$$\gamma_{ij} \equiv -V\left(\frac{\partial T_{ij}}{\partial U}\right)_{\mathbf{u}}, \tag{46}$$

where U is the internal energy. The correct microscopic definition must be found so as to be consistent with this definition. Equation (3) may be written

$$T_{ij} = \rho\frac{\mathrm{d}\bar{\phi}}{\mathrm{d}u_{ij}} + \rho\sum_{\nu}\frac{\mathrm{d}\ln\omega_\nu}{\mathrm{d}u_{ij}}\left(\frac{\partial A_q}{\partial\ln\omega_\nu}\right)_T. \tag{47}$$

By defining

$$\gamma^{\nu}_{ij} \equiv -\frac{1}{2}\frac{\mathrm{d}\ln\omega_\nu^2}{\mathrm{d}u_{ij}}, \tag{48}$$

and substituting into (47), we can get, using the Grüneisen approximation (i.e. assuming γ^{ν}_{ij} to be independent of ν),

$$\left(\frac{\partial T_{ij}}{\partial U_q}\right)_{\mathbf{u}} = -\rho\gamma_{ij}, \tag{49}$$

to which (46) reduces in the present approximation.

Now, substituting the expansion (39) into the definition (48), suppressing the index ν, and using (5), (13) and (15), one obtains

$$\gamma_{ij} = -\frac{\omega_0^2}{4\omega^2}(G_{ki}G_{lj} + G_{li}G_{kj})(g_{kl} + h_{klmn}E_{mn} + \cdots). \tag{50}$$

Evaluating this and its derivative at $\mathbf{E} = 0$, one can derive that

$$g_{ij} = -2\gamma^0_{ij}, \tag{51}$$

$$h_{ijkl} = -2\left(\frac{\partial\gamma_{ij}}{\partial s_{kl}}\right)_0 + g_{ij}g_{kl} + g_{ik}\delta_{jl} + g_{jk}\delta_{il}. \tag{52}$$

From the definitions, in (39), of g_{ij} and h_{ijkl} and the symmetry of E_{ij}, it may be seen that g_{ij}, and hence γ_{ij}, is symmetric in i and j, and that h_{ijkl} has the full Voigt symmetry, in analogy with the effective elastic moduli, c_{ijkl}.

Again, similar development in terms of $\boldsymbol{\eta}$ yields

$$g'_{ij} = -2\gamma^0_{ij} = g_{ij}, \tag{53}$$

$$h'_{ijkl} = -2\left(\frac{\partial\gamma_{ij}}{\partial s_{kl}}\right)_0 + g_{ij}g_{kl} - g_{ik}\delta_{jl} - g_{jk}\delta_{il}. \tag{54}$$

If the material has cubic symmetry, the number of independent parameters g_{ij} and h_{ijkl} is reduced. Thus γ_{ij}, and hence g_{ij}, reduces to a scalar multiple of the unit tensor[2]:

$$\gamma_{ij} = \gamma\delta_{ij}. \tag{55}$$

Also, h_{ijkl}, in analogy with the elastic moduli, reduce to three independent components, h_{1111}, h_{1122} and h_{1212}, or, in the Voigt abbreviated notation, h_{11}, h_{12} and h_{44}. The bulk parameters g and h defined in Paper I (the actual notation was h'') can be related to g_{ij} and h_{ijkl} by comparing (39) with the corresponding scalar expansion in Paper I:

$$g = g_{ii},\ h = h_{iikk}. \tag{56}$$

Thus, for cubic symmetry,

$$g_{ij} = \frac{1}{3}g\delta_{ij},\ h = 3(h_{11} + 2h_{12}). \tag{57}$$

Then the general expression (52) reduces to

$$h_{1111} = -2\left(\frac{\partial\gamma_{11}}{\partial s_{11}}\right)_0 + \frac{g^2}{9} + \frac{2g}{3}, \tag{58}$$

$$h_{1122} = -2\left(\frac{\partial\gamma_{11}}{\partial s_{22}}\right)_0 + \frac{g^2}{9}, \tag{59}$$

$$h_{1212} = -2\left(\frac{\partial\gamma_{12}}{\partial s_{12}}\right)_0 + \frac{g}{3}. \tag{60}$$

Similarly, (43) gives

$$r^0_{11} = \bar{\phi}^0_{11} + \frac{1}{4}(2h_{11} - g^2/9)U^0_q - g^2TC^0_q/36, \tag{61}$$

$$r^0_{12} = \bar{\phi}^0_{12} + \frac{1}{4}(2h_{12} - g^2/9)U^0_q - g^2TC^0_q/36, \tag{62}$$

$$r^0_{44} = \bar{\phi}^0_{44} + \frac{1}{2}h_{44}U^0_q, \tag{63}$$

where $\bar{\phi}_{\alpha\beta}$ is the appropriate combination of derivatives of $\bar{\phi}$.

The analogues of (58–60) are, from (54),

$$h'_{1111} = -2\left(\frac{\partial\gamma_{11}}{\partial s_{11}}\right)_0 + \frac{g^2}{9} - \frac{2g}{3}, \tag{64}$$

$$h'_{1122} = -2\left(\frac{\partial\gamma_{11}}{\partial s_{22}}\right)_0 + \frac{g^2}{9}, \tag{65}$$

$$h'_{1212} = -2\left(\frac{\partial\gamma_{12}}{\partial s_{12}}\right)_0 - \frac{g}{3}. \tag{66}$$

The analogues of (61–63), derived from (45), have exactly the same form, but with h'_{ijkl} replacing h_{ijkl}.

