Definition of a Transcendental Order Parameter for Reconstructive Phase Transitions

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We propose a generalization of the Landau theory of phase transitions which applies to reconstructive transitions. For the first time an order parameter is defined for this category of transition. This order parameter is shown to be a transcendental function of the large atomic displacements arising at the transition. The absence of a group-subgroup relationship between the symmetries of the phases is proved to be the consequence of specific displacements. The approach is introduced through examples of reconstructive transitions found in crystals of the elements.

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The possibility of our defining an order parameter is a preliminary condition for applying the symmetry and thermodynamic concepts which underlie the Landau theory of phase transitions.[1] Such a definition presupposes that a group-subgroup relationship is realized between the phases surrounding the transition. This is always verified for second- and first-order structural transitions in which the rearrangement of structure is such that only small displacements of the atoms take place. By contrast, for reconstructive transitions[2] in which large displacements and drastic reordering take place, a group-subgroup relationship is in many cases absent, and no order parameter has been defined up to now. For this category of transitions which is found in most of the elements,[3] in a number of alloys,[4] and in some insulators,[5] it is usually admitted that the Landau theory cannot be used, and only crystallographic and atomistic models have been proposed[3–5] in order to describe their mechanism.

In contrast to the preceding ideas, we show in this Letter that an *an order parameter can be defined for reconstructive transitions.* It is shown to be a transcendental function of the average atomic displacements (or of some other variational parameter associated with the transitions mechanism) and not a linear function of the displacements as assumed in the standard Landau theory of phase transitions.[1] For specific values of the displacements, and *enlargement* of the symmetry groups of one phase is shown to take place and subsequently *the group-subgroup relationship with respect to the other phase is lost.* The equilibrium states of the system are obtained by minimization of the thermodynamic potential of the transition *with respect to the shifts and not with respect to the order-parameter components,* in contrast to the traditional procedure[1] but in agreement with the statistical mechanics methods.[1] Aside from the usual Landau phases, which are connected with the high-symmetry parent phase by a group-subgroup relationship, the minimization procedure provides additional *non-Landau* phases which do not correspond, in most cases, to subgroups of the parent phase and possess distinctive properties, as, for example, a constant value for the transition order-parameter *below* the transition point.

As a first illustrative example to our approach, let us focus on the β-ω transition reported for Ti, Zr, and Hf.[6–9] The average shifting of the Ti atoms from one phase to the other, as deduced from the superstructure observed from electron diffraction and x-ray patterns,[6,7] takes place along the [111] cubic direction [Fig. 1(a)] and can be conveniently represented in the $(0\bar{1}1)$ cubic plane [Fig. 1(b)]. Depending on the magnitude of the displacements along [111], *five phases* may arise: (1) *the β phase*, corresponding to unshifted atoms. It has the parent O_h^9 symmetry with a number of atoms $Z=1$ in the elementary unit cell; (2) *the hexagonal ω phase*,[6] which appears as the result of a shift of $a\sqrt{3}/12$. It possesses the symmetry D_{6h}^1 with $Z=3$; (3) *the β' phase*, isostructural to β which is induced by a shift of $a\sqrt{3}/6$ and can be deduced from β by a rotation of 60° around [111]; (4) *the h phase*, arising for a shift of $a\sqrt{3}/3$. It has the same hexagonal symmetry as the ω phase but with $Z=1$; (5) *the rhombohedral ω phase*,[8] associated with any general shift along [111]. Its space group is D_{3d}^3 with $Z=3$.

As stressed by de Fontaine,[9] the shifting of the Ti atoms in the hexagonal ω phase with respect to their positions in the β phase can be expressed as combinations of three independent basic vectors, denoted by $\mathbf{a}_\beta$, $\mathbf{b}_\beta$,

