Hexagonal crystal system

Similar to cubic materials, the Wallace tensor for hexagonal materials can be expressed in terms of the Cauchy stress component σ_{33} and the deformed elastic constants, both of which can be derived from the SOEC's, TOEC's and the applied strain ξ along the c-axis. For this crystal system, we have 5 independent SOEC's, taken to be C_{11}, C_{12}, C_{13}, C_{33} and C_{44}. Further, the 10 independent TOEC's are taken in this work to be UPDATE. Employing Eq. 21 and subsequently symmetrizing according to Eq. 25 yields the symmetrized Wallace tensor (in Voigt notation) as shown in 28.

$$\bar{B}_{ij} = \begin{bmatrix} C'_{11} & C'_{12} & C'_{13} - \frac{\sigma_{33}}{2} & 0 & 0 & 0 \\ C'_{12} & C'_{11} & C'_{13} - \frac{\sigma_{33}}{2} & 0 & 0 & 0 \\ C'_{13} - \frac{\sigma_{33}}{2} & C'_{13} - \frac{\sigma_{33}}{2} & C'_{33} + \sigma_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C'_{44} + \frac{\sigma_{33}}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & C'_{44} + \frac{\sigma_{33}}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{C'_{11} - C'_{12}}{2} \end{bmatrix} \tag{28}$$

III. DERIVATION OF DEFORMED ELASTIC CONSTANTS

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A. Cubic crystal system

B. Hexagonal crystal system

IV. DETAILS OF CALCULATING TOEC'S

A. General method

Below is an outline of the method used to calculate the third-order elastic constants.
The third-order elastic constants are defined as

$$C_{ijklmn} = \frac{1}{V_0} \frac{\partial^3 F}{\partial\eta_{ij}\partial\eta_{kl}\partial\eta_{mn}}|_{\eta=0}, \tag{29}$$

where F is the Helmholtz free energy, η_{ij}, the Green-Lagrange strain, and V_0, the volume of the primitive unit cell. Using Voigt notation this can be written as

$$C_{ijk} = \frac{1}{V_0} \frac{\partial^3 F}{\partial\eta_i\partial\eta_j\partial\eta_k}|_{\eta=0}. \tag{30}$$

If the TOEC contains Voigt symmetry, but no point symmetry other than the identity, the sixth-order elastic tensor will consist of 56 unique constants. By evaluating the second derivative of the stress components with respect to η for 21 unique strain states defined as

$$\boldsymbol{\eta}^1 = \begin{pmatrix}\eta & 0 & 0 & 0 & 0 & 0\end{pmatrix} \tag{31a}$$
$$\boldsymbol{\eta}^2 = \begin{pmatrix}0 & \eta & 0 & 0 & 0 & 0\end{pmatrix} \tag{31b}$$
$$\boldsymbol{\eta}^3 = \begin{pmatrix}0 & 0 & \eta & 0 & 0 & 0\end{pmatrix} \tag{31c}$$
$$\boldsymbol{\eta}^4 = \begin{pmatrix}0 & 0 & 0 & 2\eta & 0 & 0\end{pmatrix} \tag{31d}$$
$$\boldsymbol{\eta}^5 = \begin{pmatrix}0 & 0 & 0 & 0 & 2\eta & 0\end{pmatrix} \tag{31e}$$
$$\boldsymbol{\eta}^6 = \begin{pmatrix}0 & 0 & 0 & 0 & 0 & 2\eta\end{pmatrix} \tag{31f}$$
$$\boldsymbol{\eta}^7 = \begin{pmatrix}\eta & \eta & 0 & 0 & 0 & 0\end{pmatrix} \tag{31g}$$
$$\boldsymbol{\eta}^9 = \begin{pmatrix}\eta & 0 & \eta & 0 & 0 & 0\end{pmatrix} \tag{31h}$$
$$\boldsymbol{\eta}^{10} = \begin{pmatrix}\eta & 0 & 0 & 2\eta & 0 & 0\end{pmatrix} \tag{31i}$$
$$\boldsymbol{\eta}^{11} = \begin{pmatrix}\eta & 0 & 0 & 0 & 2\eta & 0\end{pmatrix} \tag{31j}$$
$$\boldsymbol{\eta}^{12} = \begin{pmatrix}\eta & 0 & 0 & 0 & 0 & 2\eta\end{pmatrix} \tag{31k}$$
$$\boldsymbol{\eta}^{13} = \begin{pmatrix}0 & \eta & 0 & 2\eta & 0 & 0\end{pmatrix} \tag{31l}$$
$$\boldsymbol{\eta}^{14} = \begin{pmatrix}0 & \eta & 0 & 0 & 2\eta & 0\end{pmatrix} \tag{31m}$$
$$\boldsymbol{\eta}^{15} = \begin{pmatrix}0 & \eta & 0 & 0 & 0 & 2\eta\end{pmatrix} \tag{31n}$$
$$\boldsymbol{\eta}^{16} = \begin{pmatrix}0 & 0 & \eta & 2\eta & 0 & 0\end{pmatrix} \tag{31o}$$
$$\boldsymbol{\eta}^{17} = \begin{pmatrix}0 & 0 & \eta & 0 & 2\eta & 0\end{pmatrix} \tag{31p}$$
$$\boldsymbol{\eta}^{18} = \begin{pmatrix}0 & 0 & \eta & 0 & 0 & 2\eta\end{pmatrix} \tag{31q}$$
$$\boldsymbol{\eta}^{19} = \begin{pmatrix}0 & 0 & 0 & 2\eta & 2\eta & 0\end{pmatrix} \tag{31r}$$
$$\boldsymbol{\eta}^{20} = \begin{pmatrix}0 & 0 & 0 & 2\eta & 0 & 2\eta\end{pmatrix} \tag{31s}$$
$$\boldsymbol{\eta}^{21} = \begin{pmatrix}0 & 0 & 0 & 0 & 2\eta & 2\eta\end{pmatrix} \tag{31t}$$
$$\tag{31u}$$

