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ON SHEAR-INDUCED PHASE TRANSITIONS IN PERFECT CRYSTALS

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Abstract—This is an analysis of structural phase transitions in b.c.t. crystals controlled by tensile loading along a crystallographic axis.

1. INTRODUCTION

This work aims to provide a model analysis of phase transitions induced by the non-hydrostatic loading of perfectly elastic single crystals. We pursue an approach initiated in[1], allowing changes where the crystal lattice ceases to be a simple lattice. The calculations of[1] have to do with transitions controlled by temperature in unloaded body-centred (b.c.) crystals, and the emphasis is placed there upon a systematic formulation of the symmetry aspects of the problem. Perhaps the most striking result of[1] is that the isothermal elastic Green strain moduli are discontinuous at any transition point which involves a change in structure of the lattice. Here we concentrate upon the stability aspects of phase transitions in b.c. tetragonal (b.c.t.) crystals controlled by tensile loading in the direction of the exceptional crystallographic axis.

Imagine the following situation. An unloaded b.c.t. crystal sits in equilibrium with the lattice spacing in the 1-direction, say, strictly less than the lattice spacings in the other two equivalent crystallographic directions. A tensile load is monotonely applied in the 1-direction. If the crystal responds to the loading by stretching in the 1-direction and by contracting in the 2- and 3-directions equally, then it will reach a stage where the three lattice spacings are equal, so that there the configuration is b.c. cubic (b.c.c.). By the symmetry of the b.c.c. configuration, the loading there must be hydrostatic and therefore the load in the 1-direction must vanish as do the loads on the "lateral" faces of the crystal. This conflicts with the supposed monotone increase of the load.

It is easy to formalize this hypothetical behaviour; in infinitesimal isotropic elasticity, the presumption would be that both Young's modulus and Poisson's ratio are positive. The conflict regarding the load is avoided if there are unstable points on the primary equilibrium path from the unloaded b.c.t. configuration to the final b.c.c. configuration, for then the cubic state is not accessible in the experiment. Clearly, there is an analogous situation in compression. We choose to discuss the tension test so as to avoid inessential discussions of axes of equilibrium and also some subtleties of symmetry.

As in[2], we may categorize the instabilities as being of the second "kind" or of the first "kind" according as to whether or not the crystal geometry changes continuously at the transition. The analysis deals explicitly only with transitions of the second kind, which we divide, as in[1], into configurational and structural "types". In configurational changes, the b.c.t. lattice deforms as a simple lattice, the atoms of the lattice move as if they were embedded in the homogeneous deformation of a continuum. Contrastingly, in structural changes sublattices which compose the crystal begin to move independently of one another, for example, the lattice consisting of the "centre atoms" of the b.c.t. crystal may begin to move independently of the sublattice based upon the conventional crystallographic axes. In fact, the analysis deals with just this one possibility.

So as to give prominence only to the essential points of the analysis, various simplifications are introduced. Specifically, and without further reference, "genericity" is used to discount "excess" relations between material parameters, in the sense that the one degree of freedom afforded by the tensile load allows only one relation between material parameters. Also, only transitions to configurations with at least orthorhombic symmetry are allowed, as in[1], and, correspondingly, elastic stability is assessed only with respect to orthorhombic variations in the unit cell geometry. There would be formidable algebraic problems were these simplifications not employed, and this is taken as sufficient justification at this early stage.

We shall use the following jargon. A transition is *possible* when there is a bifurcation from the primary equilibrium path in any geometric variable, i.e. at a critical point on that path. If the critical point is stable, we shall say that a transition of the second kind is *observable* there, otherwise, we presume that there will be a transition of the first kind. It will be shown that *the kind of the transition and the type of the transition depend critically on the nature of the loading device employed in the assessment of elastic stability.*