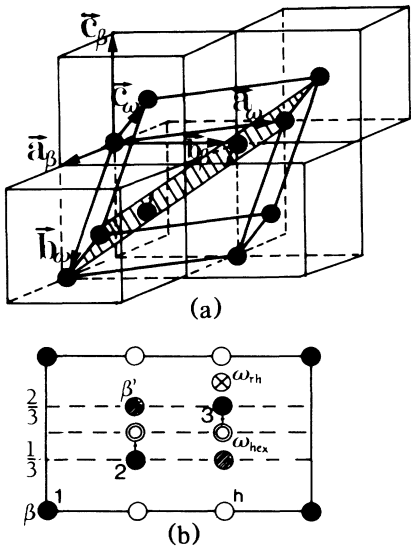

FIG. 1. (a) Primitive unit cells of the β and hexagonal ω phases. The shifting of the atoms at the β-ω transition takes place within the $(0\bar{1}1)$ hatched plane. (b) Shifts of the atoms within the $(0\bar{1}1)$ cubic plane. Filled, circled, hatched, open, and crossed atoms represent the positions of the atoms in this plane for the β, hexagonal ω, β', h, and rhombohedral ω phases, respectively. In (a) and (b), the direction of the shifts, symbolized by arrows, in along the [111] cubic direction which corresponds to the side of the plane in (b), scaled in $a\sqrt{3}/2$ units.

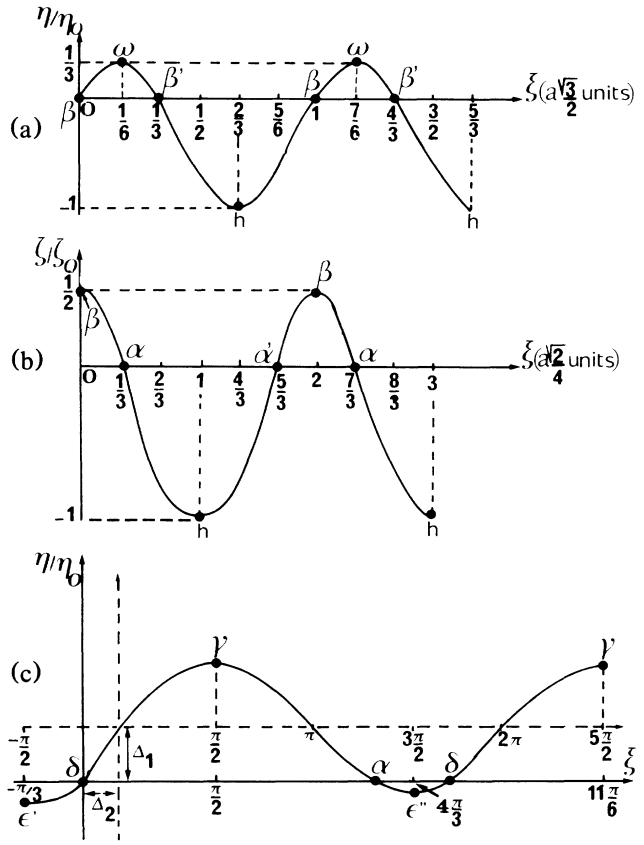

FIG. 2. Periodic dependence of the order parameter for the (a) β-ω transition and (b) β-α transition in titanium, and for the (c) δ-γ transition in iron. Here $\Delta_1 = \sin(\arccos\frac{1}{3} - \frac{1}{2}\pi)$, and $\Delta_2 = -\arccos\frac{1}{3}$.

and $\mathbf{c}_\beta$, associated with the primitive cubic β unit cell [Fig. 1(a)]:

$$\mathbf{a}_\omega = \mathbf{a}_\beta - \mathbf{b}_\beta, \quad \mathbf{b}_\omega = \mathbf{b}_\beta - \mathbf{c}_\beta, \quad \mathbf{c}_\omega = \mathbf{a}_\beta + \mathbf{b}_\beta + \mathbf{c}_\beta. \tag{1}$$

