

## Thermodynamics at finite deformation of an anisotropic elastic solid

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(Received 20 February 1996)

This article presents various thermodynamic relations of anisotropic elastic solids subjected to finite deformation caused by arbitrary stresses. They include the conversion relations between the adiabatic and isothermal values for the effective elastic stiffness coefficients, effective elastic compliance coefficients, effective Young's modulus, and Poisson's ratio. Also expressed are the relations between the thermal-expansion coefficients at constant (Cauchy) stress and at constant thermodynamic (second Piola-Kirchhoff) stress and those between the specific heats at constant strain, at constant thermodynamic stress and at constant stress. Particular emphasis is given to the deformation of a specimen of orthotropic symmetry where the thermodynamic relations are expressed in a simple form readily applicable to engineering problems. [S0163-1829(96)08933-3]

### I. INTRODUCTION

Thermodynamics of infinitesimal deformation under thermodynamic equilibrium for an isotropic elastic solid has been extensively described in literature including many textbooks. Extension to anisotropic elastic solids including crystals was given by Voigt<sup>1</sup> and described also elsewhere.<sup>2</sup> Some useful thermodynamic relations under hydrostatic pressures for anisotropic solids were given by Overton.<sup>3</sup> Thurston<sup>4,5</sup> and Wallace<sup>6,7</sup> gave a detailed description on thermodynamics of anisotropic elastic media subjected to finite deformation with particular emphasis on solids under hydrostatic pressures. They gave good theoretical accounts for most of experimental data obtained to investigate higher-order elastic constants, anharmonic properties, and equations of state of solids, etc. However, to the author's knowledge, useful thermodynamic relations for anisotropic solids subjected to finite deformation under arbitrary stresses are wanting, which may account for subtle differences in physical quantities measured under various thermodynamic conditions.

For example, in an attempt to estimate residual stresses, engineers sometimes use acoustoelastic birefringence formulas where texture and birefringence constants are measured in a tension/compression test and they combine ultrasonic adiabatic data with isothermal static tension/compression data (see Pao, Sachse, and Fukuoka<sup>8</sup>). The effective elastic stiffness/compliance coefficients obtained under finite deformation lack in general symmetry relations found in those under infinitesimal deformation and these effective coefficients can be measured either isothermally by a static load test or adiabatically by dynamic wave propagation measurements. One may naturally ask how these quantities obtained under different thermodynamic conditions are related to each other.

Another example is a specimen under ultrahigh pressure obtained inside diamond and carbide anvils, where a pressure exceeding well above 100 GPa (1 Mbar) is achievable (see Ruoff, Xia, and Xia<sup>9</sup>) and may not be exactly hydrostatic. It may be better described as a triaxial compressive state of three principal stresses. Under such conditions various thermodynamic properties of the specimen would be changed

and one may seek to understand the relations between them.

A thermodynamic stress  $\tau_{ij}$ , which is usually referred to as second Piola-Kirchhoff stress in engineering literature, is as important a variable as an ordinary Cauchy stress  $\sigma_{ij}$ , which is defined as a force divided by an area, for description of finite deformation processes. Conversion relations between the adiabatic and isothermal elastic moduli, and those between the specific heats obtained at constant strain and at constant  $\tau_{ij}$ , are given in literature,<sup>1-7</sup> which also treat extensively thermodynamics of solids under hydrostatic pressures. One may still ask what are the relations for the thermal-expansion coefficients and the specific heats, which are, respectively, measured at constant thermodynamic stress  $\tau_{ij}$  and at constant stress  $\sigma_{ij}$  for a specimen subjected to finite deformation under arbitrary stresses. We also derive the formulas for the effective Young's modulus and Poisson's ratios for the specimen, which are significant to engineering applications, and the conversion relations between their adiabatic and isothermal values. In this paper we will address these questions in the following sections. These relations are very complicated for lower symmetry materials under arbitrary stresses. Particular emphasis is given to orthotropic or higher symmetry of homogeneous deformation, where the relations are reduced to a simplified form and still useful to many engineering applications.

### II. DESCRIPTION OF DEFORMATION STATE AND SYMBOLS

Consider a stress-free specimen, which is called to be in a natural state. The Cartesian coordinates of the particle in a natural state is denoted by vector  $\mathbf{a}$ . Under an arbitrarily acting stress the specimen undergoes a finite elastic deformation  $\mathbf{U}$  from the natural state. We call this state an initial state, the Cartesian coordinates of which is denoted by  $\mathbf{X}$ . The initial state can be any state, which can include a natural state, since  $\mathbf{U}$  is arbitrary. Finally a small deformation  $\mathbf{u}$  is superposed on the initial state. We call this state a current or present state and denote its Cartesian coordinates by  $\mathbf{x}$ . We denote the density of the natural, initial, and current states by  $\rho_a$ ,  $\rho_X$ , and  $\rho_x$ , respectively, and the stress at the correspond-

ing states by  $\sigma_{ij}(\mathbf{a})$ ,  $\sigma_{ij}(\mathbf{X})$ , and  $\sigma_{ij}(\mathbf{x})$ , respectively. The deformation  $\mathbf{u}$  is expressed as

$$\mathbf{u} = \mathbf{x} - \mathbf{X}. \quad (1)$$

The strain matrices referred to the natural and initial states are given by

$$\eta_{ij} = \frac{1}{2} \left( \frac{\partial x_m}{\partial a_i} \frac{\partial x_m}{\partial a_j} - \delta_{ij} \right), \quad (2)$$

$$\begin{aligned} \xi_{ij} &= \frac{1}{2} \left( \frac{\partial x_m}{\partial X_i} \frac{\partial x_m}{\partial X_j} - \delta_{ij} \right) = \frac{1}{2} \left( \frac{\partial u_i}{\partial X_j} + \frac{\partial u_j}{\partial X_i} + \frac{\partial u_k}{\partial X_i} \frac{\partial u_k}{\partial X_j} \right) \\ &= \varepsilon_{ij} + \frac{1}{2} \frac{\partial u_k}{\partial X_i} \frac{\partial u_k}{\partial X_j} \end{aligned} \quad (3)$$

$$\varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial X_j} + \frac{\partial u_j}{\partial X_i} \right) = (1/2)(u_{i,j} + u_{j,i}), \quad (4)$$

where  $u_{i,j} = \partial u_i / \partial X_j$  is a displacement gradient.

A thermodynamic stress  $\tau_{ij}^X$  also called the second Piola-Kirchhoff stress, with reference to the initial state, is defined as

$$\tau_{ij}^X = \rho_X \left( \frac{\partial U}{\partial \xi_{ij}} \right)_S = \rho_X \left( \frac{\partial F}{\partial \xi_{ij}} \right)_T, \quad (5)$$

where  $U$  and  $F$  are, respectively, the internal energy and the Helmholtz's free energy of the current state per unit mass,  $S$  denotes the entropy, and  $T$  the temperature. The energy equations of the current state for nondissipative thermoelastic media using  $U$ ,  $F$ , the enthalpy  $H$ , and the Gibb's free energy  $G$  per unit mass are expressed as

$$dU = T dS + (1/\rho_X) \tau_{ij}^X d\xi_{ij}, \quad (6)$$

$$dF = -S dT + (1/\rho_X) \tau_{ij}^X d\xi_{ij}, \quad (7)$$

$$dH = T dS - (1/\rho_X) \xi_{ij} d\tau_{ij}^X, \quad (8)$$

$$dG = -S dT - (1/\rho_X) \xi_{ij} d\tau_{ij}^X. \quad (9)$$

In the special case that the initial state represents the stress-free natural state, which is chosen as the reference configuration, the thermodynamic potentials are expressed by replacing  $\rho_X$ ,  $\xi_{ij}$ , and  $\tau_{ij}^X$  in Eqs. (6)–(9) by  $\rho_a$ ,  $\eta_{ij}$ , and  $\tau_{ij}^a$ , respectively. Equation (5) indicates that the thermodynamic stress depends on the choice of a coordinate system. For example,  $\tau_{ij}^X$  is related to  $\tau_{kl}^a$ , the thermodynamic stress with reference to the natural state, by

$$\tau_{ij}^X = \tau_{ij}^a \frac{\rho_X}{\rho_a} \frac{\partial X_i}{\partial a_k} \frac{\partial X_j}{\partial a_l} \tau_{kl}^a. \quad (10)$$

It was shown by Murnaghan<sup>10</sup> that the stress  $\sigma_{ij}(\mathbf{x})$  at the current state is related to the thermodynamic stresses by

$$\sigma_{ij} = \frac{\rho_X}{\rho_x} \frac{\partial x_i}{\partial X_k} \frac{\partial x_j}{\partial X_l} \tau_{kl} = \frac{\rho_X}{\rho_a} \frac{\partial x_i}{\partial a_k} \frac{\partial x_j}{\partial a_l} \tau_{kl}^a. \quad (11)$$

Using the Jacobians, the density ratios above can be written as

$$J = J^{xX} = \det \left| \frac{\partial(x_1, x_2, x_3)}{\partial(X_1, X_2, X_3)} \right| = \frac{\rho_X}{\rho_x},$$

$$J^{xa} = \det \left| \frac{\partial(x_1, x_2, x_3)}{\partial(a_1, a_2, a_3)} \right| = \frac{\rho_a}{\rho_x}. \quad (12)$$

For most cases in this article, a coordinate system chosen is with reference to the initial state. Hence, when the thermodynamic stress and Jacobian are written without superscript, as shown in Eqs. (10) and (12), it is understood that they are referring to the initial state unless otherwise specified.