2. LOADING DEVICES AND ELASTIC STABILITY

(a) *Configurational changes*

In configurational changes, the lattice geometry is specified by the behaviour of the usual lattice vectors, i.e. the three orthogonal e_i which are the edges of the conventional b.c.t. unit cell. On the primary path of deformation, where the crystal is b.c.t.,

$$|e_1| \leq |e_2| = |e_3|. \tag{1}$$

The centre atom of the unit cell remains exactly in the centre in any configurational change, so that the crystal deforms throughout as a simple lattice. The e_i are assumed to vary smoothly through the change, and we suppose that

$$e_i = AE_i, \tag{2}$$

where the E_i are the reference values of the e_i, in the unloaded b.c.t. configuration, and A is the matrix of macroscopic deformation gradients. The strain energy per unit volume of the crystal, w say, presumably depends only on the e_i, and via (2),

$$w = w(A). \tag{3}$$

By the frame indifference of w, putting

$$C = A^T A, \tag{4}$$

with A^T the transpose of A, (3) reduces to

$$w = w(C) = w(E) = w(\Lambda), \tag{5}$$

in a loose notation, with E the Green strain and Λ the symmetric and positive definite right stretch tensor in the polar decomposition

$$A = R\Lambda, \tag{6}$$

with R orthogonal.

Consider, first of all, the dead loading device, where the surface tractions are compatible with a fixed uniform value of the nominal stress, N^0 say. The potential energy of the system is then

$$\phi_d(A) \overset{\text{def}}{=\!=} w(A) - \operatorname{tr} N^0 A, \tag{7}$$

where tr N^0A represents the trace of the matrix product N^0A. On the given primary path of deformation, with the unloaded configuration as reference, N^0 is symmetric and so identical to the symmetrized Biot stress, τ^0 say, which is the stress tensor associated with Λ via work conjugacy. In orthorhombic configurations of the crystal, where A is diagonal, there is then the identity

$$\phi_d(A) \equiv \phi_s(\Lambda) \overset{\text{def}}{=\!=} w(\Lambda) - \operatorname{tr}(\tau^0\Lambda). \tag{8}$$

The potential $\phi_s(\Lambda)$ corresponds to a "stretch" loading device. The stretch and dead loading devices are identical in this instance, by virtue of (8), as noted in[3]. Henceforward, we shall refer to the stretch device in preference to the dead loading device.

Consider, secondly, the "Green strain" loading device, where the vector representing the surface tractions behaves as if it were embedded in the deformation. The corresponding potential energy is

$$\phi_g(E) \overset{\text{def}}{=\!=} w(E) - \operatorname{tr}(t^0 E), \tag{9}$$

where t^0 is the stress tensor conjugate to E, sometimes called the second Piola-Kirchhoff stress tensor, whose components are identical to the contravariant components of the Kirchhoff stress tensor on an embedded basis coincident with the background axes in the reference state.

With these potentials and their arguments denoted generically by ϕ and q_{rs} respectively (with $q_{rs} = q_{sr}$), equilibrium points of the system are given by the stationary points of ϕ, where

$$\frac{\partial \phi}{\partial q_{rs}} = 0. \tag{10}$$

If there is more than one equilibrium path, $q_{rs}(\epsilon)$ say, through such a stationary point, then, by differentiating (10) with respect to ϵ,

$$\frac{\partial^2 \phi}{\partial q_{ij} \partial q_{kl}} \delta \bar{q}_{kl} = 0, \tag{11}$$

for some non-trivial

$$\delta \bar{q}_{kl} = \frac{\mathrm{d} q_{kl}}{\mathrm{d}\epsilon} \delta\epsilon. \tag{12}$$

The trivial path through the stationary point is q_{rs} = constant. When (11) holds,

$$\det \frac{\partial^2 \phi}{\partial q_{ij} \partial q_{kl}} = 0, \tag{13}$$

where det stands for the determinant, so the implicit function theorem fails at such critical points. When (11) or (13) holds, there is the possibility of a configurational transition.

Adopting the traditional energy criterion of stability, a stationary point is judged stable if and only if the potential there is a strict absolute minimum. It is necessary for stability, therefore, that

$$\frac{\partial^2 \phi}{\partial q_{ij} \partial q_{kl}} \delta q_{ij} \delta q_{kl} \geq 0, \tag{14}$$

for all increments δq_{ij}. We suppose that (14) holds strictly in the reference configuration. When (14) first fails to be strict on the primary path of deformation, (11) holds. The stability of a critical point rests upon the positive definiteness of the higher order terms, in an expansion of ϕ with respect to q_{ij}. It is clearly necessary for stability, via (11), that

$$\frac{\partial^3 \phi}{\partial q_{ij} \partial q_{kl} \partial q_{mn}} \delta \bar{q}_{ij} \delta \bar{q}_{kl} \delta \bar{q}_{mn} = 0. \tag{15}$$

If (15) fails, the critical point is unstable. These third order terms must vanish solely by virtue of the symmetry of the configuration. They may not vanish by virtue of some equality between material parameters, for that would not be a generic property (the one allowed relation between material parameters being (13)). This is the kind of argument used by Landau[2].

