Int. J. Solids Structures, Vol. 17, pp. 361–378, 1981
Printed in Great Britain.

0020-7683/81/040361-18$02.00/0
Pergamon Press Ltd.

ON PHASE TRANSITIONS INVOLVING INTERNAL STRAIN

GARETH P. PARRY†

Department of Mechanics, The Johns Hopkins University, Baltimore, Maryland, U.S.A.

(*Received* 16 *September* 1980)

Abstract—This is an analysis of continuous phase transitions at body centred tetragonal configurations of nonlinearly elastic monatomic crystals. The aim is to assess the implications of molecular theory with regard to a thermoelastic description of the transitions by means of a prototype calculation which models a change in invariance of the constitutive equation. As a by-product of the investigation, the status of the Cauchy–Born hypothesis becomes evident. The most striking result is that the isothermal elastic moduli suffer a finite discontinuity precisely at the transition point.

INTRODUCTION

This is an analysis of a specific class of phase transitions in monatomic crystals. The spirit of the work is very much that of the classical theory of Landau[1], in the sense that the starting assumption is the analyticity of a certain potential and in the sense that the analysis relies on notions of genericity. The aim of this paper is to elaborate Landau's ideas and to give fairly detailed coverage of the implications of molecular theory for the thermoelastic description of the transitions.

The phase transitions considered here occur with changes of invariance of the consitiutive equation. Most continuum models of material behaviour do not allow such changes of invariance. Hopefully, then, the calculations would be of interest if they served only to model this phenomenon. The work shows that a change in invariance induces a roughness in various potentials, notably the thermoelastic potential. This is, perhaps, the main result of the analysis and it puts in perspective those calculations which presume the analyticity, or smoothness, of the thermoelastic potential.

Additionally, in the context of thermoelasticity, the analysis makes clear the status of the Cauchy–Born hypothesis. This hypothesis, that lattice vectors are embedded in the macroscopic deformation of the crystal, has been used almost unquestioningly in the past. It will be evident that the hypothesis holds for some sets of lattice vectors, but not for others. Then, there is indeed a consistent route to thermoelasticity theory.

Leaving the first order transitions aside, we consider only transitions which occur with continuous changes in the geometry of a crystal. Landau's theory of the physics of such changes is concerned in part with the prediction of exclusion rules, disallowing some changes on the grounds of generic stability. It is convenient, at the outset, to divide these continuous changes into two categories. In the first category place changes consequent upon the homogeneous deformation of a unit cell of a simple lattice, such as the cubic-tetragonal transition which arises from the stretching of a cubic crystal lattice parallel to one of the cubic axes. These changes are reflected in a change of symmetry in the macroscopic configuration of the crystal, so we shall label these as "configurational transitions". In the second category place transitions arising from the relative displacement of lattices which compose the crystal, e.g. the cubic-tetragonal transition deriving from the displacement, parallel to one of the cubic axes, of a lattice composed of the "centre atoms" of a body centered cubic (b.c.c.) crystal. Here the symmetry change comes from an "internal" change in the crystal. Loosely, the lattice vectors describing the macroscopic configuration do not alter, but there is a definite change of symmetry. We shall call these "structural transitions". Only in this latter category is there a change in invariance of the constitutive equation. The symmetry change in the first category is a change of symmetry of the equilibrium configuration, not of the constitutive equation.

Both categories of change fall under Landau's concept of transitions of the second kind. Landau's treatment of these transitions is based upon the notion of order parameters, which

†On leave from the School of Mathematics, University of Bath, Bath, Avon, England.

measure the deviation of the system from a given symmetrical configuration and upon the assumption that the thermodynamic potential is a smooth function of these parameters. In the first mentioned example, a suitable order parameter would be the strain in the direction of stretching; in the second example, the displacement of a typical centre atom would suffice.

As noted by Ericksen[2], there are some difficulties with Landau's formulation of the problem. Using Landau's ideas, Anderson and Blount[3] have shown that the transition point corresponding to a configurational cubic-tetragonal transition is generically unstable in the sense of the traditional energy criterion of stability. On the other hand, Batterman and Barrett[4] claim to have observed a cubic-tetragonal transition of the second kind in the superconducting material vanadium silicon V_3Si. If we accept Batterman and Barrett's conclusions, then this leads us to suspect that either there is a flaw in Landau's theory or that the observed transition is not a configurational change, in the words of Anderson and Blount, involving "some change in internal symmetry other than mere strain." Landau himself points out a possible deficiency of this analysis, "we must expect that mathematically a phase transition point of the second kind is a singularity of the thermodynamic quantities and in particular of the thermodynamic potential Φ; the nature of the singularity is not yet known... It must be emphasized that the possibility of..an expansion (of Φ in terms of the order parameters) is by no means obvious *a priori*. Moreover... there is every reason to suppose that such an expansion cannot be continued to terms of arbitrarily high order... Here we shall give a theory based on the assumption that the presence of the singularity does not affect the terms of the expansion that are used." It is therefore of interest to assess the implications of less stringent smoothness requirements than those employed by Landau and Ericksen[2] has done this recently in the context of thermoelasticity theory. In that paper, Ericksen shows that the exclusion rule derived by Anderson and Blount, using Landau's ideas, can fail if one uses ideas of genericity appropriate to rougher function spaces. This at least relieves us of the contradiction between Anderson and Blount's theory and Batterman and Barrett's experiment.

The other possibility that Anderson and Blount did not cover explicitly is that the V_3Si change is a structural change. As a first step to understanding such transitions, we shall deal with the change from body centered tetragonal (b.c.t.) states of a monatomic crystal to states where the lattice of "centre atoms" is displaced relative to the centre. The analysis covers in particular transitions from b.c.c. to tetragonal states. With an assumption like that of Landau regarding the free energy, it follows that the transition point may be stable but that the isothermal elastic moduli in the corresponding thermoelasticity theory are discontinuous at the transition. The transitions are not then of second order, in the sense that Ericksen[2], say, understands the term. (They are, of course, of the second kind.) One can argue that sufficiently refined experiments will show that no transition is of second order. Indeed, Mynuck[5] states "..it is now impossible to find even one well documented example of a second order transition! Even the example chosen by Landau and Lifshitz for a typical second order transition... has been shown to be incorrect." However, Batterman and Barrett state that the V_3Si transition is "consistent with a second order... phase transformation." The analysis in this paper applies only to monatomic crystals, so we cannot say unreservedly that the V_3Si transitions fit this mould and therefore that the theory, as it stands, is inadequate in some respect. Nevertheless it seems likely that a theory of V_3Si which allows a *second order* cubic-tetragonal structural phase transition will have more ingredients than the one we pursue here.

The plan of the paper is as follows. We begin with a description of the geometry of the crystal and a discussion of the appropriate invariance conditions. This convinces us that there is indeed a change of invariance of the constitutive equation in a structural transition. The analysis of the bifurcation then shows that the change of invariance *requires* discontinuities in some second derivatives at the transition point. An appraisal of the Cauchy–Born hypothesis then allows the derivation of the corresponding thermoelasticity theory and the results are related to those of Landau by a consideration of the behaviour of the order parameters. Finally we present a table of the various genericity hypotheses which allow the main conclusions of the work.

It is worth noting that this plan is quite different to that which a pure analyst would follow. Such an analyst would presumably eliminate "irrelevant" variables like the Cauchy–Green tensor *before* considering the bifurcation and so miss entirely the discontinuities in the second derivatives of the thermoelastic potential.

BASIC IDEAS

The problem is the description of a structural phase transition at a b.c.t. configuration of a monatomic crystal. The kinematic parameters which characterize the transition are the lattice vectors and the vector displacement of the lattice of centre atoms. The control variable is the temperature θ. There is a structural transition at $\theta = \theta_0$ if and only if the displacement of the centre atoms is incipiently non-zero at that temperature.

In the terminology of Pitteri[6], the b.c.t. lattice is a 1- lattice, or simple lattice, one of the fourteen catalogued by Bravais. Thus the points x of a 1-lattice are integer linear multiples of three linearly independent basis vectors, $\bar{e}_a$ say,

$$x = n^a \bar{e}_a, \tag{1}$$

the n^a being any integers, and the summation convention operating on repeated indices. The points of the lattice do not determine the basis vectors, for any choice

$$\bar{e}^*_a = \gamma_a{}^b \bar{e}_b, \tag{2}$$

is also a set of basis vectors, provided that the elements $\gamma_a{}^b$ are integers, and that

$$\det(\gamma_a{}^b) = \pm 1, \tag{3}$$

where det stands for the determinant. Conversely, every basis of the lattice is of the form given by (2) and (3). The set of matrices γ with integer elements $\gamma_a{}^b$ satisfying (3) forms an infinite discrete group, G say, with respect to the composition of the matrices as group operation.

