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Thermodynamic Substate Variables for a Solid

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A set of tensorial thermodynamic substate variables V_{ij} has been found such that under hydrostatic pressure the enthalpy H of a solid, defined by $H \equiv U - \tau_{ij} V_{ij}$, where $\tau_{ij} \equiv (\partial U / \partial V_{ij})_S$, reduces to the conventional enthalpy $U + pV$. U is the internal energy per unit mass, p the pressure, V the specific volume, and S the entropy per unit mass. Previously used tensorial variables (e.g., the Lagrangian strain components) lead to a different enthalpy. The new variables are defined by $V_{ij} = (1/3\bar{\rho}) D^{(3/2)}{}_{ij}$, $D_{ij} = (\partial x_k / \partial X_i)(\partial x_k / \partial X_j)$. Here the X_i are the Cartesian coordinates of the particles of the body in some arbitrarily stressed reference configuration of density $\bar{\rho}$ and stresses $\bar{T}_{ij}$, x_i are the present coordinates, and $D^{(3/2)}{}_{ij}$ is a symbol for the *ij* element of the positive real 3/2 power of the tensor D_{ij}. Under these definitions, the enthalpy of a solid of arbitrary symmetry has been proved to reduce to $U + pV$ whenever $\mathbf{x}$ and $\mathbf{X}$ both correspond to states in which the stress in hydrostatic pressure. As a special case, $\mathbf{X}$ may of course be an unstressed configuration. The above choice of variables is not unique. In fact, the enthalpy reduces to $U + pV$ if V_{ij} is any matrix function of D_{ij} whose determinant is proportional to the 3/2 power of the determinant of the matrix D_{ij}. However, the above choice of V_{ij} has the additional desirable property that when evaluated at $\mathbf{x} = \mathbf{X}$, the thermodynamic tensions τ_{ij} equal the stresses T_{ij}. In the case of cubic crystals and isotropic media under hydrostatic pressure, the present V_{ij} and τ_{ij} reduce to $V_{ij} = \frac{1}{3} V \delta_{ij}$, $\tau_{ij} = -p\delta_{ij}$.

I. INTRODUCTION

The enthalpy under hydrostatic pressure is conventionally defined as

$$H = U + pV = U + p/\rho, \tag{1.1}$$

where U is the internal energy per unit mass, p is the pressure, and $V = 1/\rho$ is the specific volume, ρ being the density. For general states of stress, the enthalpy has been defined as[1]

$$H_1 = U - t_{ij} \eta_{ij} / \rho_0, \tag{1.2}$$

where η_{ij} denotes the Lagrangian strain components, referred to a natural unstressed state at which the density is ρ_0, and the quantities t_{ij} are the *thermodynamic tensions*[2] conjugate to η_{ij}/ρ_0, i.e., by definition,

$$t_{ij} = \rho_0 (\partial U / \partial \eta_{ij})_S. \tag{1.3}$$

The choice of η_{ij}/ρ_0 as thermodynamic substate variables has been found useful, but it has the aesthetic flaw and minor inconvenience that the enthalpy (1.2) does not reduce to (1.1) when the stress is hydrostatic pressure. In the present paper, we find a set of substate variables V_{ij} and thermodynamic tensions $\tau_{ij} \equiv (\partial U / \partial V_{ij})_S$ such that the enthalpy

$$H = U - \tau_{ij} V_{ij} \tag{1.4}$$

does reduce to (1.1) when the stress is hydrostatic pressure.

With the revised enthalpy, there is achieved the advantage that all four classical thermodynamic potentials in solids, U, $U - TS$, H, and $G = H - TS$, are identical with the corresponding functions as conventionally defined for fluids whenever the stress is hydrostatic. With the usual definitions, H and G do not have this property.

For fluids, the specific volume is a most convenient choice of substate variable. Not only is it subject to fairly direct experimental determination, but its conjugate thermodynamic tension is the pressure, which is also a readily measurable and widely used experimental variable. These same remarks apply to solids when the stress tensor is perfectly spherical (i.e., when the pressure is perfectly hydrostatic). It therefore seems advantageous to have available a set of tensor substate variables with the property that thermodynamic functions of solids, defined on the entire space of thermodynamic states, will reduce to the functions as conventionally defined for fluids in the subspace where the stress is hydrostatic.

In high-pressure work, it is common practice to treat solids as fluids and use the conventional thermodynamics of fluids, even when the stress tensor is not perfectly spherical. This is often done, for example, in discussions of shock waves in solids. With the variables given here, it is possible to treat departures from hydrostatic stress in terms of thermodynamic functions that all reduce precisely to the usual ones when the stress is hydrostatic.