Additionally to (15), the corresponding fourth order terms must be strictly positive definite, discounting semidefiniteness via genericity. This requirement amounts to inequalities among material parameters, so that *if* (15) *holds at a critical point, a configurational transition is observable in some materials.*

(b) *Structural changes*

The geometry of a structural change requires the specification of the vector representing the position of a typical "centre atom" of a b.c.t. cell, p say, as well as the lattice vectors e_i. When the lattice is b.c.,

$$p = \frac{1}{2}\sum_i e_i. \tag{16}$$

We envisage a change where

$$\pi \overset{\text{def}}{=\!=} p - \frac{1}{2}\sum_i e_i, \tag{17}$$

becomes non-zero. When $\pi \neq 0$, the crystal lattice is generally no longer a simple lattice, and it is most simply viewed as the superposition of two congruent simple lattices, in the terminology of [4] as a 2-lattice. The strain energy function is determined solely by the geometry, so that

$$w = w(\pi, e_i). \tag{18}$$

By frame indifference, we can write

$$w = w(\pi_i, \eta_{jk}), \tag{19}$$

with

$$(\pi)_i = \pi_i \overset{\text{def}}{=\!=} \pi \cdot e_i, \quad \eta_{jk} \overset{\text{def}}{=\!=} e_j \cdot e_k, \tag{20}$$

with $(\pi)_i$ connoting the i component of the triplet π. Further, via (2),

$$w = w(\pi, C) = w(\pi, E) = w(\pi, \Lambda), \tag{21}$$

in a loose notation, with the assumption that the e_i are embedded in the macroscopic deformation. Note that, from [1],

$$w(\pi, C) = w(-\pi, C), \tag{22}$$

via the symmetry and monatomicity of the crystal.

With this flexibility of geometry, the potential energies corresponding to the Green strain and stretch loading devices are given by

$$\phi_g(\pi, E) = w(\pi, E) - \operatorname{tr}(t^0 E), \tag{23}$$

$$\phi_s(\pi, \Lambda) = w(\pi, \Lambda) - \operatorname{tr}(\tau^0 \Lambda), \tag{24}$$

assuming that there are no applied forces which do work in changing π.

Stability must now be assessed with respect to variations of π as well as with respect to (diagonal) variations in E and Λ. With the potentials and their arguments denoted generically by ϕ and π_i, q_{jk} respectively, we choose first to all to determine the absolute minimum of ϕ at a given q_{ij}. Thus we determine the stationary points of ϕ with respect to π via

$$\frac{\partial \phi}{\partial \pi_i} = 0, \tag{25}$$

giving $\pi_i = \pi_i(q_{jk})$, and then determine the absolute minimum amongst the branches of this function. When

$$\det\left(\frac{\partial^2\phi}{\partial\pi_i\partial\pi_j}\right) \neq 0, \tag{26}$$

there is an unique solution of (25), and via (22), (23) and (24) that is the trivial solution $\pi_i = 0$. On the other hand, when

$$\det\left(\frac{\partial^2\phi}{\partial\pi_i\partial\pi_j}\right) = 0, \tag{27}$$

there is the possibility of a structural transition, and there is generally a non-trivial solution $\pi_i = \pi_i(q_{jk})$ of (25). The third order derivatives of ϕ with respect to π_i vanish in any b.c. configuration, again via (22), (23) and (24), so that there is a range of materials where the critical point corresponds to a strict relative minimum of ϕ with respect to variations of π_i. The absolute minimum of ϕ is given by

$$\bar{\phi}(q_{jk}) \overset{\text{def}}{=\!=} \min\{\phi(\pi_i(q_{jk}), q_{jk})\}, \tag{28}$$

where the minimisation is over all the branches of the function $\pi_i(q_{jk})$. If the equilibrium path corresponding to this absolute minimum of ϕ is not the trivial path, then *there is an observable structural transition* in some materials, for stability with respect to variations of q_{jk} rests solely upon *inequalities* arising from the positive definiteness of the second order terms of $\bar{\phi}(q_{jk})$.