Brugger<sup>11</sup> defined the adiabatic and isothermal elastic stiffness coefficients  $c$  and compliance coefficients  $s$  of the  $n$ th order for  $n \geq 2$  with reference to the natural state as

$$c_{ijkl\dots}^S = \rho_a (\partial^n U / \partial \eta_{ij} \partial \eta_{kl} \dots),$$

$$c_{ijkl\dots}^T = \rho_a (\partial^n F / \partial \eta_{ij} \partial \eta_{kl} \dots)_T,$$

$$s_{ijkl\dots}^S = -\rho_a (\partial^n H / \partial \tau_{ij}^a \partial \tau_{kl}^a \dots)_S,$$

$$s_{ijkl\dots}^T = -\rho_a (\partial^n G / \partial \tau_{ij}^a \partial \tau_{kl}^a \dots)_T. \quad (13)$$

With reference to the initial state we define the adiabatic and isothermal thermodynamic elastic stiffnesses  $C$  and compliances  $S$  of the second order as

$$C_{ijkl}^S = \rho_X (\partial^2 U / \partial \xi_{ij} \partial \xi_{kl})_S = (\partial \tau_{ij} / \partial \xi_{kl})_S,$$

$$C_{ijkl}^T = \rho_X (\partial^2 F / \partial \xi_{ij} \partial \xi_{kl})_T = (\partial \tau_{ij} / \partial \xi_{kl})_T$$

$$S_{ijkl}^S = -\rho_X (\partial^2 H / \partial \tau_{ij} \partial \tau_{kl})_S = (\partial \xi_{ij} / \partial \tau_{kl})_S,$$

$$S_{ijkl}^T = -\rho_X (\partial^2 G / \partial \tau_{ij} \partial \tau_{kl})_T = (\partial \xi_{ij} / \partial \tau_{kl})_T. \quad (14)$$

Since the initial state is arbitrary, we are interested in evaluating various thermodynamic quantities at the initial state. For this purpose  $\mathbf{u}$  is hence restricted to a small displacement and therefore the strain  $\xi_{ij}$  from the initial state becomes an infinitesimal strain  $\varepsilon_{ij}$ . We also define the effective elastic stiffnesses  $M$  and  $K$  and the effective elastic compliance  $Q$ , which all indicate the measure of *in situ* material strength, as (see Thurston<sup>12</sup>)

$$\begin{aligned} M_{ijkl}^{S \text{ or } T} &= (\partial \sigma_{ij} / \partial u_{k,l})_{S \text{ or } T; \mathbf{X}} \\ &= C_{ijkl}^{S \text{ or } T}(\mathbf{X}) - \sigma_{ij}(\mathbf{X}) \delta_{kl} + \sigma_{il}(\mathbf{X}) \delta_{jk} + \sigma_{jl}(\mathbf{X}) \delta_{ik}, \end{aligned} \quad (15)$$

$$\begin{aligned} K_{ijkl}^{S \text{ or } T} &= (\partial \sigma_{ij} / \partial \varepsilon_{kl})_{S \text{ or } T; \mathbf{X}} = (1/2)(M_{ijkl}^{S \text{ or } T} + M_{ijlk}^{S \text{ or } T}) \\ &= C_{ijkl}^{S \text{ or } T}(\mathbf{X}) - \sigma_{ij}(\mathbf{X}) \delta_{kl} + (1/2)[\sigma_{ik}(\mathbf{X}) \delta_{jl} \\ &\quad + \sigma_{il}(\mathbf{X}) \delta_{jk} + \sigma_{jk}(\mathbf{X}) \delta_{il} + \sigma_{jl}(\mathbf{X}) \delta_{ik}], \end{aligned} \quad (16)$$

$$Q_{ijkl}^{S \text{ or } T} = (\partial \varepsilon_{ij} / \partial \sigma_{kl})_{S \text{ or } T; \mathbf{X}}. \quad (17)$$

When the superscript  $S$  or  $T$  is omitted in the notations of the elastic stiffnesses and compliances defined in Eqs. (13)–(17), it is hence understood that they refer to both adiabatic and isothermal processes.

Since the strains and the (thermodynamic) stresses are symmetric, it is convenient to introduce the Voigt notation:<sup>1</sup> 11~1, 22~2, 33~3, 23~4, 13~5, 12~6. By convention we define

$$\xi_{ij} = (1/2)(1 + \delta_{ij})\xi_{\mu}, \quad \varepsilon_{ij} = (1/2)(1 + \delta_{ij})\varepsilon_{\mu},$$

$$\eta_{ij} = (1/2)(1 + \delta_{ij})\eta_{\mu}, \quad (18)$$

$$\tau_{ij} = \tau_{\mu} \quad \text{and} \quad \sigma_{ij} = \sigma_{\mu}, \quad (19)$$

where the indices  $i$  and  $j$  run from 1 to 3, and the index  $\mu$  runs from 1 to 6. With abbreviated Voigt notation, it is noted that while  $c_{\mu\nu}$  and  $s_{\mu\nu}$  in Eq. (13) and  $C_{\mu\nu}$  and  $S_{\mu\nu}$  in Eq. (14) are symmetric with respect to indices  $\mu$  and  $\nu$ ,  $K_{\mu\nu}$  in Eq. (16) and  $Q_{\mu\nu}$  in Eq. (17) are not symmetric, unless the stress acting on the specimen is hydrostatic, i.e.,  $\sigma_{ij} = s\delta_{ij}$ , where  $s$  is a positive or negative scalar variable. However, they all satisfy the reciprocal relation  $c_{\mu\nu}s_{\nu\lambda} = C_{\mu\nu}S_{\nu\lambda} = K_{\mu\nu}Q_{\nu\lambda} = \delta_{\mu\lambda}$ .

We introduce other thermodynamic variables evaluated at the initial state. The thermal pressures  $\phi$  and  $\varphi$  at constant strain  $\xi$  are, respectively, defined as

$$\phi_{ij} = -(\partial\tau_{ij}/\partial T)_{\xi, X}, \quad \phi_{\mu} = -(\partial\tau_{\mu}/\partial T)_{\xi, X}, \quad (20)$$

$$\varphi_{ij} = -(\partial\sigma_{ij}/\partial T)_{\xi, X}, \quad \varphi_{\mu} = -(\partial\sigma_{\mu}/\partial T)_{\xi, X}. \quad (21)$$

The linear thermal-expansion coefficients at constant stress  $\sigma$ , at constant hydrostatic pressure  $p$ , and at constant thermodynamic stress  $\tau$ , are expressed as

$$\alpha_{ij}^{\sigma} = (\partial\xi_{ij}/\partial T)_{\sigma, X}, \quad \alpha_{\mu}^{\sigma} = (\partial\xi_{\mu}/\partial T)_{\sigma, X},$$

$$\alpha_{ij}^p = (\partial\xi_{ij}/\partial T)_{p, X}, \quad \alpha_{\mu}^p = (\partial\xi_{\mu}/\partial T)_{p, X},$$

$$\alpha_{ij}^{\tau} = (\partial\xi_{ij}/\partial T)_{\tau, X}, \quad \alpha_{\mu}^{\tau} = (\partial\xi_{\mu}/\partial T)_{\tau, X}. \quad (22)$$

The specific heat per unit mass of the initial state evaluated at constant stress  $\sigma$ , at constant hydrostatic pressure  $p$ , at constant thermodynamic stress  $\tau$ , at constant strain  $\xi$ , and at constant (specific) volume  $V$ , are, respectively, defined as

$$C_{\sigma} = T(\partial S/\partial T)_{\sigma}, \quad C_p = T(\partial S/\partial T)_p = (\partial H/\partial T)_p,$$

$$C_{\tau} = T(\partial S/\partial T)_{\tau} = (\partial H/\partial T)_{\tau},$$

$$C_{\xi} = T(\partial S/\partial T)_{\xi} = (\partial U/\partial T)_{\xi},$$

$$C_V = T(\partial S/\partial T)_V = (\partial U/\partial T)_V. \quad (23)$$

Finally, we introduce the dimensionless thermodynamic Grüneisen parameter  $\gamma$  defined at the initial state as

$$\gamma_{ij} = -\frac{1}{T} \left( \frac{\partial T}{\partial \xi_{ij}} \right)_{S, X}, \quad \gamma_{\mu} = -\frac{1}{T} \left( \frac{\partial T}{\partial \xi_{\mu}} \right)_{S, X}. \quad (24)$$

The relations between strain  $\xi$ , the stresses  $\sigma$  and  $\tau$ , the entropy  $S$ , and the temperature  $T$  are schematically shown in Figs. 1(a) and 1(b), which are similar to Figs. (10.2a) and (10.2b) in the book of Nye.<sup>2</sup> Useful mathematical methods in thermodynamics are described in the book of Margenau and Murphy.<sup>13</sup> It is worth mentioning that because the initial state can represent the natural state, various thermodynamic