The above expressions for the temperature dependence of the r^n_{ijkl} and t^n_{ijkl} are for the isothermal parameters, i.e. for the parameters entering the finite strain expansions of the isothermal elastic moduli. The modifications to the derivation necessary to derive the isentropic parameters are simple generalizations of those made in Paper I. The resulting isentropic analogue of (43), for instance, is

$$r^{0s}_{ijkl} = \bar{\phi}^0_{ijkl} + \frac{1}{4}(2h_{ij} - g_{ij}g_{kl})U^0_q. \tag{67}$$

Note, in particular, that

$$r_{44}^{0s} = \bar{\phi}_{44}^{0} + \frac{1}{2} h_{44} U_q^0 \tag{68}$$

which is identical to its isothermal analogue. Thus there is no difference between c_{44}^s and c_{44}^T. This is a well known result.

4. THERMODYNAMIC RELATIONS

In the "isotropic strain" theory of Paper I, the Grüneisen parameter and its volume derivative were related to the bulk modulus and its pressure and temperature derivatives through thermodynamic identities. These identies must be generalized for the present case. The initial part of the treatment given here is similar to that given by Mason[16]. The infinitesimal symmetric strain s defined by (7) will be used in this section. The temperature and entropy will be denoted by θ and σ, respectively, to avoid confusion with the stress, **T**, and the strain, **s**.

It is convenient to consider first the relation between isothermal and isentropic elastic moduli. From the first and second laws of thermodynamics, the change of internal energy per unit volume of a system in a reversible process is given by

$$\mathrm{d}U = T_i\, \mathrm{d}s_i + \theta\, \mathrm{d}\sigma, \tag{69}$$

where the stress and strain are written in the Voigt notation, as will be all relations henceforth, unless otherwise noted. The Helmholtz free energy, A, is defined by

$$A = U - \theta\sigma, \tag{70}$$

whence

$$\mathrm{d}A = T_i\, \mathrm{d}s_i - \sigma\, \mathrm{d}\theta, \tag{71}$$

and

$$T_i = \left(\frac{\partial A}{\partial s_i}\right)_\theta, \quad \sigma = -\left(\frac{\partial A}{\partial \theta}\right)_s. \tag{72}$$

With s_i and θ as independent variables, we may write

$$\mathrm{d}\sigma = \lambda_i\, \mathrm{d}s_i + \left(\frac{\partial \sigma}{\partial \theta}\right)_s \mathrm{d}\theta, \tag{73}$$

where

$$\lambda_i = \left(\frac{\partial \sigma}{\partial s_i}\right)_\theta = -\left(\frac{\partial T_i}{\partial \theta}\right)_s, \tag{74}$$

using equation (72). In a reversible process, the quantity of heat absorbed by the system is

$$\mathrm{d}Q = \theta\, \mathrm{d}\sigma = \theta\lambda_i\, \mathrm{d}s_i + \theta\left(\frac{\partial \sigma}{\partial \theta}\right)_s \mathrm{d}\theta, \tag{75}$$

from which we can make the identification

$$\left(\frac{\partial \sigma}{\partial \theta}\right)_s = \frac{\rho C_s}{\theta}, \tag{76}$$

where ρ is density and C_s is the specific heat at constant strain. In an isentropic process, i.e. $\mathrm{d}\sigma = 0$, the change in temperature is, from (73),

$$\mathrm{d}\theta = -\frac{\theta\lambda_i}{\rho C_s}\, \mathrm{d}s_i. \tag{77}$$

Now, again in terms of s_i and θ, the change in stress is

$$\mathrm{d}T_i = c_{ij}^{\theta}\, \mathrm{d}s_j - \lambda_i\, \mathrm{d}\theta \tag{78}$$

where

$$c_{ij}^{\theta} = \left(\frac{\partial T_i}{\partial s_j}\right)_\theta \tag{79}$$

is the isothermal elastic modulus. Thus, using (77), the isentropic change in stress is

$$\mathrm{d}T_i = \left(c_{ij}^{\theta} + \frac{\theta\lambda_i\lambda_j}{\rho C_s}\right) \mathrm{d}s_j, \tag{80}$$

from which the isentropic elastic modulus is

$$c_{ij}^{\sigma} = c_{ij}^{\theta} + \frac{\theta\lambda_i\lambda_j}{\rho C_s}. \tag{81}$$

Using the chain rule of differentiation, we see that

$$\lambda_i = \left(\frac{\partial s_j}{\partial \theta}\right)_T \left(\frac{\partial T_i}{\partial s_j}\right)_\theta = \alpha_j c_{ij}^{\theta}, \tag{82}$$

where α_i is the thermal expansion tensor.

Next, consider the Grüneisen parameter and its strain derivatives. From the thermodynamic definition (46) of the generalized Grüneisen parameter (using the Voigt notation, and recalling that U is now energy per unit volume),

$$\begin{aligned} \gamma_i &= -\left(\frac{\partial T_i}{\partial \theta}\right)_s \left(\frac{\partial \theta}{\partial U}\right)_s \\ &= V\lambda_i / C_s = V\alpha_j c_{ij}^{\theta} / C_s, \end{aligned} \tag{83}$$

which generalizes the usual Grüneisen relation.

Equation (83) can be differentiated with respect to s_k, and, using the relations

$$\left(\frac{\partial V}{\partial s_k}\right)_\theta = V\delta_k, \tag{84}$$

where

$$\begin{aligned} \delta_k &= 1 \quad \text{if} \quad k = 1, 2, 3, \\ \delta_k &= 0 \quad \text{if} \quad k = 4, 5, 6, \end{aligned} \tag{85}$$

and

$$\left(\frac{\partial \lambda_i}{\partial s_k}\right)_\theta = -\left(\frac{\partial c_{ik}^{\theta}}{\partial \theta}\right)_s, \tag{86}$$