3. CONFIGURATIONAL TRANSITIONS

According to Section 2(a), the symmetry of the crystal decides whether or not a configurational transition is possible. With G any element of the tetragonal point group, corresponding to the symmetry of the unloaded reference configuration,

$$w(C) = w(G^TCG). \tag{29}$$

At the common fixed points of the mappings

$$C \to G^TCG, \tag{30}$$

where the crystal configuration is at least tetragonal, there are then the relations

$$\frac{\partial w}{\partial c_{ij}} = g_{ip}g_{jq}\frac{\partial w}{\partial c_{pq}}, \quad \frac{\partial^2 w}{\partial c_{ij}\partial c_{kl}} = g_{ip}g_{jq}g_{kr}g_{ls}\frac{\partial^2 w}{\partial c_{pq}\partial c_{rs}}, \tag{31}$$

where c_{ij} and g_{ij} are the elements of C and G, respectively. It follows from $(31)_1$ that

$$\frac{\partial w}{\partial c_{ij}} = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & b \end{pmatrix}_{ij}, \tag{32}$$

say, with the exceptional axis in the 1-direction, and from $(32)_2$ that

$$\frac{\partial^2 w}{\partial c_{ii}\partial c_{jj}} = \begin{pmatrix} l & n & n \\ n & m & p \\ n & p & m \end{pmatrix}_{ij}, \tag{33}$$

where the summation convention is suspended.

In a Green strain loading device, with

$$\delta e_{ij} = \frac{1}{2}\begin{pmatrix} \delta c_{11} & 0 & 0 \\ 0 & \delta c_{22} & 0 \\ 0 & 0 & \delta c_{33} \end{pmatrix}_{ij}, \tag{34}$$

corresponding to the allowed orthorhombic variations, the determinantal condition allowing the possibility of a configurational transition becomes

$$(p - m)(2n^2 - l\{m + p\}) = 0. \tag{35}$$

Corresponding to the relation $2n^2 = l\{m + p\}$, there is the eigenmode

$$-\frac{l}{2n}\delta e_{11} = \delta e_{22} = \delta e_{33}, \tag{36}$$

and corresponding to the relation $p = m$, there is the eigenmode

$$\delta e_{11} = 0, \quad \delta e_{22} = -\delta e_{33}. \tag{37}$$

To assess the stability of these two critical points, and the associated eigenmodes, we have to consider the third order terms of (15). The terms may be calculated directly, by equations like (31), or we can observe, from [5], that any polynomial satisfying (29) is expressible as a polynomial in the three quantities

$$c_{11}, \quad c_{22}c_{33}, \quad c_{22} + c_{33}, \tag{38}$$

in orthorhombic configurations. By equations like (31), it is clear that the polynomial

$$\xi(\delta c_{ij}) = \frac{\partial^3 w}{\partial c_{ij}\partial c_{kl}\partial c_{mn}}\delta c_{ij}\delta c_{kl}\delta c_{mn}, \tag{39}$$

has the property

$$\xi(\delta c_{ij}) = \xi(g_{ip}g_{jq}\delta c_{pq}). \tag{40}$$

Since ξ is a homogeneous polynomial of degree three, it follows that

$$\xi(\delta c_{ij}) = \alpha\delta c_{11}\delta c_{22}\delta c_{33} + \beta\delta c_{11}^2(\delta c_{22} + \delta c_{33}) + \gamma\delta c_{22}\delta c_{33}(\delta c_{22} + \delta c_{33}), \tag{41}$$

for some α, β, γ, in orthorhombic configurations.

None of the three linearly independent terms in (41) vanishes in the first eigenmode, but they all vanish in the second eigenmode. Thus the critical point corresponding to $2n^2 = l\{m + p\}$ is unstable, but there is an observable, plane, isochoric, configurational, tetragonal-orthorhombic transition, corresponding to $p = m$, in the Green strain device.