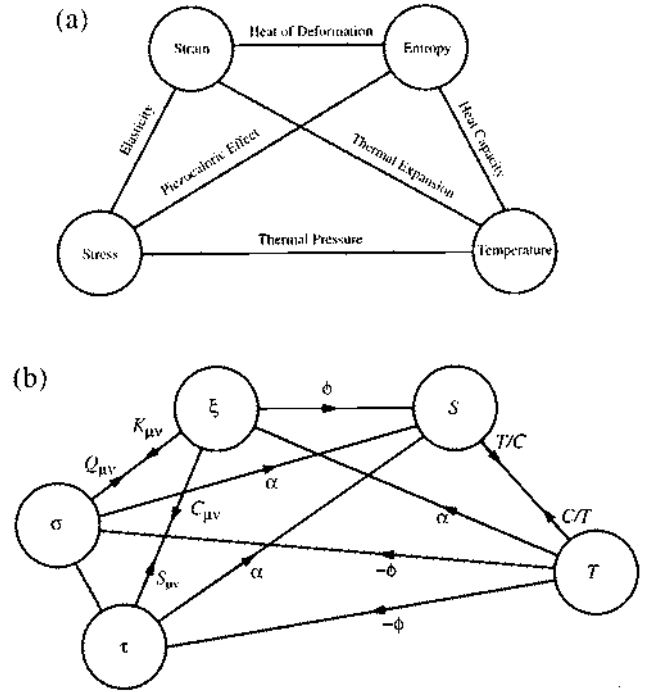


FIG. 1. Schematic diagram showing the relations between various thermodynamic variables. (a) The names of the properties and the variables. (b) The corresponding symbols.

relations developed with respect to the natural state, such as those found in the papers of Thurston<sup>4,5</sup> and Wallace,<sup>6,7</sup> hold valid, when the thermodynamic variables  $\tau_{ij}^a$ ,  $\eta_{ij}$ ,  $\rho_a$ ,  $\alpha$ ,  $C$  (specific heat), and the second-order  $c_{\mu\nu}$  and  $s_{\mu\nu}$  in Eq. (13), which are all referred to the natural state, are, respectively, replaced by  $\tau_{ij}^X$ ,  $\xi_{ij}$ ,  $\rho_X$ ,  $\alpha$ ,  $C$ , and  $C_{\mu\nu}$  and  $S_{\mu\nu}$  in Eq. (14), which are now all referred to the initial state.

It is noted that while the effective elastic coefficients  $K$  and  $Q$  defined in Eqs. (16) and (17) are easily measurable quantities, the thermodynamic elastic coefficients  $C$  and  $S$  appearing in Eq. (14) are difficult to measure. The thermal-expansion coefficient and specific heat can be measured at constant stress and are difficult to measure at other constant thermodynamic quantities. It is mentioned that at the natural state the distinctions between  $C$ ,  $K$ , and the second-order  $c$ , between  $S$ ,  $Q$ , and the second-order  $s$ , between  $\phi$  and  $\varphi$ , between  $\alpha^{\sigma}$  and  $\alpha^{\tau}$ , and between  $C_{\sigma}$  and  $C_{\tau}$ , vanish.

### III. THERMAL-EXPANSION COEFFICIENT

#### A. Relation between $\alpha^{\sigma}$ and $\alpha^{\tau}$

Thermal-expansion coefficient can be evaluated either at constant stress or at constant thermodynamic stress. To find the difference, we take  $\xi_{ij}$  and  $\tau_{kl}$  as dependent variables and  $\sigma_{rs}$  and  $T$  as independent variables by considering the form  $\xi_{ij} = \xi_{ij}[\tau_{kl}(\sigma_{rs}, T), T]$ , the derivative of which with respect to  $T$  is

$$\left( \frac{\partial \xi_{ij}}{\partial T} \right)_{\sigma} = \left( \frac{\partial \xi_{ij}}{\partial T} \right)_{\tau} + \left( \frac{\partial \xi_{ij}}{\partial \tau_{kl}} \right)_{T} \left( \frac{\partial \tau_{kl}}{\partial T} \right)_{\sigma}. \quad (25)$$

For simplicity of notation we introduce

$$x_{i,j} = \partial x_i / \partial X_j, \quad u_{i,j} = \partial u_i / \partial X_j,$$

$$x_{i,j}^{\sigma'} = (\partial x_{i,j} / \partial T)_{\sigma} = (\partial u_{i,j} / \partial T)_{\sigma} = u_{i,j}^{\sigma'}, \quad (26)$$

where the prime denotes the differentiation with respect to temperature and superscript  $\sigma$  indicates an evaluation at constant stress. Considering the  $x_{i,j}$  as the  $ij$ th element of the matrix  $(x_{i,j})$ , its inverse element is found to be

$$\frac{\partial x_i}{\partial X_j} \frac{\partial X_j}{\partial x_k} = \delta_{ik}, \quad x_{j,k}^{-1} = \partial X_j / \partial x_k; \quad (27)$$

$$\begin{aligned} \left( \frac{\partial \tau_{kl}}{\partial T} \right)_{\sigma} &= \left[ \frac{1}{\partial T} \left( J \sigma_{rs} \frac{\partial X_k}{\partial x_r} \frac{\partial X_l}{\partial x_s} \right) \right]_{\sigma} = \sigma_{rs} \left[ \frac{\partial X_k}{\partial x_r} \frac{\partial X_l}{\partial x_s} \left( \frac{\partial J}{\partial T} \right)_{\sigma} \right. \\ &\quad \left. + J \frac{\partial}{\partial T} \left( \frac{\partial X_k}{\partial x_r} \frac{\partial X_l}{\partial x_s} \right) \right]_{\sigma}. \end{aligned} \quad (28)$$

Substituting the volumetric thermal-expansion coefficient  $\beta^{\sigma} = (\partial J / \partial T)_{\sigma} / J$  at constant stress and using the notations in Eqs. (26) and (27), Eq. (28) is expressed as

$$\begin{aligned} (\partial \tau_{kl} / \partial T)_{\sigma} &= J \sigma_{rs} [\beta^{\sigma} x_{k,r}^{-1} x_{l,s}^{-1} - (x_{k,p}^{-1} x_{p,q}^{\sigma'} x_{q,r}^{-1} x_{l,s}^{-1} \\ &\quad + x_{l,p}^{-1} x_{p,q}^{\sigma'} x_{q,s}^{-1} x_{k,r}^{-1})]. \end{aligned} \quad (29)$$

At the initial state  $J=1$  and  $x_{i,j} = x_{i,j}^{-1} = \delta_{ij}$ , and therefore Eq. (28) becomes at the initial state

$$(\partial \tau_{kl} / \partial T)_{\sigma} = \beta^{\sigma} \sigma_{kl} - \sigma_{rs} (u_{k,r}^{\sigma'} \delta_{ls} + u_{l,s}^{\sigma'} \delta_{kr}). \quad (30)$$

The evaluation of Eq. (25) at the initial state yields

$$\alpha_{ij}^{\sigma} = \alpha_{ij}^{\tau} + S_{ijkl}^T [\beta^{\sigma} \sigma_{kl} - \sigma_{rs} (u_{k,r}^{\sigma'} \delta_{ls} + u_{l,s}^{\sigma'} \delta_{kr})]. \quad (31)$$

We restrict ourselves to an orthotropic or higher symmetry where a loading direction coincides with the direction of the principal axes. Then,  $\sigma_{rs} = \sigma_r \delta_{rs}$  and  $u_{k,r}^{\sigma'} = u_{k,r}^{\sigma'} \delta_{kr} = \alpha_{kk}^{\sigma}$  ( $k$  not summed). Using the Voigt's notation for  $\alpha$  and  $S$ , Eq. (31) reduces to

$$\alpha_{ij}^{\sigma} = \alpha_{ij}^{\tau} + S_{ijkl}^T \sigma_k (\beta^{\sigma} - 2\alpha_{kk}^{\sigma}), \quad ij = 11, 22, 33; \quad k = 1, 2, 3,$$

$$\begin{aligned} \alpha_{\mu}^{\sigma} &= \alpha_{\mu}^{\tau} + S_{\mu 1}^T \sigma_1 (\beta^{\sigma} - 2\alpha_1^{\sigma}) + S_{\mu 2}^T \sigma_2 (\beta^{\sigma} - 2\alpha_2^{\sigma}) \\ &\quad + S_{\mu 3}^T \sigma_3 (\beta^{\sigma} - 2\alpha_3^{\sigma}), \quad \mu = 1, 2, 3, \end{aligned} \quad (32)$$

where  $\beta^{\sigma} = \alpha_1^{\sigma} + \alpha_2^{\sigma} + \alpha_3^{\sigma}$ .