A simplification in the thermodynamics of cubic crystals and isotropic solids provides still additional motivation for the present work. The specific heat and expansion coefficients are defined formally as derivatives with respect to temperature, taken at constant thermodynamic tensions, whereas they are commonly measured at constant pressure. With the older definitions, zero pressure corresponds to zero thermodynamic tensions for all temperatures, but at any other pressure, a temperature change at constant pressure causes a change in the thermodynamic tensions. This results in the awkwardness that even under hydrostatic pressure, the specific heat and expansion coefficient at constant pressure are not the same functions of pressure as the specific heat and expansion coefficient at constant thermodynamic tensions! Moreover, the conversions from one set of functions to the other are rather complicated. For isotropic media and cubic crystals under hydrostatic pressure, the tensor substate variables given here reduce simply to $V_{ij} = \frac{1}{3} V \delta_{ij}$ and the conjugate thermodynamic tensions are the stresses: $\tau_{ij} = -p\delta_{ij}$. Clearly, constant pressure corresponds to constant thermodynamic tensions for all pressures. Thus, for isotropic media and cubic crystals under hydrostatic pressure, this choice of variables removes the awkward distinction between derivatives at constant pressure and at constant thermodynamic tensions.

II. NOTATION AND PRELIMINARY FUNDAMENTALS

An equilibrium state of the solid will be assumed to be specified by its configuration and one other variable, either temperature T or entropy S. A configuration is specified by giving the positions of all particles in the body. The particles may be identified by their positions (A_1, A_2, A_3) in a master reference configuration, here taken as an unstressed configuration at some prescribed temperature T_M. The corresponding positions in an unstressed configuration at any other temperature T_0 may be expressed as

$$a_i = f_i(T_0, A_1, A_2, A_3), \tag{2.1}$$

with

$$A_i = f_i(T_M, A_1, A_2, A_3), \qquad i = 1, 2, 3. \tag{2.2}$$

Since any rigid rotation or translation of an unstressed configuration is also an unstressed configuration, the functions f_i can be completely specified only if some constraints are imposed. Appropriate constraints for Eq. (2.1) could correspond to the mounting of the sample in a setup for measuring thermal expansion. However, it is frequently not necessary to specify the constraints explicitly, since only the *relative* positions of the particles are important.

We shall refer to (a) a *natural* unstressed state with coordinates a_i, temperature T_0, entropy S_0, and density ρ_0; (b) an *initial* homogeneously deformed state of coordinates X_i, temperature $\bar{T}$, entropy $\bar{S}$, density $\bar{\rho}$, and stresses $\bar{T}_{ij}$; (c) a *present* or current state of coordinates x_i, temperature T, entropy S, density ρ, and stresses T_{ij}. All of the positions are referred to the same Cartesian coordinate system. In general, a bar over a quantity indicates evaluation at the "initial" reference state of coordinates X_i, temperature $\bar{T}$.

In discussing small-amplitude wave propagation in elastically deformed crystals,[3] it has proved convenient to specify $\bar{T} = T_0$ and $S = \bar{S}$. Obviously one could also make other associations of natural, initial, and present states. For the present purpose, this point can be left open.

We define C_{ij}, η_{ij}, D_{ij}, and S_{ij} by the relations

$$C_{ij} = (\partial x_s/\partial a_i)(\partial x_s/\partial a_j) = \delta_{ij} + 2\eta_{ij}, \tag{2.3}$$

$$D_{ij} = (\partial x_s/\partial X_i)(\partial x_s/\partial X_j) = \delta_{ij} + 2S_{ij}. \tag{2.4}$$

The quantities η_{ij}, being referred to an unstressed state, are the classical Lagrangian strain components which appear in Eqs. (1.2) and (1.3). The analogous quantities S_{ij} are referred to an arbitrary "initial" state.