For the stretch device, we need the symmetry properties of the derivatives of w with respect to Λ. Note that in the mapping

$$A \to AG = (RG)(G^T\Lambda G), \tag{42}$$

by the uniqueness of the polar decomposition, there is induced

$$\Lambda \to G^T\Lambda G, \tag{43}$$

so that the tetragonal symmetry of the reference configuration requires that

$$w(\Lambda) = w(G^T\Lambda G). \tag{44}$$

Comparing (29) and (44), it is evident that the discussion runs exactly parallel to that of the Green strain device.

Some limited comparison of the stability criteria corresponding to the two devices is possible, as in [3, 6]. By virtue of the relation,

$$\frac{\partial^2 \phi_s}{\partial \Lambda_{ij} \partial \Lambda_{kl}} = \text{symm}\left\{\Lambda_{jm}\Lambda_{ln}\frac{\partial^2 \phi_g}{\partial e_{im}\partial e_{kn}} + t^0_{ik}\delta_{jl}\right\}, \tag{45}$$

noted in[3], where symm denotes symmetrization with respect to the interchanges $i \leftrightarrow j$, $k \leftrightarrow 1$, and δ_{jl} is the Kronecker delta, it follows that under tensile load

$$\frac{\partial^2 \phi_g}{\partial e_{ij}\partial e_{kl}}\delta e_{ij}\delta e_{kl} > 0 \rightarrow \frac{\partial^2 \phi_s}{\partial \Lambda_{ij}\partial \Lambda_{kl}}\delta \Lambda_{ij}\delta \Lambda_{kl} > 0. \tag{46}$$

That is to say, a configurational transition in the Green strain device necessarily *precedes* a transition in the stretch device, on the primary loading path. Let us denote the applied tensile load by σ. If the first and second critical points in the Green strain device occur when $\sigma = \sigma_{g1}$ and σ_{g2} respectively, and in the stretch device when $\sigma = \sigma_{s1}$ and σ_{s2} respectively, then

$$\min(\sigma_{g1}, \sigma_{g2}) < \min(\sigma_{s1}, \sigma_{s2}). \tag{47}$$

4. STRUCTURAL TRANSITIONS

The analysis of[1] provides the basis of this section. The main points of that work are summarized below.

With w depending only on the current configuration of the atoms in the crystal lattice, w must be indifferent to any rearrangement of the atoms in the 2-lattice. Thus

$$w(p, e_i) = w(p + x, M_{ij}e_j), \tag{48}$$

where x is in the lattice generated by the e_i, and M_{ij} is unimodular with integer entries[7]. Via frame indifference, which gives

$$w(p, e_i) = w(p \cdot e_i, \eta_{jk}), \tag{49}$$

eqn (48) translates to

$$w(p \cdot e_i, \eta_{jk}) = w(M_{ij}e_j \cdot (p + x), M_{jr}M_{ks}\eta_{rs}), \tag{50}$$

identically in $p \cdot e_i$ and η_{jk}. For those M_{ij} where there exists such an x that

$$p \cdot e_i = M_{ij}e_j \cdot (p + x), \quad \eta_{jk} = M_{jr}M_{ks}\eta_{rs}, \tag{51}$$

there are the relations

$$\frac{\partial w}{\partial(p \cdot e_i)} = M_{ji}\frac{\partial w}{\partial(p \cdot e_j)}, \quad \frac{\partial w}{\partial \eta_{jk}} = M_{rj}M_{sk}\frac{\partial w}{\partial \eta_{rs}}, \text{ etc.} \tag{52}$$

The M_{ij} so selected generally form a subgroup of the lattice group[8], conjugate to the tetragonal point group. In the case at hand, all of these groups are identical, so that, rewriting equations like (52) in terms of the arguments π_i and η_{jk}, we have

$$\frac{\partial w}{\partial \eta_{jk}} = g_{rj}g_{sk}\frac{\partial w}{\partial \eta_{rs}}, \quad \frac{\partial^2 w}{\partial \pi_i \partial \pi_j} = g_{ri}g_{sj}\frac{\partial^2 w}{\partial \pi_r \partial \pi_s}, \text{ etc.} \tag{53}$$