For example, the basis vectors of the body centered (b.c.) lattice may be chosen as

$$\bar{e}_1 = \frac{1}{2}(e_1 + e_2 + e_3),\ \bar{e}_2 = e_2,\ \bar{e}_3 = e_3, \tag{4}$$

where the e_a represent the edges of the conventional b.c. unit cell of the lattice. The vector $\bar{e}_1$ then represents the position of the centre atom of that cell. In the case of the b.c.t. lattice, the

$$e_a \text{ are mutually orthogonal,} \tag{5}$$

and may be chosen so that

$$|e_1| \neq |e_2| = |e_3|. \tag{6}$$

It is natural to suppose that the Helmholtz free energy per unit mass is given as a function of the form

$$\phi_1 = \phi_1(\bar{e}_a, \theta), \tag{7}$$

where the subscript 1 indicates that the crystal is represented as a 1-lattice. This "1-lattice description" of the crystal allows only configurational transitions, a structural transition cannot be described at this level. To describe a transition where the lattice of centre atoms moves independently of the remaining atoms, the configuration must be described as a "2-lattice", that is, as a superposition of two congruent and parallel simple lattices. So each constituent 1-lattice, of a 2-lattice, is generated by the same basis vectors and the 1-lattices may be brought to coincidence by a uniform translation. Let the polarization vector, or shift, representing the separation of the lattices (the vector difference of any two points, one from each lattice) be denoted p. Thus in a b.c configuration, $p = \bar{e}_1$, with $\bar{e}_1$ given by $(4)_1$. If the centre atoms of a b.c lattice are displaced, each similarly, the resulting configuration is a 2-lattice, but is is generally no longer a 1-lattice.

Correspondingly, suppose that the Helmholtz free energy per unit mass of the 2-lattice may

be written as

$$\phi_2 = \phi_2(e_a, p, \theta), \tag{8}$$

where the e_a are the (common) lattice vectors of the constituent 1-lattices.

The "internal variable" p may be eliminated if one presumes that it adopts a value which minimizes ϕ_2 absolutely. Suppose then that $\bar{p}(e_a, \theta)$ is such a minimiser of ϕ_2, so that

$$\phi_2(e_a, p, \theta) \geq \phi_2(e_a, \bar{p}, \theta), \tag{9}$$

the equation guaranteeing classical stability against variations in p, $\bar{p}$ being the equilibrium value of p. It follows from (9) that

$$\frac{\partial \phi_2}{\partial p}(e_a, \bar{p}, \theta) = 0, \tag{10}$$

which is generally easier to solve than (9). However, there are generally many solutions of

$$\frac{\partial \phi_2}{\partial p}(e_a, q, \theta) = 0, \tag{11}$$

for $q(e_a, \theta)$, corresponding to the stationary points of ϕ_2 with respect to p. These many solutions for $q(e_a, \theta)$ generate in turn many sheets of $\phi_2(e_a, q(e_a, \theta), \theta)$, which are indexed by the superscript i, so that each $\phi_2{}^i(e_a, q(e_a, \theta), \theta)$ is a single valued function. Define

$$\bar{\phi}_2(e_a, \theta) = \min_i \phi_2{}^i(e_a, q(e_a, \theta), \theta) = \phi_2(e_a, \bar{p}(e_a, \theta), \theta), \tag{12}$$

so that $\bar{\phi}_2$ corresponds to an absolute minimiser, and is single valued.

Notice that, in this structure, the shift p fits exactly Tisza's description, in [7], of a quasi-thermodynamic variable. In that paper, Tisza provides sufficient conditions for a local minimum (as does Landau in [1]).

By hypothesis, there exists a b.c.t. equilibrium configuration of the crystal. Therefore, (10) has at least one solution for $\bar{p}$ for some orthogonal e_a satisfying (6) and for some θ_0. If

$$\det \left\| \frac{\partial^2 \phi_2}{\partial p^2}(e_a, \bar{e}_1, \theta_0) \right\| \neq 0, \tag{13}$$

with $\bar{e}_1$ given by $(4)_1$, then this branch of solutions is unique in some neighbourhood of e_a, θ_0, by the implicit function theorem. With (13), there is no possibility of a relative displacement of the lattice of centre atoms, and there is no structural transition.

On the other hand, if

$$\det \left\| \frac{\partial^2 \phi_2}{\partial p^2}(e_a, \bar{e}_1, \theta_0) \right\| = 0, \tag{14}$$

then there is generally more than one solution of (11) in the neighbourhood of e_a, θ_0 and so there is the possibility of a continuous transition.

GEOMETRY

The discussion is facilitated by a brief consideration of the various groups connected with the geometry of the latices. More detail is given by Ericksen in [2, 8, 9]. To begin with, consider the 1-lattices. Equation (2) defines a transformation of the basis vectors and implies that the 1-lattice is mapped onto itself by the elements of G and only by those elements.

For each element $\gamma_a{}^b$ of G, define a linear transformation g via

$$g\bar{e}_a = \gamma_a{}^b \bar{e}_b. \tag{15}$$

Then the set of such elements forms a group $\mathcal{G}$, say, conjugate to G. The crystallographic point group $\mathcal{P}$ associated with the basis vectors $\bar{e}_a$ consists of the orthogonal elements of $\mathcal{G}$, that is, $\mathcal{P}$ consists of the orthogonal transformations Q such that

$$Q\bar{e}_a = \gamma_a{}^b \bar{e}_b, \tag{16}$$

for some choice of $\gamma_a{}^b \in G$. Thus the elements of the point group are the orthogonal transformations of the 1-lattice onto itself.

The lattice group, P say, is in turn conjugate to $\mathcal{P}$ and consists of those elements $\gamma_a{}^b$ of G which satisfy (16) for some orthogonal Q. Thus

$$\gamma_a{}^b = \bar{e}^b \cdot Q\bar{e}_a, \tag{17}$$

where $\bar{e}^b$ is the triad reciprocal to $\bar{e}_b$, and the dot denotes the scalar product. Ericksen has argued convincingly in [8] that the lattice groups distinguish changes in symmetry better than do the point groups. In addition, the kinematic rules governing the possible transitions of the second kind are neatly expressed in terms of the fixed sets corresponding to the lattice groups, see [8] for details.

Let

$$\bar{\eta}_{ab} = \bar{e}_a \cdot \bar{e}_b, \tag{18}$$

and let $\bar{\eta}$ be the matrix with elements, $\bar{\eta}_{ab}$. From (16) and (18)

$$\bar{\eta} = \gamma\bar{\eta}\gamma', \tag{19}$$

where the dash signifies the transpose. The strains compatible with a given lattice group are thus the common fixed points of the maps

$$\bar{\eta} \to \gamma\bar{\eta}\gamma', \quad \gamma \in P. \tag{20}$$

These fixed points are significant as far as the evaluation of material parameters is concerned.

In a 2-lattice, $\mathcal{P}$ and P are defined via the basis vectors of the constituent 1-lattices and they are independent of the shift p. Under the action of the point group, defined via (16), the shift becomes Qp. The 2-lattice is regenerated in the corresponding orthogonal transformation provided that

$$Qp = p + x, \tag{21}$$

for some x of the form (1). It is straightforward to show that (21) singles out a subgroup of $\mathcal{P}$, and we denote this subgroup $\mathcal{P}^*$. For the b.c.t 2-lattice, $\mathcal{P} = \mathcal{P}^*$. Let the corresponding subgroup of P be P^*.

Consider now in particular the b.c.t configuration, which may be described as a 1-lattice with basis $\bar{e}_a$, given by (4), (5) and (6), or as a 2-lattice with basis e_a, given by (5) and (6), and shift $\bar{e}_1$, given by $(4)_1$. For convenience, write

$$M_b{}^a \bar{e}_a = e_b, \tag{22}$$

where

$$M = (M_b{}^a) = \begin{Vmatrix} 2 & -1 & -1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{Vmatrix}, \tag{23}$$

regarding e_a and $\bar{e}_a$ as row vectors. As a 1-lattice, the b.c.t configuration is regenerated by

mappings of the form

$$\bar{e}_a \to \gamma_a{}^b \bar{e}_b, \quad \gamma \in G, \tag{24}$$

which induce the mappings

$$e_a \to (M\gamma M^{-1})_a{}^b e_b, \tag{25}$$

of the basis e_a of the constituent 1-lattices and the mapping

$$p \to \frac{1}{2} \sum_a (M\gamma M^{-1})_a{}^b e_b, \tag{26}$$

of the shift $p = 1/2 \sum_a e_a$.