results in a vector, $\boldsymbol{\tau}$, containing 126 terms that consist of the 56 TOEC. Writing the TOEC as a 56×1 array, $\boldsymbol{\xi}$, the 126×56 matrix, $\boldsymbol{A}$, can be defined as

$$A_{ik} = \frac{\partial \tau_i}{\partial \xi_k} \tag{32}$$

Defining $\boldsymbol{B}$ to be the pseudoinverse of $\boldsymbol{A}$ the TOEC can be defined as

$$\xi_i = B_{ik}\tau_k \tag{33}$$

The components of $\boldsymbol{\tau}$ were evaluated numerically using the finite difference method. A 9 point central difference stencil about $\eta = 0$ was used to calculate the second derivative of the 2nd Piola-Kirchoff stress components. While the maximum strain used in the finite difference calculations is system dependent and determined from convergence testing with respect to the TOEC, a maximum strain of $\eta_{max} = 0.05$ has been shown to be appropriate for most systems studied.

In the calculation of the TOEC no considerations with regards to symmetry are given. In the case where the point group of the crystal is larger than the identity or it is desired to approximate the closest tensor of a higher symmetry (such as in the case of a solid solution), the TOEC must be symmetrized as follows

$$\hat{C}_{ijklmn} = \frac{1}{n_G}\sum_{\alpha=1}^{n_G} a_{ip}^{(\alpha)} a_{jq}^{(\alpha)} a_{kr}^{(\alpha)} a_{ls}^{(\alpha)} a_{mt}^{(\alpha)} a_{nv}^{(\alpha)} C_{pqrstu} \tag{34}$$

where n_G is the number of elements in the group, and $a_{ip}^{(\alpha)}$, the transformation matrix associated with the α^{th} element of the group. Note that Einstein summation is applied to all latin subscripts.

B. Deformation Gradients

$$\left.\begin{aligned} t_1(\eta_1) = \rho_0 \frac{\partial E}{\partial \eta_1}\Big|_{\eta_2=\eta_3=\eta_4=\eta_5=\eta_6=0} = \frac{C_{111}\eta_1^2}{2} + C_{11}\eta_1 \\ \boldsymbol{F} = \begin{bmatrix} 1+\delta & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{aligned}\right\} \tag{35}$$

$$\left.\begin{aligned} t_2(\eta_1) = \rho_0 \frac{\partial E}{\partial \eta_2}\Big|_{\eta_2=\eta_3=\eta_4=\eta_5=\eta_6=0} = \frac{C_{112}\eta_1^2}{2} + C_{12}\eta_1 \\ \boldsymbol{F} = \begin{bmatrix} 1+\delta & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{aligned}\right\} \tag{36}$$

$$\left.\begin{aligned} t_1(\eta_2,\eta_3) = \rho_0 \frac{\partial E}{\partial \eta_1}\Big|_{\substack{\eta_1=\eta_4=\eta_5=\eta_6=0 \\ \eta_2=\eta_3}} = C_{12}\eta_3 + C_{12}\eta_2 + C_{123}\eta_2\eta_3 + C_{112}\frac{\eta_2^2}{2} + C_{112}\frac{\eta_3^2}{2} \\ \boldsymbol{F} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1+\delta & 0 \\ 0 & 0 & 1+\delta \end{bmatrix} \end{aligned}\right\} \tag{37}$$