In a special case where the stress acting on an orthotropic specimen is hydrostatic, i.e.,  $\sigma_{rs} = -p \delta_{rs}$ , Eq. (32) becomes

$$\begin{aligned} \alpha_{\mu}^p &= \alpha_{\mu}^{\tau} - p [S_{\mu 1}^T (\beta^p - 2\alpha_1^p) + S_{\mu 2}^T (\beta^p - 2\alpha_2^p) \\ &\quad + S_{\mu 3}^T (\beta^p - 2\alpha_3^p)], \quad \mu = 1, 2, 3, \end{aligned} \quad (33)$$

where the superscript  $p$  means an evaluation at constant hydrostatic pressure. For a specimen of cubic symmetry under hydrostatic pressures,  $\alpha_1 = \alpha_2 = \alpha_3 = \alpha$ ,  $\beta = 3\alpha$ , and there are

only three nonzero elastic compliances (or stiffnesses). Equation (33) for a cubic symmetry yields

$$\alpha_{\mu}^p = \alpha_{\mu}^{\tau} - p \alpha^p (S_{11}^T + 2S_{12}^T) = \alpha_{\mu}^{\tau} - p \alpha^p / (C_{11}^T + 2C_{12}^T),$$

$$\alpha^{\tau} = \alpha^p [1 + p / (C_{11}^T + 2C_{12}^T)]. \quad (34)$$

The difference between  $\alpha^{\sigma}$  and  $\alpha^{\tau}$  can be expressed in terms of the effective elastic compliance defined in Eq. (17). Writing  $\xi_{ij} = \xi_{ij}[\sigma_{kl}(\tau_{rs}, T), T]$  and proceeding in a similar way as above, one obtains at the initial state

$$(\partial \sigma_{kl} / \partial T)_{\tau} = -\beta^{\tau} \sigma_{kl} + \sigma_{rs} (u_{k,r}^{\tau'} \delta_{ls} + u_{l,s}^{\tau'} \delta_{kr}), \quad (35)$$

$$\alpha_{ij}^{\tau} = \alpha_{ij}^{\sigma} + Q_{ijkl}^T [-\beta^{\sigma} \sigma_{kl} + \sigma_{rs} (u_{k,r}^{\tau'} \delta_{ls} + u_{l,s}^{\tau'} \delta_{kr})]. \quad (36)$$

For a specimen of orthotropic or higher symmetry loaded in the principal-axis direction, Eq. (36) reduces to

$$\alpha_{ij}^{\tau} = \alpha_{ij}^{\sigma} - Q_{ijkk}^T \sigma_k (\beta^{\tau} - 2\alpha_{kk}^{\tau}), \quad ij = 11, 22, 33; \quad k = 1, 2, 3,$$

$$\begin{aligned} \alpha_{\mu}^{\tau} &= \alpha_{\mu}^{\sigma} - Q_{\mu 1}^T \sigma_1 (\beta^{\tau} - 2\alpha_1^{\tau}) - Q_{\mu 2}^T \sigma_2 (\beta^{\tau} - 2\alpha_2^{\tau}) \\ &\quad - Q_{\mu 3}^T \sigma_3 (\beta^{\tau} - 2\alpha_3^{\tau}), \quad \mu = 1, 2, 3. \end{aligned} \quad (37)$$

In a special case that the stress acting on the orthotropic specimen is hydrostatic, i.e.,  $\sigma_{rs} = -p \delta_{rs}$ , Eq. (37) yields

$$\begin{aligned} \alpha_{\mu}^{\tau} &= \alpha_{\mu}^p + p [Q_{\mu 1}^T (\beta^{\tau} - 2\alpha_1^{\tau}) + Q_{\mu 2}^T (\beta^{\tau} - 2\alpha_2^{\tau}) \\ &\quad + Q_{\mu 3}^T (\beta^{\tau} - 2\alpha_3^{\tau})], \quad \mu = 1, 2, 3 \end{aligned} \quad (38)$$

$$\beta^p = \beta^{\tau} (1 - p/B^T) + 2p Q_{iikk}^T \alpha_{kk}^{\tau}, \quad (39)$$

where the use of the isothermal compressibility  $\chi^T = 1/B^T = Q_{iikk}^T$  is made for derivation of Eq. (39). Further, it is readily shown from Eqs. (32), (37), and (38) that for cubic symmetry

$$\frac{\beta^{\tau}}{\beta^p} = \frac{\alpha^{\tau}}{\alpha^p} = \frac{S_{iikk}^T}{Q_{iikk}^T} = \frac{K_{iikk}^T}{C_{iikk}^T} = B^T S_{iikk}^T, \quad (40)$$

$$\alpha_{\mu}^{\tau} = \alpha_{\mu}^p + p \alpha^{\tau} (Q_{11}^T + 2Q_{12}^T) = \alpha_{\mu}^p + p \alpha^{\tau} / (K_{11}^T + 2K_{12}^T),$$

$$\alpha^p = \alpha^{\tau} (1 - p/3B^T), \quad (41)$$

where  $B^T = (K_{11}^T + 2K_{12}^T)/3$  is known as the isothermal bulk modulus of a cubic specimen at an arbitrary hydrostatic pressure level.

## B. Dependence of thermal-expansion coefficient on stress

The dependence of the thermal-expansion coefficient on stress is significant and its behavior may even exhibit a small degree of nonlinearity with stress for some materials. However, we assume that its variation with stress is linear in the range of the stresses below an elastic limit, which falls below 1 GPa for most engineering materials. The stress derivative at the initial stress is the same as that at the natural state where the distinction between the thermodynamic stress and real stress vanish. In the following Eqs. (42)–(44),  $\mathbf{X}$  and  $\mathbf{a}$

mean evaluation at the initial and natural states, respectively. The thermal-expansion coefficient at the initial state can be approximated by

$$\alpha_{ij}^{\sigma \text{ or } \tau}(\mathbf{X}) = \alpha_{ij}^{\sigma \text{ or } \tau}(\mathbf{a}) + \left( \frac{\partial \alpha_{ij}^{\sigma \text{ or } \tau}}{\partial \sigma_{kl}} \right)_{T;\mathbf{a}} \sigma_{kl}(\mathbf{X}). \quad (42)$$

It is easy to show that

$$\begin{aligned} \left( \frac{\partial \alpha_{ij}^{\sigma}}{\partial \sigma_{kl}} \right)_{T;\mathbf{X}} &= \left( \frac{\partial \alpha_{ij}^{\sigma}}{\partial \sigma_{kl}} \right)_{T;\mathbf{a}} = \left[ \frac{\partial}{\partial \sigma_{kl}} \left( \frac{\partial \varepsilon_{ij}}{\partial T} \right)_{\sigma=0} \right]_T \\ &= \left[ \frac{\partial}{\partial T} \left( \frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}} \right) \right]_{T;\sigma=0} = \left( \frac{\partial Q_{ijkl}^T}{\partial T} \right)_{\sigma=0}. \end{aligned} \quad (43)$$

Using the temperature variations of  $Q_{ijkl}^T$  data tabulated by Simmons and Wang<sup>14</sup> at the natural state,  $[(1/\alpha^\sigma)(\partial \alpha^\sigma / \partial \sigma_\mu)]_{T;\mathbf{a}}$  ( $\mu=1,2,3$ ) is calculated to be 0.43/GPa and 0.36/GPa for aluminum and copper, respectively.

It can be readily shown from Eq. (32) or (37) that for the orthotropic specimen loaded along the principal-axis direction

$$\begin{aligned} \left( \frac{\partial \alpha_\mu^\tau}{\partial \sigma_\nu} \right)_{T;\mathbf{a}} &= \left( \frac{\partial Q_{\mu\nu}^T}{\partial T} \right)_{\sigma=0} - [Q_{\mu\nu}^T(\beta^\sigma - 2\alpha_\nu^\sigma)]_{\sigma=0} \\ &(\nu \text{ not summed}; \mu, \nu = 1, 2, 3), \end{aligned} \quad (44)$$

where the use of  $\beta^\tau = \beta^\sigma$  and  $\alpha^\tau = \alpha^\sigma$  is made at the natural state. The values of  $Q_{ijkl}$  and its temperature variations are tabulated by Simmons and Wang<sup>14</sup> and Hearmon.<sup>15</sup>

#### IV. THERMAL PRESSURE AND GRÜNEISEN PARAMETER

The thermal pressures  $\phi$  and  $\varphi$  defined by Eqs. (20) and (21) are equal to each other, since

$$\begin{aligned} \varphi_{ij} &= - \left( \frac{\partial \sigma_{ij}}{\partial T} \right)_{\xi;\mathbf{X}} = - \left( \frac{\partial \sigma_{ij}}{\partial \tau_{kl}} \right)_{\xi;\mathbf{X}} \left( \frac{\partial \tau_{kl}}{\partial T} \right)_{\xi;\mathbf{X}} \\ &= - \left( \frac{x_{i,k} x_{j,l}}{J} \right)_{\mathbf{X}} \left( \frac{\partial \tau_{kl}}{\partial T} \right)_{\xi;\mathbf{X}} = - \left( \frac{\partial \tau_{ij}}{\partial T} \right)_{\xi;\mathbf{X}} = \phi_{ij}. \end{aligned} \quad (45)$$

The use of the Maxwell's relations and the definitions of Eq. (14) yields

$$\begin{aligned} \phi_\mu &= \varphi_\mu = - \left( \frac{\partial \tau_\mu}{\partial T} \right)_{\xi;\mathbf{X}} = \rho_X \left( \frac{\partial S}{\partial \xi_\mu} \right)_{T;\mathbf{X}} \\ &= \rho_X \left( \frac{\partial S}{\partial \tau_\lambda} \right)_{T;\mathbf{X}} \left( \frac{\partial \tau_\lambda}{\partial \xi_\mu} \right)_{T;\mathbf{X}} = \alpha_\lambda^\tau C_{\lambda\mu}^T, \\ \alpha_\lambda^\tau &= \varphi_\mu S_{\mu\lambda}^T. \end{aligned} \quad (46)$$