From (53), it follows that

$$\frac{\partial^2 w}{\partial \pi_i \partial \pi_j} = \begin{pmatrix} r & 0 & 0 \\ 0 & s & 0 \\ 0 & 0 & s \end{pmatrix}_{ij}, \tag{54}$$

say, so that the determinantal condition (26) allowing the possibility of structural changes becomes

$$rs^2 = 0. \tag{55}$$

So if either r or s vanishes, then by Section 2(b) there is a range of materials where a structural transition may be observed. It is as well to be sure that the inequalities arising from the stability conditions are self-consistent, for there are some novel features in the analysis of [1]. Let us assume that $r = 0$ when $\sigma = \sigma_r$ say. Then, from [1], there are three solutions of the equations corresponding to (25) in the Green strain device, and they are the trivial solution together with

$$\pi_1 = \pm(-N_1/b_1)^{1/2}, \quad \pi_2 = \pi_3 = 0, \tag{56}$$

when $N_1/b_1 < 0$, to lowest order in the increments δe_{ij}, with

$$N_1 \stackrel{\text{def}}{=\!=} \sum_i \frac{1}{4} \frac{\partial^2 w}{\partial \pi_1{}^2 \partial e_{ii}} \delta e_{ii}, \tag{57}$$

$$b_1 \stackrel{\text{def}}{=\!=} \frac{1}{4!} \frac{\partial^4 w}{\partial \pi_1{}^4}. \tag{58}$$

By tests like those in [2, 9], the critical point is found to be a relative minimum provided b_1 is positive. Substituting the trivial solution $\pi_i = 0$ into $\phi_g\ (\pi_i, \delta e_{jk})$, we obtain

$$\phi_{g0} \stackrel{\text{def}}{=\!=} \phi_g(0, \delta e_{jk}). \tag{59}$$

Each of the solutions (56), on substitution, gives

$$\phi_{g1} \stackrel{\text{def}}{=\!=} -\frac{N_1{}^2}{b_1} + \phi_g(0, \delta e_{jk}), \tag{60}$$

when N_1 is negative. There is no real branch of solutions otherwise. Evidently,

$$\phi_{g1} < \phi_{g0}, \tag{61}$$

when N_1 is negative. So the absolute minimum of ϕ_g, with respect to variations of π, corresponds to the trivial path when N_1 is positive, (for the trivial path is then the only branch of solutions), it corresponds to one of the paths given by (56) when N_1 is negative, by virtue of (61). Thus, the stability of the critical point rests finally upon the positive definiteness of the second order terms of the function.

$$\bar{\phi}_g(\delta e_{ij}) = \left.\begin{matrix} \phi_{g0}, & N_1 > 0 \\ \phi_{g1}, & N_1 < 0 \end{matrix}\right\}. \tag{62}$$

It is clear that if the second order term in an expansion of ϕ_{g0} is positive definite, so is the corresponding term in an expansion of ϕ_{g1}, provided the parameters

$$\left(\frac{\partial^2 w}{\partial \pi_1{}^2 \partial e_{ii}} \cdot \frac{\partial^2 w}{\partial \pi_1{}^2 \partial e_{jj}}\right) \Big/ b_1 \tag{63}$$

are small enough, by virtue of (57) and (60). Thus the inequalities are self consistent, and we can expect to observe a transition to an eigenmode of the form (56) in some materials. The non trivial path here corresponds to a tetragonal configuration of the crystal, since only π_1 is non-zero in (56). The existence of such a tetragonal–tetragonal transition would be inferred in practice by the discontinuity of the first order Green strain moduli that is evident from (60).

There is a more careful discussion of the transition in[1]. One point to note is that $\bar{\phi}_g$ does not differentiate between π and $-\pi$, via (22). When the crystal reaches the critical point on the trivial path, it cannot select either one of these (stable) branches in preference to the other. So it seems rather likely that the equilibrium configurations of the crystal will be twinned beyond the critical point. There are similar remarks in[10].

Here we are interested primarily in the comparison of the transitions which occur in the Green strain and stretch devices.