$$\left.\begin{aligned} t_4(\eta_4) = \rho_0 \frac{\partial E}{\partial \eta_4}\Big|_{\eta_1=\eta_2=\eta_3=\eta_5=\eta_6=0} = C_{44}\eta_4 \\ \boldsymbol{F} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \sqrt{1-\delta^2} & \delta \\ 0 & \delta & \sqrt{1-\delta^2} \end{bmatrix} \end{aligned}\right\} \tag{38}$$

$$\left.\begin{aligned} t_4(\eta_1,\eta_4) = \rho_0 \frac{\partial E}{\partial \eta_4}\Big|_{\substack{\eta_2=\eta_3=\eta_5=\eta_6=0 \\ \eta_1=\eta_4}} = C_{44}\eta_4 + C_{144}\eta_1\eta_4 \\ \boldsymbol{F} = \begin{bmatrix} \frac{\delta}{2} + \sqrt{\delta\sqrt{1-\delta^2} - \frac{3\delta^2}{4} + 1} & 0 & 0 \\ 0 & \sqrt{1-\delta^2} & \delta \\ 0 & \delta & \sqrt{1-\delta^2} \end{bmatrix} \end{aligned}\right\} \tag{39}$$

$$\left.\begin{aligned} t_5(\eta_1,\eta_5) = \rho_0 \frac{\partial E}{\partial \eta_5}\Big|_{\substack{\eta_2=\eta_3=\eta_4=\eta_6=0 \\ \eta_1=\eta_5}} = C_{44}\eta_5 + C_{155}\eta_1\eta_5 \\ \boldsymbol{F} = \begin{bmatrix} \frac{\delta}{2} + \sqrt{\delta\sqrt{1-\delta^2} - \frac{3\delta^2}{4} + 1} & 0 & \delta \\ 0 & 1 & 0 \\ \delta & 0 & \sqrt{1-\delta^2} \end{bmatrix} \end{aligned}\right\} \tag{40}$$

$$\left.\begin{aligned} t_4(\eta_4,\eta_5,\eta_6) = \rho_0 \frac{\partial E}{\partial \eta_4}\Big|_{\substack{\eta_1=\eta_2=\eta_3=0 \\ \eta_4=\eta_5=\eta_6}} = C_{44}\eta_4 + C_{456}\eta_5\eta_6 \\ \boldsymbol{F} = \begin{bmatrix} \sqrt{1-2\delta^2} & \delta & \delta \\ \delta & \sqrt{1-2\delta^2} & \delta \\ \delta & \delta & \sqrt{1-2\delta^2} \end{bmatrix} \end{aligned}\right\} \tag{41}$$

$$\left.\begin{aligned} t_1(\eta_1) = \rho_0 \frac{\partial E}{\partial \eta_1}\Big|_{\eta_2=\eta_3=\eta_4=\eta_5=\eta_6=0} = \frac{C_{111}\eta_1^2}{2} + C_{11}\eta_1 \\ \boldsymbol{F} = \begin{bmatrix} 1+\delta & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{aligned}\right\} \tag{42}$$

$$\left.\begin{aligned} t_2\left(\eta_2\right) = \rho_0 \frac{\partial E}{\partial \eta_2}\Big|_{\eta_1=\eta_3=\eta_4=\eta_5=\eta_6=0} = \frac{C_{222}\eta_2^2}{2} + C_{11}\eta_2 \\ \boldsymbol{F} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1+\delta & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{aligned}\right\} \tag{43}$$

$$\left.\begin{aligned} t_3\left(\eta_3\right) = \rho_0 \frac{\partial E}{\partial \eta_3}\Big|_{\eta_1=\eta_2=\eta_4=\eta_5=\eta_6=0} = \frac{C_{333}\eta_3^2}{2} + C_{33}\eta_3 \\ \boldsymbol{F} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1+\delta \end{bmatrix} \end{aligned}\right\} \tag{44}$$

$$\left.\begin{aligned} t_3\left(\eta_1\right) = \rho_0 \frac{\partial E}{\partial \eta_3}\Big|_{\eta_2=\eta_3=\eta_4=\eta_5=\eta_6=0} = \frac{C_{113}\eta_1^2}{2} + C_{13}\eta_1 \\ \boldsymbol{F} = \begin{bmatrix} 1+\delta & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{aligned}\right\} \tag{45}$$

$$\left.\begin{aligned} t_1\left(\eta_3\right) = \rho_0 \frac{\partial E}{\partial \eta_1}\Big|_{\eta_1=\eta_2=\eta_4=\eta_5=\eta_6=0} = \frac{C_{133}\eta_3^2}{2} + C_{13}\eta_3 \\ \boldsymbol{F} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1+\delta \end{bmatrix} \end{aligned}\right\} \tag{46}$$