Using the Maxwell's relation and Eq. (46), the thermodynamic Grüneisen parameter  $\gamma_{ij}$  defined in Eq. (24) is expressed as

$$\gamma_{ij} \equiv - \frac{1}{T} \left( \frac{\partial T}{\partial \xi_{ij}} \right)_{S;\mathbf{X}} = - \frac{1}{\rho_X T} \left( \frac{\partial \tau_{ij}}{\partial S} \right)_{T;\mathbf{X}} = \frac{\phi_{ij}}{\rho_X C_\xi} = \frac{C_{ijkl}^T \alpha_{kl}^\tau}{\rho_X C_\xi}, \quad (47)$$

which yields the thermal-expansion coefficients at constant  $\tau$ :

$$\alpha_{ij}^\tau = \rho_X C_\xi S_{ijkl}^T \gamma_{kl}, \quad \beta^\tau = \alpha_{ii}^\tau = \rho_X C_\xi S_{iikk}^T \gamma_{kl}. \quad (48)$$

For orthotropic or higher symmetry,  $\gamma_{ij} = \gamma_{ij} \delta_{ij} = \gamma_{ii}$  ( $i$  not summed;  $i=1,2,3$ ). For cubic and isotropic materials under arbitrary hydrostatic pressures,  $\gamma = \gamma_{11} = \gamma_{22} = \gamma_{33}$  and it is easy to show from Eqs. (40), (47), and (48) that

$$\gamma = \frac{\beta^\tau C_{iikk}^T}{9 \rho_X C_\xi} = \frac{\beta^\tau (S_{iikk}^T)^{-1}}{\rho_X C_\xi} = \frac{\beta^p B^T}{\rho_X C_\xi} = \frac{\beta^p B^T}{\rho_X C_V} = \frac{\beta^p B^S}{\rho_X C_p}, \quad (49)$$

where  $C_\xi = C_V$  [refer to Eq. (60)] and  $B^S/B^T = C_p/C_V$  are utilized. The last two parts of Eq. (49) are familiar relations in the field of equation of state of solids.  $\gamma$  is shown to be approximately independent of temperature except at low temperatures for many cubic solids (see Wallace<sup>7</sup>).

#### V. SPECIFIC HEAT

The difference between the specific heats at constant thermodynamic stress  $C_\tau$  and constant strain  $C_\xi$  is given by many authors<sup>1,2,4-7</sup> and the difference between the specific heats at constant hydrostatic pressure  $C_p$  and at constant volume  $C_V$  has been treated in literature.<sup>1,2-7</sup>  $C_\tau$  is related to  $C_\xi$  by

$$C_\tau = C_\xi + T \alpha_\mu^\tau \alpha_\nu^\tau C_{\mu\nu}^T / \rho_X = C_\xi + T \alpha_\nu^\tau \phi_\nu / \rho_X, \quad (50)$$

where subscript indices  $\mu$  and  $\nu$  are the abbreviated Voigt notations and  $\phi_\nu = \alpha_\mu^\tau C_{\mu\nu}^T$  is the thermal pressure given in Eq. (46). The ratio  $C_r = C_\tau / C_\xi$  is given by

$$C_r = \frac{C_\tau}{C_\xi} = 1 + \frac{T \alpha_\mu^\tau \alpha_\nu^\tau C_{\mu\nu}^S}{\rho_X C_\tau} = \frac{\alpha_\mu^\tau C_{\mu\nu}^S}{\alpha_\mu^\tau C_{\mu\nu}^T}. \quad (51)$$

To find the relation between  $C_\tau$  and  $C_\sigma$ , we choose  $\sigma_{rs}$  and  $T$  as independent variables and  $S$  and  $\tau_{kl}$  as dependent variables by considering the form  $S = S[\tau_{kl}(\sigma_{rs}, T), T]$ , which on differentiation with respect to  $T$  yields

$$\left( \frac{\partial S}{\partial T} \right)_\sigma = \left( \frac{\partial S}{\partial T} \right)_\tau + \left( \frac{\partial S}{\partial \tau_{kl}} \right)_T \left( \frac{\partial \tau_{kl}}{\partial T} \right)_\sigma. \quad (52)$$

Multiplying Eq. (52) by  $T$ , and using Eqs. (23) and (30) and the Maxwell's relation

$$(\partial S / \partial \tau_{kl})_T = (\partial \xi_{kl} / \partial T)_\tau / \rho_X = \alpha_{kl}^\tau / \rho_X, \quad (53)$$

one obtains at the initial state

$$C_\sigma = C_\tau + (T \alpha_{kl}^\tau / \rho_X) [\beta^\sigma \sigma_{kl} - \sigma_{rs} (u_{k,r}^{\sigma'} \delta_{ls} + u_{l,s}^{\sigma'} \delta_{kr})]. \quad (54)$$

For an orthotropic specimen loaded along the principal axis,  $\alpha_{kl}^\tau = \alpha_k^\tau \delta_{kl}$  and  $\sigma_{rs} = \sigma_r \delta_{rs}$ , and therefore

$$C_\sigma = C_\tau + T \alpha_k^\tau \sigma_k (\beta^\sigma - 2\alpha_k^\sigma) / \rho_X. \quad (55)$$

Equation (55), for the case of hydrostatic pressure  $\sigma_{rs} = -p \delta_{rs}$ , becomes

$$C_p = C_\tau - Tp(\beta^\tau \beta^p - 2\alpha_k^\tau \alpha_k^p) / \rho_X, \quad (56)$$

which in the case of cubic and isotropic symmetries reduces to

$$C_\sigma = C_\tau - 3Tp\alpha^\tau \alpha^p / \rho_X. \quad (57)$$

From the books of thermodynamics (see also Refs. 1, 2, and 4–7),  $C_p - C_V$  is given by

$$C_p - C_V = T(\beta^p)^2 B^T / \rho_X. \quad (58)$$

From Eqs. (50), (56), (58), and (39), one can derive

$$\begin{aligned} C_V - C_\xi &= T[\alpha_\mu^\tau \alpha_\nu^\tau C_{\mu\nu}^T - (\beta^p)^2 B^T + p(2\alpha_k^\tau \alpha_k^p - \beta^\tau \beta^p)] / \rho_X \\ &= (T/\rho_X)[\alpha_\mu^\tau \alpha_\nu^\tau C_{\mu\nu}^T - B^T \beta^p \beta^\tau \\ &\quad + 2B^T Q_{iiij}^T \alpha_{kk}^p (\alpha_{kk}^\tau - \alpha_{jj}^\tau) p]. \end{aligned} \quad (59)$$

For materials of orthotropic or higher symmetry, there are three or less Grüneisen parameters  $\gamma_{ij}$  and the substitution of Eq. (48) into Eq. (59) yields

$$\begin{aligned} (C_V - C_\xi) / C_\xi &= B^T T [Q_{kkll}^T \alpha_{ii}^\tau \gamma_{ii} - S_{iikk}^T \alpha_{jj}^p \gamma_{kk} \\ &\quad + 2Q_{iiij}^T \alpha_{kk}^p (\alpha_{kk}^\tau - \alpha_{jj}^\tau) p / (\rho_X C_\xi)]. \end{aligned} \quad (60)$$

Neither Eq. (59) nor (60) vanishes in general. However, recalling Eqs. (40) and (49), it is readily shown that both Eqs. (59) and (60) vanish for cubic and isotropic materials. At the natural state ( $p=0$ ) for which  $Q_{ijkl}^T = S_{ijkl}^T = s_{ijkl}^T$ , Eq. (60) becomes identical with Eq. (A1.11) derived for materials of orthorhombic or higher symmetry by Barron and Munn,<sup>16</sup> who showed that Eq. (60) is less than 1% for many noncubic solids at zero pressure.

Variations of the specific heat with stress or strain are extremely small as evident in the experiments of Loriers-Susse, Bastide, and Bäckström<sup>17</sup> and Bastide and Loriers-Susse.<sup>18</sup> Its dependence on stress can be considered as linear and written as

$$C_\sigma = C_\sigma(\mathbf{a}) + \left( \frac{\partial C_\sigma}{\partial \sigma_{ij}} \right)_{T;\mathbf{a}} \sigma_{ij} = C_\sigma(\mathbf{a}) + \frac{T}{\rho_a} \left( \frac{\partial \alpha_{ij}^\sigma}{\partial T} \right)_{\sigma;\mathbf{a}} \sigma_{ij}. \quad (61)$$

The specific heat at the natural state and variations of the thermal-expansion coefficient with temperature are found in the data compiled by Touloukian.<sup>19</sup>

Note that comparison of Eq. (50) with Eq. (55) indicates that the difference between  $C_\tau$  and  $C_\xi$  is generally an order of a few percents of either value, while the difference between  $C_\sigma$  and  $C_\tau$  is much smaller in the stress range below the elastic limit, which is generally an order of a few percents of the thermodynamic stiffness coefficients  $C_{\mu\nu}^T$ . The difference  $C_\sigma - C_\tau$  may be safely ignored in most cases.