The set of matrices $M\gamma M^{-1}$ forms a group $\tilde{G}$, say, conjugate to G. Denote a typical element of $\tilde{G}$ by $\tilde{\gamma}$. Obviously $G \neq \tilde{G}$, because the entries of a typical $\tilde{\gamma}$ include half integers, so that there are elements of $\tilde{G}$ not in G. There are also elements of G not in $\tilde{G}$, such as that element corresponding to the matrix

$$H = \begin{Vmatrix} 1 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{Vmatrix}, \tag{27}$$

one of the generators of G. This is not to say that there are transformations regenerating the b.c.t lattice which arise from the 2-lattice description, but not from the 1-lattice description, for the transformations corresponding to the former description (viz. the elements of G) take no account of the behaviour of the shift. Specifically, the mapping $e_a \to H_a{}^b e_b$ takes the shift $p = 1/2(e_1 + e_2 + e_3)$ into the vector $1/2(e_1 + 2e_2 + e_3)$ and so generates an end-centred configuration of the lattice.

However, as Ericksen remarks in [9], those elements of $\tilde{G}$ which correspond to orthogonal transformations, in the sense that

$$\tilde{Q}e_a = \tilde{\gamma}_a{}^b e_b, \tag{28}$$

for some $\tilde{\gamma} \in \tilde{G}$ and for some orthogonal $\tilde{Q}$, include $\mathscr{P}$. More familiarly, the point group corresponding to the 1-lattice description includes that corresponding to the 2-lattice description. It turns out that the inclusion is strict only when

$$|e_1| = 2|e_2| = 2|e_3|, \tag{29}$$

in which case the configuration is face centred cubic (f.c.c), as is evident on drawing a diagram of adjacent cells of the b.c.t lattice. In that case, the point group corresponding to the 1-lattice description includes a rotation through $\pi/2$ not in the tetragonal point group. Specifically, this rotation corresponds to the mappings

$$e_1 \to e_2 - e_3, \; e_2 \to \frac{1}{2}(-e_1 \to e_2 \to e_3), \; e_3 \to \frac{1}{2}(e_1 + e_2 + e_3), \tag{30}$$

or equivalently,

$$\bar{e}_1 \to \bar{e}_2, \; \bar{e}_2 \to -\bar{e}_1 + \bar{e}_2 + \bar{e}_3, \; \bar{e}_3 \to \bar{e}_1. \tag{31}$$

In confirmation

$$\tilde{\gamma}^0 \overset{\text{def}}{=} \begin{Vmatrix} 0 & 1 & -1 \\ -1/2 & 1/2 & 1/2 \\ 1/2 & 1/2 & 1/2 \end{Vmatrix} = M \begin{Vmatrix} 0 & 1 & 0 \\ -1 & 1 & 1 \\ 1 & 0 & 0 \end{Vmatrix} M^{-1}. \tag{32}$$

Thus the elements $\tilde{\gamma}$ of $\tilde{G}$ corresponding to fixed points of the mapping

$$\tilde{\eta} \to \tilde{\gamma}\tilde{\eta}\tilde{\gamma}', \tag{33}$$

with (29), include elements not in the lattice group, to wit $\tilde{\gamma}^0$.

INVARIANCE OF THE CONSTITUTIVE EQUATION

Here we demonstrate that there is a change of invariance of the Helmholtz free energy as the crystal passes through the transition. Suppose that the lattices consist of indistinguishable atoms. The free energy, taking here no account of the history of deformation, must be invariant with respect to any deformation which rearranges these indistinguishable atoms. Thus ϕ_1 must be invariant under transformations of the 1-lattice onto itself.

$$\phi_1(\bar{e}_a, \theta) = \phi_1(\gamma_a{}^b \bar{e}_b, \theta), \tag{34}$$

and ϕ_2 invariant under transformations of the 2-lattice onto itself,

$$\phi_2(e_a, p, \theta) = \phi_2(\gamma_a{}^b e_b, p + x, \theta), \tag{35}$$

with $\gamma \in G$ and x of the form $n^a e_a$, n^a integers.

In any b.c configuration, the lattice may be regarded as a 1-lattice or as a 2-lattice. So the Helmholtz free energy is expressible either in the form ϕ_1 or in the form ϕ_2, for which (34) and (35) must hold respectively. Thus

$$\phi_1(\bar{e}_a, \theta) = \phi_2\left(e_a, \frac{1}{2}\sum_a e_a, \theta\right), \tag{36}$$

with $\bar{e}_a$ given by (4), and so with (34), (24)–(26) and (36)

$$\phi_2\left(e_a, \frac{1}{2}\sum_a e_a, \theta\right) = \phi_2\left(\tilde{\gamma}_a{}^b e_b, \frac{1}{2}\sum_a \tilde{\gamma}_a{}^b e_b, \theta\right), \tag{37}$$

which holds in addition to (35).

When the lattice of centre atoms is displaced, the configuration may not be represented as a 1-lattice, so that (37) does not hold. There is then a *change of invariance* in the passage from a 1-lattice to a 2-lattice, for G and $\tilde{G}$ are inequivalent. This change of invariance is characteristic of a structural transition and should not be confused with a change in the symmetry of the equilibrium configurations assumed by the crystal in the neighbourhood of the transition.

The change of invariance is reflected by a change in the point group only when the point group corresponding to G differs from that corresponding to $\tilde{G}$, which occurs only when the transition point is f.c.c. In that case the point group arising from the 2-lattice description is tetragonal, whereas that deriving from the 1-lattice description is cubic. Equation (37) is in a way more complicated than (35), which adds some labour to the determination of relations between material parameters, but opens up a whole new field to those who revel in exhaustive computation and classification.

In addition to these requirements, there is the symmetry deriving from the monatomicity of the crystal. Since the constituent 1-lattices, of the 2-lattice, then cannot tell themselves apart, there must result

$$\phi_2(e_a, p, \theta) = \phi_2(e_a, -p, \theta), \tag{38}$$

as noted by Ericksen [10].

Finally there is the standard requirement that the free energy be frame indifferent, so that

$$\phi_1(\bar{e}_a, \theta) = \phi_1(R\bar{e}_a, \theta), \tag{39}$$

and

$$\phi_2(e_a, p, \theta) = \phi_2(Re_a, Rp, \theta), \tag{40}$$

R being any orthogonal transformation. With the classical results of the theory of orthogonal invariants, we have

$$\phi_1 = \phi_1{}^+(\bar{e}_a \cdot \bar{e}_b, \theta), \tag{41}$$

$$\phi_2 = \phi_2{}^+(e_a \cdot e_b, p \cdot e_c, \theta), \tag{42}$$

in the second of these two representations using the fact that p^2 is expressible in terms of $e_a \cdot e_b$ and $p \cdot e_c$, when $\det(e_a \cdot e_b)$ is non-zero.

In all that follows, in the spirit of Landau, we assume that $\phi_2{}^+$ is smooth enough that all the derivatives employed actually exist and focus attention upon the consequent properties of $\phi_2{}^i$ and $\bar{\phi}_2$. Since the Taylor series expansion of $\phi_2{}^+$ is of central importance in the analysis of the bifurcation, we need to know the relations amongst the various derivatives. From (35) and (42), we have

$$\phi_2{}^+(e_a \cdot e_b, p \cdot e_c, \theta) = \phi_2{}^+(\gamma_a{}^r \gamma_b{}^s e_r \cdot e_s, (p + x) \cdot \gamma_c{}^t e^t, \theta), \tag{43}$$

for arbitrary $e_a \cdot e_b, p$, for all $\gamma \in G$, x in the lattice generated by e_a. Using (21), if $\gamma \in P^*$, then there exists such an x that

$$e_a \cdot e_b = \gamma_a{}^r \gamma_b{}^s e_r \cdot e_s, \tag{44}$$

$$p \cdot e_c = (p + x) \cdot \gamma_c{}^t e_t, \tag{45}$$

and the derivatives of $\phi_2{}^+$ are constrained at such points by the equations

$$\frac{\partial \phi_2{}^+}{\partial (e_a \cdot e_b)} = \gamma_r{}^a \gamma_s{}^b \frac{\partial \phi_2{}^+}{\partial (e_r \cdot e_s)}, \tag{46}$$