$$\left.\begin{aligned} t_2\left(\eta_1\right) = \rho_0 \frac{\partial E}{\partial \eta_2}\Big|_{\eta_2=\eta_3=\eta_4=\eta_5=\eta_6=0} = \frac{C_{112}\eta_1^2}{2} + C_{12}\eta_1 \\ \boldsymbol{F} = \begin{bmatrix} 1+\delta & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{aligned}\right\} \tag{47}$$

$$\left.\begin{aligned} t_4\left(\eta_4\right) = \rho_0 \frac{\partial E}{\partial \eta_4}\Big|_{\eta_1=\eta_2=\eta_3=\eta_5=\eta_6=0} = C_{44}\eta_4 \\ \boldsymbol{F} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \sqrt{1-\delta^2} & \delta \\ 0 & \delta & \sqrt{1-\delta^2} \end{bmatrix} \end{aligned}\right\} \tag{48}$$

$$\left.\begin{aligned} t_3\left(\eta_3,\eta_5\right) = \rho_0 \frac{\partial E}{\partial \eta_3}\Big|_{\substack{\eta_1=\eta_2=\eta_4=\eta_6=0 \\ \eta_3=\eta_5}} = \frac{C_{333}\eta_3^2}{2} + C_{33}\eta_3 + \frac{C_{344}\eta_5^2}{2} \\ \boldsymbol{F} = \begin{bmatrix} \sqrt{1-\delta^2} & 0 & \delta \\ 0 & 1 & 0 \\ \delta & 0 & \frac{\delta}{2} + \sqrt{\delta\sqrt{1-\delta^2} - \frac{3\delta^2}{4} + 1} \end{bmatrix} \end{aligned}\right\} \tag{49}$$

$$\left.\begin{aligned} t_5\left(\eta_3,\eta_5\right) = \rho_0 \frac{\partial E}{\partial \eta_5}\Big|_{\substack{\eta_1=\eta_2=\eta_4=\eta_6=0 \\ \eta_3=\eta_5}} = C_{44}\eta_5 + C_{344}\eta_3\eta_5 \\ \boldsymbol{F} = \begin{bmatrix} \sqrt{1-\delta^2} & 0 & \delta \\ 0 & 1 & 0 \\ \delta & 0 & \frac{\delta}{2} + \sqrt{\delta\sqrt{1-\delta^2} - \frac{3\delta^2}{4} + 1} \end{bmatrix} \end{aligned}\right\} \tag{50}$$

$$\left.\begin{aligned} t_3(\eta_1,\eta_2) = \rho_0 \frac{\partial E}{\partial \eta_3}\Big|_{\substack{\eta_3=\eta_4=\eta_5=\eta_6=0\\ \eta_1=\eta_2}} = \frac{C_{113}\eta_1^2}{2} + C_{123}\eta_1\eta_2 + C_{13}\eta_1 + \frac{C_{113}\eta_2^2}{2} + C_{13}\eta_2 \\ \boldsymbol{F} = \begin{bmatrix} 1+\delta & 0 & 0 \\ 0 & 1+\delta & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{aligned}\right\} \tag{51}$$

$$\left.\begin{aligned} t_4(\eta_1,\eta_4) = \rho_0 \frac{\partial E}{\partial \eta_4}\Big|_{\substack{\eta_2=\eta_3=\eta_5=\eta_6=0\\ \eta_1=\eta_4}} = C_{44}\eta_4 + C_{144}\eta_1\eta_4 \\ \boldsymbol{F} = \begin{bmatrix} \frac{\delta}{2} + \sqrt{\delta\sqrt{1-\delta^2} - \frac{3\delta^2}{4} + 1} & 0 & 0 \\ 0 & \sqrt{1-\delta^2} & \delta \\ 0 & \delta & \sqrt{1-\delta^2} \end{bmatrix} \end{aligned}\right\} \tag{52}$$

$$\left.\begin{aligned} t_5(\eta_1,\eta_5) = \rho_0 \frac{\partial E}{\partial \eta_5}\Big|_{\substack{\eta_2=\eta_3=\eta_4=\eta_6=0\\ \eta_1=\eta_5}} = C_{44}\eta_5 + C_{155}\eta_1\eta_5 \\ \boldsymbol{F} = \begin{bmatrix} \frac{\delta}{2} + \sqrt{\delta\sqrt{1-\delta^2} - \frac{3\delta^2}{4} + 1} & 0 & \delta \\ 0 & 1 & 0 \\ \delta & 0 & \sqrt{1-\delta^2} \end{bmatrix} \end{aligned}\right\} \tag{53}$$