## VI. EFFECTIVE ELASTIC STIFFNESS/COMPLIANCE COEFFICIENTS

Equations (32), (46)–(48), and (50) are expressed in terms of the thermodynamic elastic coefficients  $S$  or  $C$ , which are difficult to measure but can be evaluated by using the relations between the thermodynamic elastic coefficients and the effective elastic coefficients  $Q_{\mu\nu}$  and  $K_{\mu\nu}$ , which can be easily measured. In this section we derive these relations. We also discuss the conversion relationships between the adiabatic and isothermal effective elastic coefficients:  $Q_{\mu\nu}^S$  and  $Q_{\mu\nu}^T$ ;  $K_{\mu\nu}^S$  and  $K_{\mu\nu}^T$ .  $K_{\mu\nu}^S$  can be obtained from the wave speed measurements of ultrasonic waves propagating in various directions of an elastic medium.  $Q_{\mu\nu}^S$  is then obtained by inverting the  $K_{\mu\nu}^S$  matrix.

The differences between  $C_{\alpha\beta}^S$  and  $C_{\alpha\beta}^T$  and between  $S_{\mu\nu}^S$  and  $S_{\mu\nu}^T$  are expressed as<sup>1,4–7</sup>

$$C_{\alpha\beta}^S = C_{\alpha\beta}^T + \frac{T\phi_\alpha \phi_\beta}{\rho_X C_\xi} = C_{\alpha\beta}^T + \frac{T\alpha_\mu^\tau \alpha_\nu^\tau C_{\mu\alpha}^T C_{\nu\beta}^T}{\rho_X C_\xi}, \quad (62)$$

$$S_{\mu\nu}^S = S_{\mu\nu}^T - \frac{T\alpha_\mu^\tau \alpha_\nu^\tau}{\rho_X C_\tau}. \quad (63)$$

To find the difference  $Q_{\mu\nu}^S - Q_{\mu\nu}^T$ , we consider  $\varepsilon_{mn}$  and  $S$  as independent variables and  $\sigma_{kl}$  and  $T$  as dependent variables:

$$\begin{aligned} d\varepsilon_{mn} &= \left( \frac{\partial \varepsilon_{mn}}{\partial \sigma_{kl}} \right)_T d\sigma_{kl} + \left( \frac{\partial \varepsilon_{mn}}{\partial T} \right)_\sigma dT, \\ dS &= \left( \frac{\partial S}{\partial \sigma_{kl}} \right)_T d\sigma_{kl} + \left( \frac{\partial S}{\partial T} \right)_\sigma dT. \end{aligned} \quad (64)$$

Under adiabatic condition  $dS=0$ , Eq. (64) can be written as

$$d\varepsilon_{mn} = \left( \frac{\partial \varepsilon_{mn}}{\partial \sigma_{kl}} \right)_T (d\sigma_{kl})_S - \frac{(\partial \varepsilon_{mn} / \partial T)_\sigma (\partial S / \partial \sigma_{kl})_T}{(\partial S / \partial T)_\sigma} (d\sigma_{kl})_S,$$

which on division by  $(d\sigma_{kl})_S$  yields at the initial state

$$\begin{aligned} Q_{mnl}^S &= Q_{mnl}^T - \frac{T\alpha_{mn}^\sigma}{C_\sigma} \left( \frac{\partial S}{\partial \sigma_{kl}} \right)_T \\ &= Q_{mnl}^T - \frac{T\alpha_{mn}^\sigma}{C_\sigma} \left( \frac{\partial S}{\partial \varepsilon_{ij}} \right)_T \left( \frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}} \right)_T \\ &= Q_{mnl}^T - \frac{T\alpha_{mn}^\sigma}{\rho_X C_\sigma} \alpha_{rs}^\tau C_{rsij}^T Q_{ijkl}^T, \end{aligned} \quad (65)$$

where the Maxwell's relation

$$\begin{aligned} \rho_X (\partial S / \partial \varepsilon_{ij})_{T;\mathbf{X}} &= \rho_X (\partial S / \partial \xi_{ij})_{T;\mathbf{X}} = -(\partial \tau_{ij} / \partial T)_{\xi;\mathbf{X}} = \phi_{ij} \\ &= \alpha_{rs}^\tau C_{rsij}^T \end{aligned} \quad (66)$$

is used for derivation. Using Eq. (16) and  $K_{rsij} Q_{ijkl} = (\delta_{rk} \delta_{sl} + \delta_{rl} \delta_{sk}) / 2$ , Eq. (65) is written as

$$Q_{mnkl}^S = Q_{mnkl}^T - \frac{T\alpha_{mn}^\sigma}{\rho_X C_\sigma} [\alpha_{kl}^\tau + \alpha_{rs}^\tau \sigma_{rs} Q_{iikl}^T - \alpha_{rs}^\tau (Q_{iskl}^T \sigma_{ri} + Q_{sjkl}^T \sigma_{rj} + Q_{irkl}^T \sigma_{si} + Q_{rjkl}^T \sigma_{sj})/2], \quad (67)$$

For an orthotropic specimen loaded along the principal-axis direction,  $\alpha_{rs}^\tau = \alpha_r^\tau \delta_{rs}$  and  $\sigma_{ij} = \sigma_i \delta_{ij}$ , therefore Eq. (67) is simplified to

$$Q_{mnkl}^S = Q_{mnkl}^T - \frac{T\alpha_{mn}^\sigma}{\rho_X C_\sigma} [\alpha_{kl}^\tau + \alpha_r^\tau \sigma_r (Q_{iikl}^T - 2Q_{rrkl}^T)], \quad (68)$$

which is expressed with the abbreviated Voigt's notation as

$$Q_{\mu\nu}^S = Q_{\mu\nu}^T - \frac{T\alpha_\mu^\sigma \alpha_\nu^\tau}{\rho_X C_\sigma} (1 + r_t), \quad (69)$$

where

$$r_t = (\alpha_1^\tau / \alpha_\nu^\tau) \sigma_1 (Q_{2\nu}^T + Q_{3\nu}^T - Q_{1\nu}^T) + (\alpha_2^\tau / \alpha_\nu^\tau) \sigma_2 (Q_{3\nu}^T + Q_{1\nu}^T - Q_{2\nu}^T) + (\alpha_3^\tau / \alpha_\nu^\tau) \sigma_3 (Q_{1\nu}^T + Q_{2\nu}^T - Q_{3\nu}^T). \quad (70)$$

In Eq. (69) no summation over the Voigt's index  $\nu$  is implied.  $\alpha_\mu^\sigma = \alpha_\nu^\tau = 0$  for  $\mu$  or  $\nu = 4, 5, \text{ or } 6$ , and therefore

$$Q_{44}^S = Q_{44}^T, \quad Q_{55}^S = Q_{55}^T, \quad Q_{66}^S = Q_{66}^T. \quad (71)$$

Noting that  $Q_{\mu\nu} = Q_{\nu\mu}$  and using Eq. (38) for an orthotropic specimen under hydrostatic pressure  $\sigma_{ij} = -p \delta_{ij}$ , one finds from Eq. (69) that

$$Q_{\mu\nu}^S = Q_{\mu\nu}^T - \frac{T\alpha_\mu^\sigma \alpha_\nu^\tau}{\rho_X C_p}, \quad (72)$$

which is a familiar result in the field of high-pressure equations of state.

The compressibility  $\chi^S$  or  $T$  of a material can be expressed in terms of the effective compliance coefficients  $Q_{\mu\nu}^S$  or  $T$  as (see Refs. 1, 2, and 4–7)

$$\chi^S \text{ or } T = - \left( \frac{\partial V}{V \partial p} \right)_{S \text{ or } T; X} = Q_{iikk}^S \text{ or } T = Q_{11}^S \text{ or } T + Q_{22}^S \text{ or } T + Q_{33}^S \text{ or } T + 2(Q_{12}^S \text{ or } T + Q_{23}^S \text{ or } T + Q_{13}^S \text{ or } T), \quad (73)$$

where  $V = 1/\rho_X$  is the specific volume and the symmetry property of  $Q_{\mu\nu} = Q_{\nu\mu}$  under hydrostatic pressures is utilized. Then the bulk modulus  $B^S$  or  $T$  of a material is obtained simply by taking the reciprocal of  $\chi^S$  or  $T$ . The difference between the adiabatic and isothermal values of compressibility or bulk modulus can be calculated via Eqs. (72) and (73).

The relation between  $K_{\alpha\beta}^S$  or  $T$  and  $C_{\alpha\beta}^S$  or  $T$  has already been described by Eq. (16). The general relation between  $Q_{\alpha\beta}^S$  or  $T$  and  $S_{\alpha\beta}^S$  or  $T$  is difficult to obtain. Three relations between  $Q_{\mu\nu}^T$  and  $S_{\mu\nu}^T$  can be found from Eqs. (32) and (37) for an orthotropic specimen loaded along the principal-axis direction. They are expressed as

$$S_{\mu 1}^T \sigma_1 (\beta^\sigma - 2\alpha_1^\sigma) + S_{\mu 2}^T \sigma_2 (\beta^\sigma - 2\alpha_2^\sigma) + S_{\mu 3}^T \sigma_3 (\beta^\sigma - 2\alpha_3^\sigma)$$

$$= Q_{\mu 1}^T \sigma_1 (\beta^\tau - 2\alpha_1^\tau) + Q_{\mu 2}^T \sigma_2 (\beta^\tau - 2\alpha_2^\tau) + Q_{\mu 3}^T \sigma_3 (\beta^\tau - 2\alpha_3^\tau), \quad (74)$$

where the Voigt index  $\mu = 1, 2, 3$ .