$$\frac{\partial \phi_2{}^+}{\partial (p \cdot e_c)} = \gamma_t{}^c \frac{\partial \phi_2{}^+}{\partial (p \cdot e_t)}, \tag{47}$$

omitting the common arguments. In the b.c.t configuration, $\mathcal{P}^*$ is the entire tetragonal point group. The relations between higher derivatives are easily found. Also from the 1-lattice description, via (37), we have

$$\phi_2{}^+\left(e_a \cdot e_b, \frac{1}{2}\sum_a e_a \cdot e_c, \theta\right) = \phi_2{}^+\left(\tilde{\gamma}_a{}^r \tilde{\gamma}_b{}^s e_r \cdot e_s, \frac{1}{2}\sum_a \tilde{\gamma}_a{}^r \tilde{\gamma}_c{}^s e_r \cdot e_s, \theta\right), \tag{48}$$

for arbitrary $e_a \cdot e_b$, so that at the fixed points of

$$e_a \cdot e_b \to \tilde{\gamma}_a{}^r \tilde{\gamma}_b{}^s e_r \cdot e_s, \tag{49}$$

there are the relations

$$\frac{\partial \phi_2{}^+}{\partial (e_a \cdot e_b)} + \frac{1}{4}\left(\frac{\partial \phi_2{}^+}{\partial (p \cdot e_a)} + \frac{\partial \phi_2{}^+}{\partial (p \cdot e_b)}\right) = \tilde{\gamma}_r{}^a \tilde{\gamma}_s{}^b \frac{\partial \phi_2{}^+}{\partial (e_r \cdot e_s)} + \frac{1}{2}\frac{\partial \phi_2{}^+}{\partial (p \cdot e_s)} \sum_r (\tilde{\gamma}_r{}^a \tilde{\gamma}_s{}^b + \tilde{\gamma}_r{}^b \tilde{\gamma}_s{}^a), \tag{50}$$

omitting the common arguments. These last equations give constraints different from those obtained from the 2-lattice description only when the lattice configuration is f.c.c, in which case the additional constraints come by choosing $\tilde{\gamma} = \tilde{\gamma}^0$ in (50).

It is convenient at this point to introduce the change of variable $p \cdot e_a \to \pi_a$ via

$$\pi_a = \left(p - \frac{1}{2}\sum_b e_b\right) \cdot e_a, \tag{51}$$

π_a representing the displacement of the lattice of centre atoms. Putting

$$\eta_{ab} = e_a \cdot e_b, \tag{52}$$

and writing

$$\phi_2^{+} = \phi_2^{*}(\eta_{ab}, \pi_c, \theta), \tag{53}$$

we have, by consecutive use of (35) and (38)

$$\begin{aligned}\phi_2^{*}\left(\eta_{ab}, \left(p - \frac{1}{2}\sum_b e_b\right) \cdot e_c, \theta\right) &= \phi_2^{*}\left(\eta_{ab}, \left(p + \frac{1}{2}\sum_b e_b\right) e_c, \theta\right) \\ &= \phi_2^{*}\left(\eta_{ab}, \left(-p + \frac{1}{2}\sum_b e_b\right) \cdot e_c, \theta\right)\end{aligned} \tag{54}$$

so that

$$\phi_2^{*}(\eta_{ab}, \pi_c, \theta) = \phi_2^{*}(\eta_{ab}, -\pi_c, \theta). \tag{55}$$

At any b.c configuration, $\pi_c = 0$. Thus (35) requires that all derivatives in which π_c occurs an odd number of times vanish in such configurations. The relations (46) and (47) translate into relations between the derivatives of ϕ_2^{*} via

$$\frac{\partial \phi_2^{+}}{\partial (e_a \cdot e_b)} = \frac{\partial \phi_2^{*}}{\partial \eta_{ab}} - \frac{1}{4}\left(\frac{\partial \phi_2^{*}}{\partial \pi_a} + \frac{\partial \phi_2^{*}}{\partial \pi_b}\right) = \frac{\partial \phi_2^{*}}{\partial \eta_{ab}}, \tag{56}$$

$$\frac{\partial \phi_2^{+}}{\partial (p \cdot e_a)} = \frac{\partial \phi_2^{*}}{\partial \pi_a}, \tag{57}$$

in the first of these using (55). The relation (48) becomes

$$\phi_2^{*}(\eta_{ab}, 0, \theta) = \phi_2^{*}(\tilde{\gamma}_a{}^r \tilde{\gamma}_b{}^s \eta_{rs}, 0, \theta), \tag{58}$$

and (50) simplifies to

$$\frac{\partial \phi_2^{*}}{\partial \eta_{ab}} = \tilde{\gamma}_r{}^a \tilde{\gamma}_s{}^b \frac{\partial \phi_2^{*}}{\partial \eta_{rs}}, \tag{59}$$

at the fixed points of the mapping (49).

Among other relations employed in the work are

$$\begin{aligned}\frac{\partial^2 \phi_2^{+}}{\partial (p \cdot e_a) \partial (p \cdot e_b)} &= \frac{\partial^2 \phi_2^{*}}{\partial \pi_a \partial \pi_b}, \\ \frac{\partial^3 \phi_2^{+}}{\partial (p \cdot e_a) \partial (p \cdot e_b) \partial (e_c \cdot e_d)} &= \frac{\partial^3 \phi_2^{*}}{\partial \pi_a \partial \pi_b \partial \eta_{cd}}, \\ \frac{\partial^2 \phi_2^{+}}{\partial (e_a \cdot e_b) \partial (e_c \cdot e_d)} &= \frac{\partial^2 \phi_2^{*}}{\partial \eta_{ab} \partial \eta_{cd}} - \frac{1}{16}\left(\frac{\partial^2 \phi_2^{*}}{\partial \pi_a \partial \pi_c} + \frac{\partial^2 \phi_2^{*}}{\partial \pi_a \partial \pi_d} + \frac{\partial^2 \phi_2^{*}}{\partial \pi_b \partial \pi_c} + \frac{\partial^2 \phi_2^{*}}{\partial \pi_b \partial \pi_d}\right),\end{aligned} \tag{60}$$

at the b.c.t configuration.

From (46), and similar equations, the usual point group constraints apply to derivatives of ϕ_2^+ with respect to $e_a \cdot e_b$, so that, for example with the tetragonal point group

$$\frac{\partial^2 \phi_2^+}{\partial(e_b \cdot e_b)\partial(e_d \cdot e_d)} = \begin{Vmatrix} \alpha & \beta & \beta \\ \beta & \gamma & \delta \\ \beta & \delta & \gamma \end{Vmatrix}, \quad \text{no summation} \tag{61}$$

where the rows and columns are labelled 11, 22, 33 consecutively. (We shall need only these components of the tensor.) So also one finds

$$\frac{1}{2!}\frac{\partial^2 \phi_2^+}{\partial(p \cdot e_a)\partial(p \cdot e_b)} = \begin{Vmatrix} r & 0 & 0 \\ 0 & s & 0 \\ 0 & 0 & s \end{Vmatrix}. \tag{62}$$

Then from $(60)_1$ and $(60)_3$

$$\frac{\partial^2 \phi_2^*}{\partial \eta_{bb}\partial \eta_{dd}} = \begin{Vmatrix} \alpha & \beta & \beta \\ \beta & \gamma & \delta \\ \beta & \delta & \gamma \end{Vmatrix} + \frac{1}{2}\begin{Vmatrix} r & 0 & 0 \\ 0 & s & 0 \\ 0 & 0 & s \end{Vmatrix}, \quad \text{no summation} \tag{63}$$

so that the derivatives of ϕ_2^* with respect to η also have tetragonal symmetry. Analogous remarks apply when the point group is cubic.

THE BIFURCATION

This section comprises of the elimination of the internal variable π_a by the assumption that it minimises absolutely the potential $\phi_2^*(\eta, \pi, \theta)$. This entails the determination of the relative and absolute minima of ϕ_2^* with respect to π_a. The problem is trivial when there is only one solution for $\pi_a(\eta, \theta)$ of the equation corresponding to (11), viz.,

$$\frac{\partial \phi_2^*}{\partial \pi_a}(\eta, \pi, \theta) = 0, \tag{64}$$

in the neighbourhood of the b.c.t configuration that we have specified. From (55), this one solution must be $\pi_a = 0$. On the other hand, suppose that at the b.c.t configuration corresponding to $\eta = \eta_0$, with

$$\eta_0 = \begin{Vmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & b \end{Vmatrix}, \quad \text{say,} \tag{65}$$

and at the temperature $\theta = \theta_0$, we have

$$f(\eta_0, \theta_0) \overset{\text{def}}{=} \det \frac{\partial^2 \phi_2^*}{\partial \pi_c \partial \pi_b}(\eta_0, 0, \theta_0) = 0, \tag{66}$$

allowing relative displacement of the centre atoms of the b.c.t lattice and, correspondingly, more than one solution of (64) in a neighbourhood of η_0, θ_0. Then we have in addition to select the absolute minimum from amongst the relative minima corresponding to solutions of (64).

