

ed, especially for non-cubic solids. For $2VT/\kappa_T \ddagger$ gives not the heat capacity of a constant, but that of a solid whose shape is at constant volume⁴. During the time of an experiment, a solid is in a state with a well defined entropy S and functions of the strain and temperature. The main topic. We deal only with thermo- and magnetic effects.

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um, and consider only strains which are of several atomic spacings. The strain can be defined at each point in the solid from its position before and after deformation. A superposed circle will denote a uniform strain the new positions are

$$(\delta_{ij} + u_{ij}) \hat{x}_j \quad (1)$$

plied over a repeated suffix. If the displacement is symmetric and antisymmetric parts give, to first order

$$\omega_{ij} \equiv \frac{1}{2}(u_{ij} - u_{ji}) \quad (2)$$

defined by the six e_{ij} . Specified by the e_{ij} . An arbitrary vector \hat{r} in the unstrained state becomes the vector \mathbf{r} in the strained state

$$r_i = (\delta_{ij} + u_{ij} + u_{ki}u_{kj}) \hat{r}_j \quad (3)$$

depend on the ω_{ij} as well as the e_{ij} . We can define a symmetric Lagrange finite strain tensor

$$e_{ij} = \frac{1}{2}(u_{ij} + u_{ji} + u_{ki}u_{kj}) \quad (4)$$

for infinitesimal strains. We shall use the Voigt notation

$$e_{\lambda} = \eta_{22}, \eta_{33} = \eta_{33}; \quad (5)$$

$$e_{\lambda} = 2\eta_{31}, \eta_6 = 2\eta_{12} \quad (6)$$

are introduced for later convenience. Voigt uses Greek letters λ , etc. ($\lambda = 1, \dots, 6$). A similar notation is used for 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 tensor⁸, which in the absence of couple stresses is symmetric⁹. 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

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

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 convention¹⁰ 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

$$H' \equiv U - \dot{V}t_{\lambda}\eta_{\lambda}, \quad G' \equiv A - \dot{V}t_{\lambda}\eta_{\lambda} \quad (8)$$

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

$$dU - T dS = \dot{V}t_{\lambda} d\eta_{\lambda} = dA + S dT \quad (9)$$

$$dH' - T dS = -\dot{V}\eta_{\lambda} dt_{\lambda} = dG' + S dT \quad (10)$$

Maxwell relations follow as for fluids, e.g.

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

$$(\partial T / \partial t_{\lambda})_{\eta', S} = (\partial^2 H' / \partial t_{\lambda} \partial S)_{\eta'} = -\dot{V}(\partial \eta_{\lambda} / \partial S)_{\eta'} \quad (12)$$

and two similar expressions derived from dU and dG' . Relations of this type also establish the symmetry of the isothermal elastic stiffnesses, analogous to the bulk modulus B for fluids:

$$C_{\lambda\mu}^T \equiv \left(\frac{\partial t_{\lambda}}{\partial \eta_{\mu}} \right)_{\eta', T} = \frac{1}{\dot{V}} \left(\frac{\partial^2 A}{\partial \eta_{\mu} \partial \eta_{\lambda}} \right)_{\eta', T} = C_{\mu\lambda}^T \quad (13)$$