To find the difference between  $K_{\alpha\beta}^S$  and  $K_{\alpha\beta}^T$ , we consider a small deformation from the initial state, in which  $\xi_\beta$  becomes an infinitesimal strain  $\epsilon_\beta$ . We consider the form  $\sigma_\alpha = \sigma_\alpha[\epsilon_\beta, T(\epsilon_\beta, S)]$ , where  $\epsilon_\beta$  and  $S$  are chosen as independent variables, and  $\sigma_\alpha$  and  $T$  are the dependent variables. Partial differentiation with respect to  $\epsilon_\beta$  yields

$$\left( \frac{\partial \sigma_\alpha}{\partial \epsilon_\beta} \right)_S = \left( \frac{\partial \sigma_\alpha}{\partial \epsilon_\beta} \right)_T + \left( \frac{\partial \sigma_\alpha}{\partial T} \right)_\epsilon \left( \frac{\partial T}{\partial \epsilon} \right)_S. \quad (75)$$

Using the Maxwell's relation  $(\partial T / \partial \epsilon_\beta)_S = (\partial \tau_\beta / \partial S)_\epsilon / \rho_X = -T \phi_\beta / (\rho_X C_\xi)$  and evaluating at the initial state with the aid of Eqs. (45) and (46), one obtains from Eqs. (75) and (62)

$$K_{\alpha\beta}^S - K_{\alpha\beta}^T = \frac{T \phi_\alpha \phi_\beta}{\rho_X C_\xi} = C_{\alpha\beta}^S - T_{\alpha\beta} = \frac{T \alpha_\mu^\tau \alpha_\nu^\tau C_{\mu\alpha}^T C_{\nu\beta}^T}{\rho_X C_\xi}, \quad (76)$$

which can be also derived from Eqs. (16) and (62). Note that Eq. (76) can be derived in a similar way by starting with the form  $\sigma_\alpha = \sigma_\alpha[\epsilon_\beta, S(\epsilon_\beta, T)]$ .

For an orthotropic specimen loaded along the principal-axis direction,  $\alpha_{ij}^\tau = \alpha_i^\tau \delta_{ij}$  ( $i, j = 1, 2, 3$ ), and therefore it follows from Eq. (76) that

$$K_{44}^S - K_{44}^T = C_{44}^S - C_{44}^T = 0, \quad K_{55}^S - K_{55}^T = C_{55}^S - C_{55}^T = 0, \\ K_{66}^S - K_{66}^T = C_{66}^S - C_{66}^T = 0. \quad (77)$$

For a material of cubic symmetry subjected to hydrostatic pressures  $\sigma_{rs} = -p \delta_{rs}$ , it is easy to show from Eq. (76) that

$$K_{11}^S - K_{11}^T = C_{11}^S - C_{11}^T = \frac{[(C_{11}^T + 2C_{12}^T) \alpha^\tau]^2 T}{\rho_X C_V} = C_{12}^S - C_{12}^T \\ = K_{12}^S - K_{12}^T, \quad (78)$$

where  $C_V$  is equal to  $C_\xi$  for cubic and isotropic materials [refer to Eqs. (59) and (60)]. In addition to  $K_{44}$ , we define the effective shear modulus  $K_M$  of a cubic material as

$$K_M^S = (1/2)(K_{11}^S - K_{12}^S) = (1/2)(K_{11}^T - K_{12}^T) = K_M^T. \quad (79)$$

Moreover,  $Q_{11} = Q_{22} = Q_{33}$ ,  $Q_{12} = Q_{23} = Q_{13}$ , and  $(Q_{11} + 2Q_{12})^{-1} = K_{11} + 2K_{12}$  for cubic symmetry. The adiabatic and isothermal bulk moduli,  $B^S$  and  $B^T$ , are via Eqs. (73) and (79) given by

$$B^S = -V(\partial p / \partial V)_S = (1/3)(K_{11}^S + 2K_{12}^S) = K_{11}^S - 4K_M^S/3, \quad (80)$$

$$B^T = -V(\partial p / \partial V)_T = (1/3)(K_{11}^T + 2K_{12}^T) = K_{11}^T - 4K_M^T/3 \\ = (1/3)(C_{11}^T + 2C_{12}^T + p). \quad (81)$$

The last part of Eq. (81) can be obtained by applying Eq. (16) for the case of hydrostatic pressure. It follows from Eqs. (78)–(81) that

$$B^S - B^T = K_{11}^S - K_{11}^T = \frac{[(C_{11}^T + 2C_{12}^T)\alpha^T]^2 T}{\rho_X C_V}, \quad (82)$$

which, on substitution of Eq. (41) and the last part of Eq. (81), becomes

$$B^S - B^T = 9(B^T \alpha^p)^2 T / (\rho_X C_V). \quad (83)$$

The above result has been treated in many books of thermodynamics.

### VII. EFFECTIVE YOUNG'S MODULUS AND POISSON'S RATIO

In this section we restrict ourselves to a specimen of orthotropic or higher symmetry, which is homogeneously loaded along the principal-axis directions at the initial state and then a small additional homogeneous loading is super-

posed along the principal  $X_3$  direction. The stresses at the initial state are given by  $\sigma_{ij} = \sigma_i \delta_{ij}$  and a small additional deformation is described by  $\delta\sigma_{ij} = \delta\sigma_{33}$  and  $u_{i,j} = \varepsilon_i \delta_{ij}$ . Representing the specimen gauge lengths along the principal directions by  $l_1, l_2,$  and  $l_3,$  we derive the formulas for the Young's modulus  $E_3$  and the Poisson's ratios  $\nu_{13}$  and  $\nu_{23},$  which are defined as

$$E_3 = \left( \frac{d\sigma_3}{d\varepsilon_3} \right)_X = \left[ \frac{d(\delta\sigma_3)}{dl_3/l_3} \right]_X, \quad (84)$$

$$\nu_{13} = - \left( \frac{\varepsilon_1}{\varepsilon_3} \right)_X = - \left[ \frac{dl_1/l_1}{dl_3/l_3} \right]_X, \quad \nu_{23} = - \left( \frac{\varepsilon_2}{\varepsilon_3} \right)_X = - \left[ \frac{dl_2/l_2}{dl_3/l_3} \right]_X. \quad (85)$$

In this case,  $K_{\mu\nu}$  in Eq. (16) can be expressed in matrix form as

$$[K_{\mu\nu}] = \begin{bmatrix} C_{11} + \sigma_1 & C_{12} - \sigma_1 & C_{13} - \sigma_1 & 0 & 0 & 0 \\ C_{12} - \sigma_2 & C_{22} + \sigma_2 & C_{23} - \sigma_2 & 0 & 0 & 0 \\ C_{13} - \sigma_3 & C_{23} - \sigma_3 & C_{33} + \sigma_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} + C(\sigma_2 + \sigma_3)/2 & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} + (\sigma_1 + \sigma_3)/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} + (\sigma_1 + \sigma_2)/2 \end{bmatrix}. \quad (86)$$

A small deformation process from the initial state can be either isothermal or isentropic. Using Eq. (86), Eqs. (84) and (85) can be written as

$$\nu_{13}^{T \text{ or } S} = - \frac{Q_{13}^{T \text{ or } S}}{Q_{33}^{T \text{ or } S}} = - \frac{(\mathbf{K}^{-1})_{13}^{T \text{ or } S}}{(\mathbf{K}^{-1})_{33}^{T \text{ or } S}} = \frac{(C_{13}^{T \text{ or } S} - \sigma_1)(C_{22}^{T \text{ or } S} + \sigma_2) - (C_{12}^{T \text{ or } S} - \sigma_1)(C_{23}^{T \text{ or } S} - \sigma_2)}{(C_{11}^{T \text{ or } S} + \sigma_1)(C_{22}^{T \text{ or } S} + \sigma_2) - (C_{12}^{T \text{ or } S} - \sigma_1)(C_{21}^{T \text{ or } S} - \sigma_2)}, \quad (87)$$

$$\nu_{23}^{T \text{ or } S} = - \frac{Q_{23}^{T \text{ or } S}}{Q_{33}^{T \text{ or } S}} = - \frac{(\mathbf{K}^{-1})_{23}^{T \text{ or } S}}{(\mathbf{K}^{-1})_{33}^{T \text{ or } S}} = \frac{(C_{23}^{T \text{ or } S} - \sigma_2)(C_{11}^{T \text{ or } S} + \sigma_1) - (C_{12}^{T \text{ or } S} - \sigma_2)(C_{13}^{T \text{ or } S} - \sigma_1)}{(C_{11}^{T \text{ or } S} + \sigma_1)(C_{22}^{T \text{ or } S} + \sigma_2) - (C_{12}^{T \text{ or } S} - \sigma_1)(C_{21}^{T \text{ or } S} - \sigma_2)}, \quad (88)$$

$$E_3^{T \text{ or } S} = \frac{1}{Q_{33}^{T \text{ or } S}} = \frac{1}{(\mathbf{K}^{-1})_{33}^{T \text{ or } S}} = C_{33}^{T \text{ or } S} + \sigma_3 - \nu_{13}^{T \text{ or } S}(C_{13}^{T \text{ or } S} - \sigma_1) - \nu_{23}^{T \text{ or } S}(C_{23}^{T \text{ or } S} - \sigma_2), \quad (89)$$



where  $\mathbf{K}^{-1}$  denotes the inverse matrix of the matrix  $[K_{\mu\nu}]$  and the superscripts  $T$  and  $S$  represent isothermal and adiabatic values, respectively. One recalls that in Eqs. (87)–(89)  $\sigma_1$ ,  $\sigma_2$ , and  $\sigma_3$  are the principal initial stresses. Equations (87)–(89) expresses the effective Young's modulus and Poisson's ratio in terms of the thermodynamic elastic coefficients and three principal stresses acting on an orthotropic specimen.