The analysis has to be carried out separately for the cases when the putative transition point is b.c.t, b.c.c and f.c.c, where correspondingly $a \neq b$ and $a \neq 2b$, $a = b$ and $a = 2b$. The details will be set down for each case in turn and the general features then abstracted to gain a clearer picture of the situation. To simplify matters as far as possible, we allow only the diagonal components of η to vary, so that we exclude the consideration of tetragonal-monoclinic transitions, for example.

The equation $f(\eta_0, \theta_0) = 0$ specifies a six-dimensional hypersurface in the space of η, θ. With our assumption that $\eta_{12} = \eta_{23} = \eta_{31} = 0$, a point on the surface has, loosely, three degrees of

freedom. The remarks that follow will be phrased as if η_0 had only three independent components (η_{11}, η_{22}, η_{33}), so that, e.g. the "tangent plane" to $f(\eta_0, \theta_0) = 0$ at a given θ_0 would be a 2-dimensional surface with normal $(\partial f/\partial\eta_{11}, \partial f/\partial\eta_{22}, \partial f/\partial\eta_{33})$.

(1) *b.c.t configuration*, a ≠ b *and* a ≠ 2b

From equations like (46), (47) and (56), (57), one obtains

$$\frac{1}{2}\frac{\partial^2\phi_2^*}{\partial\pi_a\partial\pi_b} = \begin{Vmatrix} r & 0 & 0 \\ 0 & s & 0 \\ 0 & 0 & s \end{Vmatrix}, \quad \frac{1}{2}\frac{\partial^3\phi_2^*}{\partial\pi_a{}^2\partial\eta_{bb}} = \begin{Vmatrix} a_1 & a_2 & a_2 \\ a_3 & a_4 & a_5 \\ a_3 & a_5 & a_4 \end{Vmatrix}, \tag{67}$$

where the summation convention is suspended, where the element in the ith row and jth column of $(67)_2$ is $(\partial^3\phi_2^*/\partial\pi_i^2\partial\eta_{jj})$, and

$$\frac{1}{4!}\frac{\partial^4\phi_2^*}{\partial\pi_a{}^2\partial\pi_b{}^2} = \begin{Vmatrix} b_1 & 1/6b_2 & 1/6b_2 \\ 1/6b_2 & b_3 & 1/6b_4 \\ 1/6b_2 & 1/6b_4 & b_3 \end{Vmatrix}. \tag{68}$$

The material parameters r, s, a_i, b_j are arbitrary at this stage and they depend upon η_0, θ_0. The Taylor series expansion of (64) about η_0, θ takes the form

$$\frac{\partial\phi_2^*}{\partial\pi_a}(\eta, \pi, \theta) = \frac{\partial^2\phi_2^*}{\partial\pi_a\partial\pi_b}(\eta_0, 0, \theta)\,\pi_b + \frac{\partial^3\phi_2^*}{\partial\pi_a\partial\pi_b\partial\eta_{cd}}(\eta_0, 0, \theta)\,\pi_b\delta\eta_{cd} + \frac{1}{3!}\frac{\partial^4\phi_2^*}{\partial\pi_a\partial\pi_b\partial\pi_c\partial\pi_d}\pi_b\pi_c\pi_d + \text{higher order terms (h.o.t)}, \tag{69}$$

where $\delta\eta$ is the increment $\eta - \eta_0$. Setting the terms given explicitly in (69) to zero, and introducing the notation,

$$\begin{aligned} N_1 &= 2(a_1\delta\eta_{11} + a_2\delta\eta_{22} + a_2\delta\eta_{33}), \\ N_2 &= 2(a_3\delta\eta_{11} + a_4\delta\eta_{22} + a_5\delta\eta_{33}), \\ N_3 &= 2(a_3\delta\eta_{11} + a_5\delta\eta_{22} + a_4\delta\eta_{33}), \end{aligned} \tag{70}$$

we find

$$\begin{aligned} 0 &= \pi_1([2r + N_1] + 4b_1\pi_1{}^2 + 2b_2[\pi_2{}^2 + \pi_3{}^2]), \\ 0 &= \pi_2([2s + N_2] + 4b_3\pi_2{}^2 + 2[b_2\pi_1{}^2 + b_4\pi_3{}^2]), \\ 0 &= \pi_3([2s + N_3] + 4b_3\pi_3{}^2 + 2[b_2\pi_1{}^2 + b_4\pi_2{}^2]). \end{aligned} \tag{71}$$

According to (64) and (67), consider separately the cases where r and s vanish. If $r = 0$, then assuming that

$$\begin{pmatrix} \pi_1 \\ \pi_2 \\ \pi_3 \end{pmatrix} = \begin{pmatrix} \pi_1{}^0 \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \end{pmatrix}, \tag{72}$$

where the ϵ_a are $0(\pi_1{}^0)$, the solutions of (71) are given to lowest order in $\pi_1{}^0$ by

$$\pi_1{}^0 = 0, \quad \pi_1{}^0 = \pm\left(-\frac{N_1}{4b_1}\right)^{1/2}, \tag{73}$$

provided $b_1 \neq 0$ and $N_1 b_1 < 0$.

Conditions such as the nonvanishing of the coefficient b_1 occur frequently in the analysis. We shall always assume that such inequalities hold (which is a looser idea than Landau's notion of the improbability of the existence of a solution of a set of more than n equations in n

unknowns). In this connection, we note the remarks of Aizu[11], "... one special relation must hold among the coefficients ... We cannot, however, find any reason why such a special relation must hold. Here, therefore, we explicitly postulate that such a relation does not hold[8]", who continues amusingly in a footnote labelled[8] "Although no natural reason can be discovered why such a special relation must hold, on the other hand, neither can a decisive reason be found why such a special relation must *not* hold in any case. It is just for this sake that we "postulate"." We prefer to think of such conditions in the following manner. It is possible that there is a crystal with $b_1 = 0$, and measurements may be made on this sample, perhaps giving "exceptional" results. Another sample of the same material will not be quite identical to the first, although the experimentalist will do his best to make them identical. Presumably, then, in the second sample, b_1 is small, in some sense, but non-zero. Thus we regard an inequality such as $b_1 \neq 0$ as valid *close* to any sample we care to choose. Loose ideas like this will be referred to as "genericity" assumptions, and henceforward inequalities involving material parameters will be assumed to be satisfied, without much comment.

By tests like those of Tisza[7] and Landau[1], one finds that the critical point is infinitesimally stable against variations in π, and therefore that the three branches of π are relative minima, provided that b_1 is positive.

To continue with the main argument, (73) gives $\pi(\eta, \theta)$ to lowest order in the amplitude of the eigenmode. The function $\pi_1{}^0(\eta, \theta)$ has three branches, and each in turn is substituted into the Taylor series expansion

$$\begin{aligned}\phi_2^*(\eta, \pi, \theta) = \phi_2^*(\eta_0, 0, \theta) &+ \frac{\partial \phi_2^*}{\partial \eta_{ab}}(\eta_0, 0, \theta)\delta\eta_{ab} \\ &+ \frac{1}{2!}\frac{\partial^2 \phi_2^*}{\partial \eta_{ab}\partial \eta_{cd}}(\eta_0, 0, \theta)\delta\eta_{ab}\delta\eta_{cd} + \frac{1}{2!}\frac{\partial^2 \phi_2^*}{\partial \pi_a \partial \pi_b}(\eta_0, 0, \theta)\pi_a\pi_b \\ &+ \frac{1}{2!}\frac{\partial^3 \phi_2^*}{\partial \pi_a \partial \pi_b \partial \eta_{cd}}(\eta_0, 0, \theta)\pi_a\pi_b\delta\eta_{cd} \\ &+ \frac{1}{4!}\frac{\partial^4 \phi_2^*}{\partial \pi_a \partial \pi_b \partial \pi_c \partial \pi_d}(\eta_0, 0, \theta)\pi_a\pi_b\pi_c\pi_d + \text{h.o.t.},\end{aligned} \tag{74}$$

to derive the corresponding potential $\phi_2^*(\eta, \pi^0(\eta, \theta), \theta)$, with π^0 denoting the vector $(\pi_1{}^0, 0, 0)$. Index the sheets of $\phi_2^*(\eta, \pi^0(\eta, \theta), \theta)$ by the superscript i and define

$$\bar{\phi}_2(\eta, \theta) = \min_i \phi_2^{*i}(\eta, \pi^0(\eta, \theta), \theta). \tag{75}$$