Fundamentally the internal energy U may be regarded as a function of the configuration and either temperature T or entropy S, entropy being the natural choice when U is regarded as a thermodynamic potential. From rotational invariance, it can be shown that all nine deformation gradients $\partial x_i/\partial A_j$ need not appear. The six independent components of the symmetric tensor $(\partial x_s/\partial A_i)(\partial x_s/\partial A_j)$, together with the entropy and prescription of the master reference temperature T_M, suffice to determine U. Similarly, with fixed natural and initial states specified, U may be regarded as a function of (C_{ij}, S) or (D_{ij}, S). In the latter cases, the parameters used to fix the natural or initial states are present as parameters, just as T_M is present as a parameter when the deformation is referred all the way back to the "master" configuration. The variables needed in addition to T or S to determine U are called *substate* variables.[4]

We use the energy equation in the form[5]

$$\dot{U} - T\dot{S} = (1/\rho) T_{ij} d_{ij}, \tag{2.5}$$

where T_{ij} is the stress, assumed nondissipative,

$$d_{ij} = \tfrac{1}{2}[(\partial v_i/\partial x_j) + (\partial v_j/\partial x_i)], \tag{2.6}$$

v_i denoting the velocity components, and where the dot denotes the time derivative at a specified particle (i.e., the *material* time derivative). By differentiation of Eq. (2.4) with $\mathbf{X}$ fixed, using (2.6) and the definition of velocity, one readily finds

$$\dot{D}_{ij} = 2d_{km}(\partial x_k/\partial X_i)(\partial x_m/\partial X_j) \tag{2.7}$$

and hence

$$d_{ij} = \tfrac{1}{2}(\partial X_p/\partial x_i)(\partial X_q/\partial x_j)\dot{D}_{pq}. \tag{2.8}$$

III. CHOICE OF THERMODYNAMIC SUBSTATE VARIABLES

We seek a set of variables V_{ij} which makes the enthalpy (1.4) reduce to (1.1) under hydrostatic pressure. Each of these V_{ij} will be regarded as a function of the nine components D_{ij} (even though, because of symmetry, only six D_{ij} are independent):

$$V_{ij} = V_{ij}(D_{11}, D_{22}, D_{33}, D_{23}, \cdots). \tag{3.1}$$

By inversion, each D_{ij} can be regarded as a function of the nine V_{ij}. We can then write

$$\dot{D}_{pq} = (\partial D_{pq}/\partial V_{ij})\dot{V}_{ij}, \tag{3.2}$$

and from (2.8) and (3.2),

$$d_{ij} = \frac{1}{2}\frac{\partial X_p}{\partial x_i}\frac{\partial X_q}{\partial x_j}\frac{\partial D_{pq}}{\partial V_{rs}}\dot{V}_{rs}. \tag{3.3}$$

By substitution from (3.3) into (2.5), writing

$$\dot{U} = (\partial U/\partial V_{rs})\dot{V}_{rs} + (\partial U/\partial S)\dot{S}, \tag{3.4}$$

we find

$$\left(\frac{\partial U}{\partial V_{rs}}-(2\rho)^{-1}T_{ij}\frac{\partial X_p}{\partial x_i}\frac{\partial X_q}{\partial x_j}\frac{\partial D_{pq}}{\partial V_{rs}}\right)\dot{V}_{rs}+\left(\frac{\partial U}{\partial S}-T\right)\dot{S}=0, \quad (3.5)$$

whence

$$T=\partial U/\partial S, \quad (3.6)$$

$$\tau_{rs}\equiv\frac{\partial U}{\partial V_{rs}}=(2\rho)^{-1}T_{ij}\frac{\partial X_p}{\partial x_i}\frac{\partial X_q}{\partial x_j}\frac{\partial D_{pq}}{\partial V_{rs}}. \quad (3.7)$$

Now when the stress is hydrostatic pressure, $T_{ij}=-p\delta_{ij}$, and therefore

$$T_{ij}\frac{\partial X_p}{\partial x_i}\frac{\partial X_q}{\partial x_j}=-p\delta_{ij}\frac{\partial X_p}{\partial x_i}\frac{\partial X_q}{\partial x_j}=-pD^{(-1)}{}_{pq}. \quad (3.8)$$

Hence, $-\tau_{rs}V_{rs}$ reduces to

$$-\tau_{rs}V_{rs}=(p/2\rho)D^{(-1)}{}_{pq}(\partial D_{pq}/\partial V_{rs})V_{rs}. \quad (3.9)$$

Clearly, in order for this to sum up to p/ρ, we must have, when the stress is hydrostatic pressure,

$$D^{(-1)}{}_{pq}(\partial D_{pq}/\partial V_{rs})V_{rs}=2. \quad (3.10)$$

$D^{(-1)}{}_{pq}$ can be expressed in terms of the derivative of $\det\|D\|$ with respect to D_{pq}. For any nonsingular 3×3 matrix A, we have the formula[6]

$$\partial(\det\|A\|)/\partial A_{ij}=A^{(-1)}{}_{ji}\det\|A\|. \quad (3.11)$$

In view of (3.11) and the symmetry of D_{pq}, (3.10) becomes

$$[\partial(\det\|D\|)/\partial D_{pq}](\partial D_{pq}/\partial V_{rs})V_{rs}=2\det\|D\|$$