A parallel analysis holds for the stretch device. Via (21), (23) and (24),

$$\frac{\partial^2 \phi_g}{\partial \pi_i \partial \pi_j}(\pi, E) = \frac{\partial^2 w}{\partial \pi_i \partial \pi_j}(\pi, E) = \frac{\partial^2 w}{\partial \pi_i \partial \pi_j}(\pi, \Lambda) = \frac{\partial^2 \phi_s}{\partial \pi_i \partial \pi_j}(\pi, \Lambda), \tag{64}$$

so that if a structural transition is possible in the Green strain device, a corresponding transition is possible in the stretch device. In fact it is evident that

$$w(\pi(E), E) = w(\pi(\Lambda), \Lambda), \tag{65}$$

when $\pi(E)$ and $\pi(\Lambda)$ are parametrisations of the same path. So as a check on the analysis, we note that, in (62), N_1 is independent of the choice of strain measure, via the measure invariance of the increment of strain energy

$$\delta w = \sum_i \frac{\partial w}{\partial q_{ii}} \delta q_{ii}. \tag{66}$$

With (65) and the implication corresponding to (46), it follows that if a structural transition may be observed, in a given material, in a Green strain device, then a corresponding transition may be observed, in the same material, in a stretch device at the identical load level, σ_r. The converse is generally false.

5. SUMMARY

With these observations, it is straightforward to catalogue the various transitions. Let us attach the label (D, K, T) to any transition, where in any one instance, D represents the loading device, either G (Green) or S (stretch), K represents the kind, either 1 (first) or 2 (second), and T represents the type, c (configurational) or s (structural) or blank (if $K = 1$). Recapping previous notation, critical points allowing configurational changes occur when $\sigma = \sigma_{g1}$ and σ_{g2} in a Green strain device, when $\sigma = \sigma_{s1}$ and σ_{s2} in a stretch device. Structural changes of the form (56) are allowed when $\sigma = \sigma_r$. (We omit all consideration of structural changes corresponding to $s = 0$.) When $\sigma = \sigma_r$, and with (46), there are three relevant possibilities:

(1) the second order terms in $\bar{\phi}_g$ are positive definite, so are those in $\bar{\phi}_s$;
(2) the second order terms in $\bar{\phi}_g$ are not positive definite, those in $\bar{\phi}_s$ are positive definite;
(3) neither set of terms in positive definite.

It is most convenient to represent the results in the form of a table, the *two* entries in each compartment of the table representing the first transitions observed in the two sorts of loading device. The rows of the table correspond to the possibilities (1), (2) and (3) above.

For the sake of brevity, we shall assume that $\sigma_{g2} < \sigma_{g1} < \sigma_{s2} < \sigma_{s1}$, and that the critical points corresponding to $\sigma = \sigma_{g2}$ and $\sigma = \sigma_{s2}$ are both stable. This choice will give the full range of results announced in the introduction. There is no difficulty in cataloguing the full range of possibilities:

Table 1.

	$\sigma_r < \sigma_{g2}$	$\sigma_{g2} < \sigma_r < \sigma_{g1}$	$\sigma_{g1} < \sigma_r < \sigma_{s2}$	$\sigma_{s2} < \sigma_r < \sigma_{s1}$	$\sigma_{s1} < \sigma_r$
(1)	$(G, 2, s)$, $(S, 2, s)$	$(G, 2, c)$, $(S, 2, s)$	$(G, 2, c)$, $(S, 2, s)$	$(G, 2, c)$, $(S, 2, c)$	$(G, 2, c)$, $(S, 2, c)$
(2)	$(G, 1,)$, $(S, 2, s)$	$(G, 2, c)$, $(S, 2, s)$	$(G, 2, c)$, $(S, 2, s)$	$(G, 2, c)$, $(S, 2, c)$	$(G, 2, c)$, $(S, 2, c)$
(3)	$(G, 1,)$, $(S, 1,)$	$(G, 2, c)$, $(S, 1,)$	$(G, 2, c)$, $(S, 1,)$	$(G, 2, c)$, $(S, 2, c)$	$(G, 2, c)$ $(S, 2, c)$

As is evident from compartments 12, 13, 22, 23, the type of the transition depends on the loading device, and from compartments 21, 32, 33, the kind of the transition depends on the loading device.

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