Then the trivial branch $\pi_1{}^0 = 0$ gives

$$\phi_2^{*0} = \phi_2^*(\eta, 0, \theta), \tag{76}$$

and the two non trivial branches of $\pi_1{}^0$ coalesce to give just one sheet

$$\phi_2^{*1} = -\frac{N_1{}^2}{16 b_1} + \phi_2^*(\eta, 0, \theta), \text{ when } N_1 < 0, \tag{77}$$

assuming that b_1 is positive. Thus, via (75),

$$\bar{\phi}_2(\eta, \theta) = \phi_2^*(\eta, 0, \theta), \qquad \text{if } N_1 > 0, \tag{78}$$

$$= -\frac{N_1{}^2}{16 b_1} + \phi_2^*(\eta, 0, \theta), \qquad \text{if } N_1 < 0. \tag{79}$$

The plane $N_1 = 0$ is locally the unique tangent plane to the surface $f(\eta_0, \theta_0) = 0$, or, equivalently, $r(\eta_0, \theta_0) = 0$. Therefore, on any path through η_0, θ_0 not tangent to that surface, N_1 changes sign and so from (78) and (79) the derivatives $(\partial \bar{\phi}_2 / \partial \eta)$ are continuous at n_0, θ_0, but

there is a finite discontinuity of the second derivatives $(\partial^2\bar{\phi}_2/\partial\eta^2)$ *precisely at* η_0, θ_0. Loosely, the change of invariance forces ϕ_2^* to be multivalued, and the minimisation with respect to π gives the roughness of $\bar{\phi}_2$.

The analysis illustrates a remark of Mayer and Streeter [12], "In the case of the second order transition, there must be some reason why the extrapolation of the higher heat capacity is meaningless, since otherwise, if the extrapolation of the phase were conceivable, the extrapolated phase would necessarily be stable." In this instance, the sheet ϕ_2^{*1} may not be continued out of the half space $N_1 < 0$, for there is no real geometrical configuration corresponding to $N_1 > 0$, by virtue of (73).

The second class of transitions from the b.c. configuration arises when $s = 0$. Assuming that

$$\begin{pmatrix}\pi_1\\ \pi_2\\ \pi_3\end{pmatrix} = \begin{pmatrix}0\\ \pi_2^0\\ \pi_3^0\end{pmatrix} + \begin{pmatrix}\epsilon_1\\ \epsilon_2\\ \epsilon_3\end{pmatrix}, \tag{80}$$

where ϵ_1 is $\pi_2^0(|\pi_2| + |\pi_3^0|)$, ϵ_2 is $\pi_2^0(\pi_2)$, ϵ_3 is $\pi_3^0(\pi_3)$, the system (71) reduces to

$$\begin{aligned} 0 &= \pi_2^0(N_2 + 4b_3\pi_2^{02} + 2b_4\pi_3^{02}),\\ 0 &= \pi_3^0(N_3 + 4b_3\pi_3^{02} + 2b_4\pi_2^{02}), \end{aligned} \tag{81}$$

There are three classes of solutions of these equations

(a) $$\pi_2^0 = \pi_3^0 = 0, \tag{82}$$

(b) $$\pi_2^0 = 0,\ \pi_3^0 = \pm\left(-\frac{N_3}{4b_3}\right)^{1/2},$$

$$\pi_3^0 = 0,\ \pi_2^0 = \pm\left(-\frac{N_2}{4b_3}\right)^{1/2}, \tag{83}$$

(c) $$\begin{pmatrix}\pi_2^{02}\\ \pi_3^{02}\end{pmatrix} = -\frac{1}{\Delta}\begin{Vmatrix} 4b_3 & -2b_4\\ -2b_4 & 4b_3\end{Vmatrix}\begin{pmatrix}N_2\\ N_3\end{pmatrix}, \tag{84}$$

where

$$\Delta = 4(4b_3^2 - b_4^2), \tag{85}$$

assuming, without comment, that $2|b_3| \neq |b_4|$. Thus there are nine branches of the function $\pi^0(\eta, \theta)$. Substituting back into (74), we find that there are four corresponding sheets of $\phi_2^*(\eta, \pi(\eta, \theta), \theta)$ viz.

$$\phi_2^{*0} = \phi_2^*(\eta, 0, \theta), \text{ corresponding to the trivial branch (a)}, \tag{86}$$

$$\phi_2^{*1} = -\frac{N_2^2}{16b_3} + \phi_2^*(\eta, 0, \theta), \text{ when } N_2 b_3 < 0, \tag{87}$$

$$\phi_2^{*2} = -\frac{N_3^2}{16b_3} + \phi_2^*(\eta, 0, \theta), \text{ when } N_3 b_3 < 0, \tag{88}$$

corresponding to the class of solutions (b), and

$$\phi_2^{*3} = -\frac{1}{\Delta}(b_3[N_2^2 + N_3^2] - b_4 N_2 N_3) + \phi_2^*(\eta, 0, \theta), \tag{89}$$

when $\Delta(b_4 N_3 - 2b_3 N_2) > 0$ and $\Delta(b_4 N_2 - 2b_3 N_3) > 0$, corresponding to the class of solutions (c). In this case, the critical point is infinitesimally stable against variations in π provided that both b_3 and Δ are positive.

Using the relations

$$\phi_2^{*3} - \phi_2^{*2} = -\frac{1}{16b_3\Delta}(2b_4N_2 - 4b_3N_3)^2, \quad \phi_2^{*3} - \phi_2^{*1} = -\frac{1}{16b_3\Delta}(2b_4N_3 - 4b_3N_2)^2, \tag{90}$$

where each is defined, the construction of $\bar{\phi}_2$ falls naturally into two cases, depending on the sign of b_4. For brevity, consider only the case where b_4 is positive. Then one finds

$$\begin{aligned}
\bar{\phi}_2 &= \phi_2^{*0}, \text{ if } N_2 > 0, N_3 > 0, \\
&= \phi_2^{*1}, \text{ if } N_2 < 0, 2b_3N_3 > b_4N_2, \\
&= \phi_2^{*2}, \text{ if } N_3 < 0, 2b_3N_2 > b_4N_3, \\
&= \phi_2^{*3}, \text{ if } b_4N_2 > 2b_3N_3, b_4N_3 > 2b_3N_2.
\end{aligned} \tag{91}$$

Evidently, on any path not in the four planes given by the vanishing of the variables N_2, N_3, $2b_3N_3 - b_4N_2$, $2b_3N_2 - b_4N_3$, each of these variables changes sign at η_0, θ_0. So, on any such path, the second derivatives $(\partial^2\bar{\phi}_2/\partial\eta^2)$ suffer a finite discontinuity. (Note that the planes $N_2 = 0$, $N_3 = 0$ are both tangent planes to the surface $f(\eta_0, \theta_0) = 0$, corresponding to the double zero $s^2(\eta_0, \theta_0) = 0$.)

(2) *b.c.c. configuration, $a = b$*

Here the symmetry requires that

$$\frac{1}{2!}\frac{\partial^2\phi_2^*}{\partial\pi_a\partial\pi_b} = \begin{Vmatrix} r & 0 & 0 \\ 0 & r & 0 \\ 0 & 0 & r \end{Vmatrix}, \tag{92}$$

$$\frac{1}{2!}\frac{\partial^3\phi_2^*}{\partial\pi_a^2\partial\eta_{bb}} = \begin{Vmatrix} a & b & b \\ b & a & b \\ b & b & a \end{Vmatrix}, \tag{93}$$

$$\frac{1}{4!}\frac{\partial^4\phi_2^*}{\partial\pi_a^2\partial\pi_b^2} = \begin{Vmatrix} d & 1/6e & 1/6e \\ 1/6e & d & 1/6e \\ 1/6e & 1/6e & d \end{Vmatrix}, \tag{94}$$

with the same conventions as case (1). With the notation

$$\begin{aligned}
N_1 &= 2(a\delta\eta_{11} + b\delta\eta_{22} + b\delta\eta_{33}), \\
N_2 &= 2(b\delta\eta_{11} + a\delta\eta_{22} + b\delta\eta_{33}), \\
N_3 &= 2(b\delta\eta_{11} + b\delta\eta_{22} + a\delta\eta_{33}),
\end{aligned} \tag{95}$$

eqns (69) become

$$0 = \pi_1(N_1 + 2r + 4d\pi_1^2 + 2e[\pi_2^2 + \pi_3^2]), \tag{96}$$

$$0 = \pi_2(N_2 + 2r + 4d\pi_2^2 + 2e[\pi_1^2 + \pi_3^2]), \tag{97}$$

$$0 = \pi_3(N_3 + 2r + 4d\pi_3^2 + 2e[\pi_1^2 + \pi_2^2]), \tag{98}$$

to lowest order. When r vanishes, there are twenty-seven branches of $\pi(\eta, \theta)$ given by the following four classes of solutions