or

$$\frac{\partial J}{\partial V_{rs}}V_{rs}=J, \quad (3.12)$$

where we have introduced

$$J^2\equiv\det\|D\|=(\bar{\rho}/\rho)^2. \quad (3.13)$$

Now (3.12) will be satisfied if

$$(\partial J/\partial V_{rs})V_{rm}=\tfrac{1}{3}J\delta_{sm}, \quad (3.14)$$

because contraction on s and m in (3.14) yields (3.12). Multiplication of (3.14) by $V^{(-1)}{}_{mk}$ and use of (3.11) gives

$$\partial J/\partial V_{ks}=\tfrac{1}{3}JV^{(-1)}{}_{sk}=\tfrac{1}{3}J(\det\|V\|)^{-1}\partial(\det\|V\|)/\partial V_{ks}. \quad (3.15)$$

To satisfy (3.15), it is sufficient to have

$$\det\|V\|=mJ^3, \quad (3.16)$$

where m is any constant. Hence, in order for the enthalpy to reduce to the usual expression under hydrostatic pressure, it is sufficient to choose the thermodynamic substate tensor variables V_{rs} such that $\det\|V\|$ is proportional to the $\frac{3}{2}$ power of $\det\|D\|$. Three examples of such a tensor V_{rs} are

$$(1/3\bar{p})J^{1/3}D_{rs}, \qquad (1/3\bar{p})J^{2/3}D^{(1/2)}{}_{rs}, \qquad (1/3\bar{p})D^{(3/2)}{}_{rs},$$

where the constant m in (3.16) has been set equal to

$$m=(3\bar{p})^{-3}$$

in order to make $\tau_{rs}=-p\delta_{rs}$ at the initial configuration where $D_{rs}=\delta_{rs}$, if the stress at the initial configuration is $\bar{T}_{km}=-p\delta_{km}$.

Let us consider in more detail the third example:

$$V_{ij}=(1/3\bar{p})D^{(3/2)}{}_{ij} \quad\text{or}\quad D_{ij}=(3\bar{p})^{2/3}V^{(2/3)}{}_{ij}. \quad (3.17)$$

From (3.17) we have

$$\partial D_{pq}/\partial V_{rs}=(3\bar{p})^{2/3}(\partial V^{(2/3)}{}_{pq}/\partial V_{rs}). \quad (3.18)$$

The derivative in (3.18) can be evaluated at the initial state by invoking the power-series expansion of $V^n{}_{pq}$. Defining

$$v_{ij}\equiv(1/k)V_{ij}-I, \qquad k\equiv1/3\bar{p} \quad (3.19)$$

we have

$$V^n{}_{ij}=k^n(I+v_{ij})^n=k^n(I+nv_{ij}+\cdots), \quad (3.20)$$

whence

$$\begin{aligned}(\partial V^n{}_{pq}/\partial V_{rs})_0&=(\partial V^n{}_{pq}/\partial v_{ij})_0(\partial v_{ij}/\partial V_{rs})_0\\&=nk^n\delta_{pi}\delta_{qj}(k^{-1}\delta_{ir}\delta_{js})\\&=nk^{n-1}\delta_{pr}\delta_{qs}.\end{aligned} \quad (3.21)$$

In (3.21), the subscript 0 indicates evaluation at the initial state where $D=I$, and hence $V=I/3\bar{p}$. Setting $k=1/3\bar{p}$ and $n=\frac{2}{3}$ to obtain the derivative needed in (3.18), we find

$$(\partial D_{pq}/\partial V_{rs})_0=2\bar{p}\delta_{pr}\delta_{qs}. \quad (3.22)$$

From (3.22) and (3.7), we find that in the configuration $\mathbf{x}=\mathbf{X}$, the thermodynamic tensions τ_{rs} equal the initial stress components $\bar{T}_{rs}$.

