ed, especially for non-cubic solids. For
$^2VT/\kappa_T$‡ gives not the heat capacity of a
onstant, but that of a solid whose shape
: at constant volume[4].

ring the time of an experiment, a solid
e state with a well defined entropy S and
ctions of the strain and temperature. The
r main topic. We deal only with thermo-
and magnetic effects.

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ım, and consider only strains which are
of several atomic spacings. The strain can
each point in the solid from its position
guration. A superposed circle will denote
or a uniform strain the new positions are

$$(\delta_{ij} + u_{ij})\, \mathring{x}_j \tag{1}$$

plied over a repeated suffix. If the displace-
ric and antisymmetric parts give, to first
ons

$$, \quad \omega_{ij} \equiv \tfrac{1}{2}(u_{ij} - u_{ji}) \tag{2}$$

fied by the six e_{ij}.
pecified by the e_{ij}. An arbitrary vector $\mathring{\mathbf{r}}$ in
n becomes the vector $\mathbf{r}$ in the strained
,6

$$_{ij} + u_{ji} + u_{ki}u_{kj})\, \mathring{r}_i \mathring{r}_j \tag{3}$$

pend on the ω_{ij} as well as the e_{ij}. We can
symmetric *Lagrange finite strain tensor*

$$_{ij} + u_{ji} + u_{ki}u_{kj}) \tag{4}$$

finitesimal strains. We shall use the *Voigt*

$$= \eta_{22}, \eta_3 = \eta_{33}; \tag{5}$$

$$_5 = 2\eta_{31}, \eta_6 = 2\eta_{12} \tag{6}$$

e introduced for later convenience. Voigt
eek letters λ, etc. ($\lambda = 1, \ldots 6$). A similar
s e_λ.

to avoid confusion with the Grüneisen function γ.

Description of stress

The stress is most directly described by the well-known *Cauchy stress tensor*[8], which in the absence of couple stresses is symmetric[9]. However, the Cauchy stress has the disadvantage for thermodynamic purposes that it does not determine the strain unless the orientation is specified (or unless the stress is isotropic). We therefore define other stress parameters, t_λ, which are thermodynamically conjugate to the strain parameters η_λ, and so depend on this prior choice of strain parameter.

The energy U and Helmholtz energy A are functions of the strain and one other variable. The stresses t_λ are defined by

$$\mathring{V} t_\lambda \equiv (\partial U/\partial \eta_\lambda)_{\eta', S} = (\partial A/\partial \eta_\lambda)_{\eta', T} \tag{7}$$

where the subscript η' denotes that all the η_μ except η_λ are kept constant during differentiation. The t_λ have the dimensions of (negative) pressure, and are sometimes called the *thermodynamic tensions*[1,2]. One may also retain tensor notation to define stresses t_{ij} by equations like 7, with this convention[10] for differentiation with respect to the components of a symmetric tensor. Write the function to be differentiated symmetrically in η_{ij} and η_{ji} and then differentiate treating all nine η_{ij} as independent. The resulting tensor is symmetric, and is related to the t_λ by a scheme like equations 5 and 6 without the factors of two.

The relation of t_{ij} to the Cauchy stress σ_{ij} is discussed in §3.

Energy functions and Maxwell relations

We define quantities analogous to the enthalpy and Gibbs energy

$$H' \equiv U - \mathring{V} t_\lambda \eta_\lambda, \qquad G' \equiv A - \mathring{V} t_\lambda \eta_\lambda \tag{8}$$

where the primes remind us that these cannot be identified with the functions H and G defined under hydrostatic pressure. The repeated subscript λ denotes summation from 1 to 6; by virtue of the factors of two in the abbreviated notation for strains but not for tensions, $t_\lambda \eta_\lambda$ is equal to $t_{ij}\eta_{ij}$.

The differentials of the functions U, A, H' and G' are given to first order by

$$\mathrm{d}U - T\,\mathrm{d}S = \mathring{V} t_\lambda\, \mathrm{d}\eta_\lambda = \mathrm{d}A + S\,\mathrm{d}T \tag{9}$$

$$\mathrm{d}H' - T\,\mathrm{d}S = -\mathring{V} \eta_\lambda\, \mathrm{d}t_\lambda = \mathrm{d}G' + S\,\mathrm{d}T \tag{10}$$

Maxwell relations follow as for fluids, e.g.

$$(\partial S/\partial \eta_\lambda)_{\eta', T} = -(\partial^2 A/\partial \eta_\lambda\, \partial T)_{\eta'} = -\mathring{V}(\partial t_\lambda/\partial T)_\eta \tag{11}$$

$$(\partial T/\partial t_\lambda)_{t', S} = (\partial^2 H'/\partial t_\lambda\, \partial S)_{t'} = -\mathring{V}(\partial \eta_\lambda/\partial S)_t \tag{12}$$

and two similar expressions derived from $\mathrm{d}U$ and $\mathrm{d}G'$. Relations of this type also establish the symmetry of the isothermal elastic stiffnesses, analogous to the bulk modulus B for fluids:

$$C^T_{\lambda\mu} \equiv \left(\frac{\partial t_\lambda}{\partial \eta_\mu}\right)_{\eta', T} = \frac{1}{\mathring{V}} \left(\frac{\partial^2 A}{\partial \eta_\mu\, \partial \eta_\lambda}\right)_{\eta', T} = C^T_{\mu\lambda} \tag{13}$$