(a) $$\pi_1 = \pi_2 = \pi_3 = 0, \tag{99}$$

(b) $$\pi_1 = \pi_2 = 0, \pi_3^2 = -N_3/4d, \text{ with two other similar,} \tag{100}$$

(c) $$\pi_1 = 0,\ \begin{pmatrix}\pi_2^2\\ \pi_3^2\end{pmatrix} = \frac{1}{4(e^2-4d^2)}\begin{Vmatrix}4d & -2e\\ -2e & 4d\end{Vmatrix}\begin{pmatrix}N_2\\ N_3\end{pmatrix},\ \text{with two other similar,} \tag{101}$$

(d) $$\begin{pmatrix}\pi_1^2\\ \pi_2^2\\ \pi_3^2\end{pmatrix} = \frac{1}{4(e^2-ed-2d^2)}\begin{Vmatrix}-e-2d & e & e\\ e & -e-2d & e\\ e & e & -e-2d\end{Vmatrix}\begin{pmatrix}N_1\\ N_2\\ N_3\end{pmatrix}. \tag{102}$$

Correspondingly, there are eight distinct sheets of $\phi_2^*(\eta, \pi(\eta,\theta),\theta)$. The calculation of $\bar{\phi}_2$ is proportionately more intricate, but again, in the neighbourhood of the transition point, the various ϕ_2^{*i} differ by terms of order $\delta\eta_{aa}\delta\eta_{bb}$ (no summation), so that the first derivatives $(\partial\bar{\phi}_2/\partial\eta)$ are continuous at the transition, but the $(\partial^2\bar{\phi}_2/\partial\eta)$ have a finite discontinuity.

(3) *f.c.c configuration, $a = 2b$*

This last case differs from the preceding two cases in that the relations between the material parameters arise from two different descriptions of the lattice, via (34) and (35). Equation (35) means, effectively, that the parameters must satisfy the standard tetragonal constraints, so that the derivatives of ϕ_2^* are of the form given for case (1). Additionally, by equations like (59), one finds other constraints on terms involving derivatives with respect to η only. For example, (59) itself, together with the tetragonal symmetry, shows that the stress must be hydrostatic in this configuration. Likewise, we find that

$$\mathscr{L}_{aabb} \overset{\text{def}}{=} \frac{\partial^2\phi_2^*}{\partial\eta_{aa}\partial\eta_{bb}}(\eta,0,\theta),\ \text{no summation,} \tag{103}$$

is constrained by just one equation,

$$4\mathscr{L}_{1111} + 2\mathscr{L}_{1122} = \mathscr{L}_{2233} + \mathscr{L}_{3333}, \tag{104}$$

and one verifies that $(\partial^2\phi_2^*/\partial\eta_{ab}\partial\eta_{cd})(\eta,0,\theta)$ is generically non-singular. The constraint (104) has no effect on the analysis of case (1), as presented. Therefore the conclusions are identical in the two cases.

COMMON FEATURES OF THE THREE CASES

The overriding feature that emerges from the consideration of these specific instances of a structural transition is that the second derivatives of the potential $\bar{\phi}_2$ are generically discontinuous precisely at the transition point. To relate this remark to thermoelasticity, the behaviour of the lattice vectors must be correlated with the macroscopic deformation. The Cauchy–Born hypothesis, that lattice vectors are embedded in the macroscopic deformation, clearly fails for some choices of lattice vectors. Specifically, the lattice vectors $\bar{e}_a$ defined via (4), which generate a b.c lattice, no longer constitute a basis of the lattice when the centre atoms are displaced infinitesimally. On the other hand, the basis e_a of the 2-lattice varies smoothly through the transition, so that if the e_a were E_a in some reference configuration of the crystal

$$e_a = FE_a, \tag{105}$$

with F the matrix of macroscopic deformation gradients. With (105), $\eta_{ab} = e_a \cdot e_b$ may be identified with the components of the Cauchy–Green tensor based on the triad reciprocal to E_a. The potential $\bar{\phi}_2(\eta,\theta)$ may then be interpreted as the thermoelastic potential, and we have the result that the *isothermal elastic moduli are generically discontinuous at a b.c.t. structural transition.*

It remains to be seen whether or not a corresponding result holds for polyatomic crystals, or for transitions where there is a multiple bifurcation. Even with these qualifications, the tacit assumption of Anderson and Blount, that the thermoelastic potential appropriate to V_3Si is of class at least $C^{(3)}$, is put in some perspective.

Note that the analysis so far has presumed nothing about the state of stress of the crystal at

η_0, θ_0 (apart from the necessary symmetry requirements). The formulation can cope with some shear-induced phase transitions. However, to complete the analysis, we consider qualitatively the behaviour of *unloaded* equilibrium paths of the crystal, parametrized by θ. Finally, we relate the work to that of Landau by a discussion of the order parameters appropriate to these paths and by putting a few words in his mouth with regard to our genericity hypotheses.

(a) *Thermoelastic stability*

With $\bar{\phi}_2$ interpreted as the thermoelastic potential, the traditional energy criterion of stability, that the point $\bar{\eta}$, θ is strictly stable provided that

$$\bar{\phi}_2(\eta, \theta) > \bar{\phi}_2(\bar{\eta}, \theta), \text{for all } \eta \neq \bar{\eta}, \tag{106}$$

is certainly fulfilled if the matrix of isothermal elastic moduli $(\partial^2\bar{\phi}_2/\partial\eta^2)(\eta, \theta)$ is strictly positive definite.

Let us check to see that structural transitions are possible for some ranges of material parameters, in the sense that there are strictly stable equilibrium paths through η_0, θ_0, with a path "in" to η_0, θ_0 corresponding to $\pi = 0$ and a path "out" of η_0, θ_0 corresponding to $\pi \neq 0$. For each case considered, the matrices $(\partial^2\phi_2^{*0}/\partial\eta^2)$ are generically non-singular. Then there is a range of material parameters where each $(\partial^2\phi_2^{*0}/\partial\eta)$ is positive definite. By inspection, the derivatives $(\partial^2\phi_2^{*i}/\partial\eta^2)$ differ from $(\partial^2\phi_2^{*0}/\partial\eta^2)$ by the *addition* of material parameters (to lowest order), so that there is a range of material parameters where $(\partial^2\phi_2^{*i}/\partial\eta^2)$ is also positive definite. For example, in (77), if the parameters a_i are small enough, or if the parameter b_1 is big enough, then $(\partial^2\phi_2^{*1}/\partial\eta^2)$ is positive definite.

The unloaded equilibrium path is the path of absolute minima, with respect to η, of $\bar{\phi}_2$ (as far as we can tell from this lowest order local analysis). At $\theta = \theta_0$, the intersection of the sheets is stress free and, from the above, the point η_0, θ_0 is assumed strictly stable in each sheet of ϕ_2^{*i} (reckoned according to the criterion $\phi_2^{*i}(\eta, \theta) > \phi_2^{*i}(\bar{\eta}, \theta)$). At different temperatures, the intersection of the sheets is generically not stress free, and indeed there is an intersection of the sheets if and only if (66) has a solution for η at the given temperature. In a neighbourhood of θ_0, this is the case provided that

$$\frac{\partial f}{\partial \theta}(\eta_0, \theta_0) \neq 0. \tag{107}$$

If (107) failed, there would be no necessary connection between the respective continuations of the sheets to different θ, and the continuation of any sheet in θ would be entirely arbitrary. In this context, Tisza[7] remarks that the smoothness of second derivatives with respect to θ, required by Landau[1] in his analysis of the behaviour of the specific heat, is not to be expected. However, with the proviso that the derivatives $(\partial^2\phi_2^{*i}/\partial\eta^2)$ vary smoothly with θ in each sheet, these derivatives remain positive definite in some neighbourhood of η_0, θ_0. Therefore, by the implicit function theorem, there is a continuous and differentiable line of relative minima of the ϕ_2^{*i}, parametrized by θ, in each sheet.