With the thermodynamic substate variables given by the V_{ij} in (3.17), it is not difficult to obtain a general formula for the thermodynamic tensions under hydrostatic pressure that applies to all crystals except those of the monoclinic and triclinic classes. With these exceptions, the conventionally chosen Cartesian axes[7,8] are principal axes of D_{ij} for any pressure p. Thus, the matrices D_{ij} and V_{ij}, considered as functions of the time-dependent pressure $p(t)$, have constant eigenvectors. It follows that in this case V_{ij} and D_{ij} commute with their time derivatives, and the time derivative of the second equation in (3.17) can be expressed as

$$\dot{D}_{pq}=\tfrac{2}{3}(3\bar{p})^{2/3}V^{(-1/3)}{}_{pr}\dot{V}_{rq}=2\bar{p}D^{(-1/2)}{}_{pr}\delta_{sq}\dot{V}_{rs}. \quad (3.23)$$

As it stands, the coefficient of $\dot{V}_{rs}$ in (3.23) does not exhibit symmetry in pq and rs, but the same sum is obtained in (3.23) if this coefficient is replaced by the following symmetrized form, which, for the special cases under consideration, seems to be an acceptable expression for $\partial D_{pq}/\partial V_{rs}$:

$$\partial D_{pq}/\partial V_{rs}=\tfrac{1}{2}\bar{\rho}(D^{(-1/2)}{}_{pr}\delta_{sq}+D^{(-1/2)}{}_{ps}\delta_{rq}+D^{(-1/2)}{}_{qr}\delta_{sp}+D^{(-1/2)}{}_{qs}\delta_{rp}). \quad (3.24)$$

Finally, from (3.7), (3.8), and (3.24), we have

$$\tau_{rs}=-pJD^{(-3/2)}{}_{rs}, \quad (3.25)$$

where $J=\bar{\rho}/\rho$ as in (3.13).

Even when the stress is not hydrostatic pressure, if the stress system is such as to preserve the eigenvectors of D, then the thermodynamic tensions are related to the stress through the expression obtained by substituting from (3.24) into (3.7).

As a special case, the initial state may be chosen to be a natural unstressed state, in which case $X_i=a_i$, and D_{ij} and $\bar{\rho}$ in the preceding formulas become C_{ij} and ρ_0. However, it is interesting to note that *any* hydrostatically compressed state may be chosen as the initial state, and the enthalpy as defined here will reduce to $U+p/\rho$ for *all* pressures, while with the V_{ij} in (3.17), the thermodynamic tensions at the initial state will be equal to the initial stress.

In the special case of cubic crystals and isotropic media under hydrostatic pressure, D_{ij} remains spherical, and the substate variables and thermodynamic tensions reduce to

$$V_{ij}=\tfrac{1}{3}V\delta_{ij}, \qquad \tau_{rs}=-p\delta_{rs}. \quad (3.26)$$

The simplification already mentioned at the end of the Introduction results from the fact that in this case constant pressure corresponds to constant thermodynamic tensions for all pressures.

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Energy Bands and the Optical Properties of LiCl*

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Using a recently developed local-orbital theory of the author's, the ground-state eigenfunctions of the LiCl crystal in the Hartree-Fock approximation have been obtained. Using these functions to form the crystal charge density, the one-electron energy bands have been computed in essentially the Hartree-Fock approximation using the mixed-basis technique. Various levels of approximation within the local-orbital approximation are investigated. Polarization corrections to the energy bands are included by the method of Fowler. Finally, using tight-binding interpolation for the valence levels and empirical pseudopotentials for the conduction bands, the density of states for the valence and conduction states are obtained, and a joint density of states is computed. Extensive experimental comparisons are made. The principal results are the following: (1) The valence bands are very wide ($3p$ band is about 8 eV wide). (2) The soft x-ray spectrum can be interpreted in terms of the band structure. (3) Polarization corrections are significant.

I. INTRODUCTION

In recent years, energy-band calculations on the alkali halide crystals have become common. While these calculations are extremely useful for qualitative interpretation of optical-absorption measurements and also electron energy-loss data, the theoretical situation is not fully satisfactory. Firstly, there is no general agreement as to how one chooses a model potential for computing alkali halide band structures, and different types of potentials can yield greatly differing results.[1] Secondly, when one chooses a model potential for such a calculation, Koopmans's theorem is violated, and the resultant one-electron eigenvalues are not the electron binding energies.[2] Thus the agreement of such a calculation with experiment is fortuitous. Most recent band calculations are of this nature.[3–6] Other recent calculations have attempted to use the correct Fock exchange.[7,8] In the cases in which the Fock exchange was used, no attempt at self-consistency was made. In addition, in the case of Oyama and Miyakawa[7] the Fock exchange was considered in an approximate way.[9] In the calculations by Kucher, Tolpygo, Tomasevich, and Evseev (KTTE),[8] the tight-binding method was employed for the conduction band, and so few states were included in the tight-binding expansion so that the accuracy of such calculations is in doubt and the d states are neglected.

Only KTTE attempt to include polarization effects in their energy-band calculations. An excellent discussion of these techniques has been recently given by