The difference between the adiabatic and isothermal values of the Young's modulus and Poisson's ratios can be conveniently obtained from Eq. (69), which can be written as

$$Q_{33}^T = Q_{33}^S \left[ 1 + \frac{\alpha_3^\sigma \alpha_3^\tau T}{Q_{33}^S \rho_X C_\sigma} (1 + r_t) \right], \quad (90)$$

where

$$r_t = (\alpha_1^\tau / \alpha_3^\tau) \sigma_1 (Q_{23}^T + Q_{33}^T - Q_{13}^T) + (\alpha_2^\tau / \alpha_3^\tau) \sigma_2 (Q_{33}^T + Q_{13}^T - Q_{23}^T) + \sigma_3 (Q_{13}^T + Q_{23}^T - Q_{33}^T). \quad (91)$$

At uniaxial compressive loading of 1 GPa in the  $x_3$  direction,  $r_t$  in Eq. (91) is estimated to be 0.0059 for high-strength steel, 0.014 for high-strength titanium alloy, 0.013 for cubic iron and 0.012 for cubic silicon. At uniaxial compressive stress  $\sigma_3 = 100$  MPa,  $r_t$  is estimated to be 0.045 for PMMA (lucite) and 0.032 for cubic NaCl. Here, the word cubic applies only to the natural state.

Taking the reciprocal of the above equation gives the following isothermal and adiabatic conversion relation for the Young's modulus:

$$E_3^T = \frac{E_3^S}{1 + (\alpha_3^\sigma \alpha_3^\tau E_3^S T / \rho_X C_\sigma) (1 + r_t)} = \frac{E_3^S}{1 + \alpha_3^\sigma \lambda E_3^S}, \quad (92)$$

$$E_3^S = \frac{E_3^T}{1 - \alpha_3^\sigma \lambda E_3^T},$$

where  $\lambda$  denotes

$$\lambda \equiv \frac{T \alpha_3^\tau (1 + r_t)}{\rho_X C_\sigma}. \quad (93)$$

Similarly we proceed to obtain

$$\nu_{13}^S = -\frac{Q_{13}^S}{Q_{33}^S} = \frac{-Q_{13}^T + \lambda \alpha_1^\sigma}{Q_{33}^T (1 - \lambda \alpha_3^\sigma E_3^T)} = \frac{\nu_{13}^T + \alpha_1^\sigma \lambda E_3^T}{1 - \alpha_3^\sigma \lambda E_3^T},$$

$$\nu_{23}^S = -\frac{Q_{23}^S}{Q_{33}^S} = \frac{\nu_{23}^T + \alpha_2^\sigma \lambda E_3^T}{1 - \alpha_3^\sigma \lambda E_3^T}, \quad (94)$$

$$\nu_{13}^T = -\frac{Q_{13}^T}{Q_{33}^T} = \frac{\nu_{13}^S - \alpha_1^\sigma \lambda E_3^S}{1 + \alpha_3^\sigma \lambda E_3^S}, \quad \nu_{23}^T = -\frac{Q_{23}^T}{Q_{33}^T} = \frac{\nu_{23}^S - \alpha_2^\sigma \lambda E_3^S}{1 + \alpha_3^\sigma \lambda E_3^S}. \quad (95)$$

The terms  $\alpha_i^\sigma \lambda E_3^T$  ( $i=1,2,3$ ) in the above equation is much smaller than unity. For example, they are estimated to be 0.0047 for aluminum, 0.0031 for copper, 0.0037 for low carbon steel, and 0.0016 for 18-Ni maraging steel. It is therefore sufficiently accurate to express Eq. (94) as

$$\nu_{13}^S = \nu_{13}^T + (\alpha_1^\sigma + \nu_{13}^T \alpha_3^\sigma) \lambda E_3^T + \alpha_3^\sigma (\alpha_1^\sigma + \nu_{13}^T \alpha_3^\sigma) (\lambda E_3^T)^2,$$

$$\nu_{23}^S = \nu_{23}^T + (\alpha_2^\sigma + \nu_{23}^T \alpha_3^\sigma) \lambda E_3^T + \alpha_3^\sigma (\alpha_2^\sigma + \nu_{23}^T \alpha_3^\sigma) (\lambda E_3^T)^2. \quad (96)$$

For an isotropic elastic solid subjected to an infinitesimal deformation at the natural state, Eqs. (92), (94), and (95) become identical with Eq. (6.8) in the book of Landau and Lifshitz.<sup>20</sup>

## VIII. DISCUSSION

The effective isothermal elastic coefficients  $K_{\mu\nu}^T$  and  $Q_{\mu\nu}^T$  of a specimen can be conveniently obtained in slow isothermal uniaxial tension (or compression) and torsion tests performed in various directions of the specimen. What are usually measured in these tests are the applied force or torque and linear or angular displacements. Since the calculation of  $K_{\mu\nu}^T$  and  $Q_{\mu\nu}^T$  involves the differentiation of stress with respect to strain, which again involves the differentiation of displacement with respect to gauge dimension, an accurate determination of  $K_{\mu\nu}^T$  and  $Q_{\mu\nu}^T$  requires very accurate measurements of the applied stress and dimensional changes. Better accuracy in determination of  $K_{\mu\nu}^T$  and  $Q_{\mu\nu}^T$  are often obtained first by measuring  $K_{\mu\nu}^S$  and  $Q_{\mu\nu}^S$  and next by using the adiabatic and isothermal conversion formulas treated in Secs. VI and VII.

The effective adiabatic elastic stiffness coefficients are conveniently obtained from measurements of ultrasonic wave speeds in various directions of a specimen (see Schreiber, Anderson, and Soga<sup>21</sup>). A transit time of an ultrasonic wave through the specimen can be accurately measured by using various techniques. Denoting the phase velocity of an elastic wave propagating along the  $x_i$  direction and polarized along the  $x_j$  direction by  $V_{ij}$ , the pure-index effective elastic coefficients  $K_{\mu\mu}$  ( $\mu$  not summed) are determined from the following equations:

$$\frac{1}{2} \rho_X [(V_{ij}^2 + V_{ji}^2)] = \begin{bmatrix} K_{11}^S & K_{66}^S & K_{55}^S \\ K_{66}^S & K_{22}^S & K_{44}^S \\ K_{55}^S & K_{44}^S & K_{33}^S \end{bmatrix}, \quad (97)$$

which indicates that the diagonal elements of the adiabatic effective elastic stiffness matrix can be obtained from the wave speeds along the principal-axis directions. The pure-index effective shear moduli  $K_{44}^S$ ,  $K_{55}^S$ , and  $K_{66}^S$  can also be obtained from the wave speed measurement of shear horizontally polarized transverse waves of the pure mode propagating at an oblique angle in symmetry planes. The mixed index elastic stiffness coefficients (off-diagonal elements) can be determined from the wave speed measurements of quasilongitudinal or quasitransverse waves propagating at an oblique angle in symmetry planes.

Thus, all the elements  $K_{\mu\nu}^S$  of the  $\mathbf{K}^S$  matrix of Eq. (86) can be obtained from the measurements of wave speeds in various directions of a stressed medium. Then, one can calculate its inverse  $\mathbf{Q}^S = [Q_{\mu\nu}^S]$ , the effective elastic compliance matrix, which is more than sufficient to determine the compressibility, bulk modulus, effective adiabatic Poisson's ratios and Young's modulus described in Secs. VI and VII. For calculation of the corresponding isothermal values one resorts to various conversion formulas shown in Secs. VI and VII.

The thermal-expansion coefficient and specific heat are difficult to measure at constant thermodynamic stress  $\tau_{ij}$  and

so is the specific heat at constant strain. For these reasons both of them are usually measured at constant stress  $\sigma_{ij}$  or constant hydrostatic pressure  $p$ . The measurement of the specific heat or thermal-expansion coefficients at constant stress  $\sigma_{ij}$  requires us to monitor the dimensional changes in three principal directions of a specimen and adjust an applied force in order to keep  $\sigma_{ij}$  constant, as in the case of an engineering creep test under constant  $\sigma_{ij}$ . This can be done without too much difficulty by adopting, e.g., a computer-controlled feedback system. Then, for an orthotropic specimen loaded parallel to the principal axis, the thermal-expansion coefficient  $\alpha_{ij}^T$  can be obtained via Eq. (32), (37), or (38) and the specific heats  $C_\tau$  and  $C_\xi$  can be calculated using Eqs. (55), (56), and (50). In the moderate stress range below the elastic limit of a material, variations of the thermal-expansion coefficient and specific heat with stress or strain are small and can be estimated to good accuracy via Eqs. (42), (44), and (61), where one can resort to the temperature dependence data of the effective elastic compliance coefficients and thermal-expansion coefficients at the stress-free natural state.

#### ACKNOWLEDGMENTS

The author greatly acknowledges the financial support from the Office of Naval Research and is indebted to Dr. Robert. N. Thurston for his valuable comments and fruitful discussions. The author thanks Professor W. Sachse for his interest in this work.

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