The equilibrium path, the line of absolute minima of $\bar{\phi}_2$, depends upon how the lines of relative minima of ϕ_2^{*i} fall with regard to the partition of the space of $\delta\eta$ in the definition of $\bar{\phi}_2$, for example in (79) or (91). (There is the tacit assumption here that the domains of the ϕ_2^{*i} are extended to the entire space of $\delta\eta$.) Consider the b.c.t case with $r = 0$ for definiteness. Generically, each component of $\delta\eta$ changes sign on any path through $\delta\eta = 0$. With the second derivatives $(\partial^2\phi_2^{*0}/\partial\eta^2)$ and $(\partial^2\phi_2^{*1}/\partial\eta^2)$, corresponding to (79), both positive definite, it is clear that there is always a structural transition corresponding to this potential, for the lines of minima of ϕ_2^{*i} are generically not tangent to $r = 0$. On the other hand, if ϕ_2^{*1} were not positive definite, e.g. if b_1 were small enough, then there would be no line of minima of ϕ_2^{*1} and so there would be no stable equilibrium path of $\bar{\phi}_2$ in $N_1 < 0$. Thus there would be no continuous transition in this case.

It is clear that cubic-tetragonal transitions are possible for some ranges of material parameters, e.g. case (2b) corresponds to such a transition (and the discussion runs parallel to

the b.c.t case above). This result may be contrasted with the corresponding result in the works of Landau and Anderson and Blount.

(b) *Order parameters*

To relate this set-up with that of Landau, consider the problem in terms of the order parameters. The b.c.t case is typical. An appropriate order parameter is

$$z = \eta_{22} - \eta_{33}, \tag{108}$$

for z vanishes if and only if the configuration is tetragonal (in our class of orthorhombic variations). The potential in any sheet of $\phi_2^{*i}(\eta, \pi(\eta, \theta), \theta)$ may be written as a function of η_{11}, $\eta_{22} + \eta_{33}$ and z. Assuming that the various matrices of "moduli" are positive definite close to the transition, so then are

$$\frac{\partial^2 \phi_2^{*i}}{\partial \eta_{11}^2}(\eta_{11}, \eta_{22}+\eta_{33}, z, \theta) \left\| \frac{\partial^2 \phi_2^{*i}}{\partial \eta_{11} \partial(\eta_{22}+\eta_{33})} \right\| (\eta_{11}, \eta_{22}+\eta_{33}, z, \theta)$$

$$\frac{\partial^2 \phi_2^{*i}}{\partial(\eta_{22}+\eta_{33})\partial \eta_{11}}(\eta_{11}, \eta_{22}+\eta_{33}, z, \theta) \left\| \frac{\partial^2 \phi_2^{*i}}{\partial(\eta_{22}+\eta_{33})^2} \right\| (\eta_{11}, \eta_{22}+\eta_{33}, z, \theta), \tag{109}$$

positive definite. By the implicit function theorem, this allows η_{11} and $\eta_{22} + \eta_{33}$ to be eliminated from ϕ_2^{*i} in favour of z and θ, using the two equations

$$\frac{\partial \phi_2^{*i}}{\partial \eta_{11}} = \frac{\partial \phi_2^{*i}}{\partial(\eta_{22}+\eta_{33})} = 0, \tag{110}$$

expressing in part the vanishing of the stress. Substitution gives

$$\tilde{\phi}_2^{*i}(z, \theta) \overset{\text{def}}{=} \phi_2^{*i}(\eta_{11}(z, \theta), (\eta_{22}+\eta_{33})(z, \theta), z, \theta), \tag{111}$$

subject to

$$\frac{\partial \tilde{\phi}_2^{*i}}{\partial z} = 0, \tag{112}$$

completing the specification of the stress on the equilibrium path. Expanding $\tilde{\phi}_2^{*i}$ about $z = 0$, we have

$$\tilde{\phi}_2^{*i}(z, \theta) = \alpha(\theta) + \beta(\theta) z + \gamma(\theta) z^2 + \text{h.o.t.} \tag{113}$$

The coefficient $\beta(\theta)$ vanishes identically if $\tilde{\phi}_2^{*i}$ is an even function of z, as is the case for $i = 0, 1$ in case (1), with $r = 0$, and for $i = 0, 3$ in case (1), with $s = 0$. On the other hand, for $i = 1, 2$ in case (1), with $s = 0$, we have only that

$$\beta(\theta_0) = 0, \tag{114}$$

because the transition point is stress free.

In the first case, minimizing with respect to z,

$$z(\gamma(\theta) + \text{h.o.t.}) = 0. \tag{115}$$

Since $\gamma(\theta_0) \neq 0$, generically, the equilibrium path in the corresponding sheets is tetragonal. Nevertheless, if the path crosses from one sheet to another, there is still a transition, reflected in the discontinuity of the moduli.

In the second case, minimizing

$$z(\theta) = -\frac{\beta(\theta)}{2\gamma(\theta)}, \tag{116}$$

to lowest order. With (114) then, generically,

$$z(\theta) \alpha\ \delta\theta, \tag{117}$$

where $\delta\theta$ is the decrement in θ.

(c) *Genericity*

Putative transition points lie on the surface $f(\eta_0, \theta_0) = 0$. With the restriction $\eta_{12} = \eta_{23} = \eta_{31} = 0$, the six degrees of freedom of a point on this surface are reduced to three, and the three equations expressing the vanishing of the stress then determine a point on this (hyper) surface. Landau would presumably say that it is infinitely improbable that any more equations are satisfied at this point. For example, he would say that $b_1(\eta_0, \theta_0)$ is generically non-zero (as we have assumed throughout). He would, presumably, then allow any consistent analysis which relies solely on inequalities, so that hopefully he would accept the analysis presented here.

It is important to realize, however, that these naive counting arguments are very probably vitiated in some more symmetrical situations (and, on a pedantic note, we remark that no finite number of experiments can contradict a probabilistic statement). To conclude, we present a table summarizing the genericity hypotheses which allow a b.c.t structural transition.

Hypotheses	Results
$b_1 \neq 0$.	Lowest order analysis reasonable. Stability against variations in π possible. $\bar{\phi}_2$ is not $C^{(2)}$.
$\det \left\| \frac{\partial^2 \phi_2^{*0}}{\partial \eta^2} \right\| \neq 0$.	Thermoelastic stability of unloaded crystal allowable.
Lines of minima of ϕ_2^{*i} are not tangent to $f(\eta_0, \theta_0) = 0$.	A b.c.t structural transition is possible.

Acknowledgement—I am grateful to Prof. J. L. Ericksen for much guidance at all stages of this work. This material is based on work supported by the National Science Foundation under Grant No. CME 79 11112.

REFERENCES

1. L. D. Landau, On the theory of phase transitions. In *Collected Papers of L. D. Landau* (Edited by D. Ter Haar), pp. 193–216. Pergamon Press and Gordon and Breach, London (1965).
2. J. L. Ericksen, Some phase transitions in crystals. *Arch. Rat'l. Mech. Analysis* **73**, 99–124 (1980).
3. P. W. Anderson and E. I. Blount, Symmetry considerations on martensitic transformations: "ferroelectric" metals?. *Phys. Rev. Lett.* **14**, 217–219 (1965).
4. B. W. Batterman and C. S. Barrett, Crystal structure of superconducting V_3Si. *Phys. Rev. Lett.* **13**, 390–392 (1964).
5. Yu. V. Mnyuck, Molecular mechanism of polymorphic transitions. *Mol. Cryst. Liq. Cryst.* **52**, 163–200 (1979).
6. M. Pitteri, Reconciliation of local and global symmetries of crystals. Pending publication.
7. L. Tisza, On the general theory of phase transitions. In *Phase Transformations in Solids* (Edited by R. Smoluchowski, J. E. Mayer and W. A. Weyl), Wiley, New York and Chapman & Hall, London (1951).
8. J. L. Ericksen, On the symmetry of deformable crystals. *Arch. Rat'l. Mech. Analysis* **72**, 1–13 (1979).
9. J. L. Ericksen, Changes in symmetry in elastic crystals. Pending publication.
10. J. L. Ericksen, Nonlinear elasticity of diatomic crystals. *Int. J. Solids Structures* **6**, 951–957 (1970).
11. K. Aizu, Possible species of ferroelectrics. *Phys. Rev.* **146**, 423–429 (1966).
12. J. E. Mayer, and S. F. Streeter, Phase transitions. *J. Chem. Phys.* **7**, 1019–1025 (1939).