We can associate to the set of $\mathbf{a}_\omega$, $\mathbf{b}_\omega$, and $\mathbf{c}_\omega$ vectors, the wave vector $\mathbf{k}_1$ pertaining to the bcc Brillouin zone which expresses the linear relationship (1). It is $\mathbf{k}_1 = \frac{1}{3}(\mathbf{a}_\beta^* + \mathbf{b}_\beta^* + \mathbf{c}_\beta^*)$, where $\mathbf{a}_\beta^*$, $\mathbf{b}_\beta^*$, and $\mathbf{c}_\beta^*$ are the reciprocal lattice vectors. As $\mathbf{k}_1$ is invariant under the operations of the point group C_{3v}, its star has eight arms[10] and the representation spanned by the components of the shifts of all the atoms from the β to the ω phase can be shown to be composed by an eight-dimensional irreducible representation (IR), denoted by $\tau_1(\mathbf{k}_1)$ which accounts for the shifts along [111], and by a sixteen-dimensional IR expressing the atomic shifts within the plane [111]. Decomposing the basis vectors ϕ_i which span the representation space in terms of symmetric coordinates for the shifts along [111], one finds that all basis vectors have zero coefficients except ϕ_1 and ϕ_2, which correspond to the arms $\pm\mathbf{k}_1$. Two space groups, subgroups of O_h^9, can be subsequently shown to be induced by $\tau_1(\mathbf{k}_1)$ and to display the superstructure (1), namely C_{3v}^1 ($Z=3$), and D_{3d}^3 ($Z=3$). One can easily verify that the first of these groups describes nonsymmetric shifts of the atoms denoted by 2 and 3 in Fig. 1(b), whereas for symmetric shifts, assumed in Fig. 1(b), one obtains the space group D_{3d}^3 which corresponds to the rhombohedral ω phase. For the specific shifts of magnitude $a\sqrt{3}/12$, where a is the cubic lattice parameter, the rhombohedral symmetry D_{3d}^3 ($Z=3$) *increases* to D_{6h}^1 ($Z=3$), which is the *actual symmetry* of the hexagonal ω phase.

Because of the magnitude of the shifts assumed in the preceding mechanism for the β-ω (O_h^9-D_{6h}^1) transition, it should be unphysical to put forward a linear relationship between the order-parameter modulus (denoted by η) and the shifts (denoted by ξ) as it is usual in the standard Landau theory of structural transitions,[1] where the shifts are assumed to be small. Let us show that a good understanding of the β-ω transition can be obtained by the introduction of a transcendental dependence of η as a function of ξ. We will take here

$$\eta = \eta_0 \left[\sin\left(\frac{4\pi\xi}{a\sqrt{3}} + \frac{\pi}{6} \right) - \frac{1}{2} \right]. \tag{2}$$

The form of the function (2) is justified in Fig. 2(a), which shows that for successive values of ξ along [111],

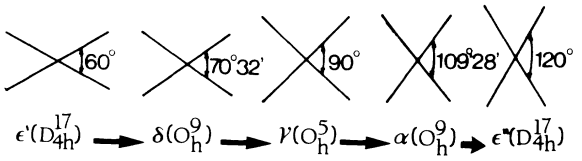

FIG. 3. Periodic character of the bcc-fcc Bain deformation of the iron unit cell, viewed by our considering the angle between the diagonals in the (110) cubic plane.

one gets periodically the sequence of β, hexagonal ω β', and h phases. More precisely, for $\xi=0,1,2,3,\ldots$ (in $a\sqrt{3}/2$ units), one has $\eta=0$ for the parent β phase; for $\xi=\frac{1}{6},\frac{7}{6},\frac{13}{6},\frac{19}{6},\ldots,$ $\eta=\frac{1}{3}$ (the ω phase); for $\xi=\frac{1}{3},\frac{4}{3},\frac{7}{3},\frac{10}{3},\ldots,$ $\eta=0$ again for the β' phase, for $\xi=\frac{2}{3},\frac{5}{3},\frac{8}{3},\frac{11}{3},\ldots,$ $\eta=-1$ (the h phase). The preceding numbers demonstrate that Eq. (2) complies with the standard definition of an order parameter (i.e., $\eta=0$ for the parent β or β' phases and $\eta\neq0$ for the ω and h phases) and that it holds *for infinite shifts.*

Taking into account the equilibrium values found for the eight-component order parameter for general shifts along [111], namely $\eta_1=\eta_2\neq0$ and $\eta_3=\cdots=\eta_8=0$, one can write the *effective* potential associated with $\tau_1(\mathbf{k}_1)$ as $F=F_0+a_1\eta^2+b\eta^3+a_2\eta^4$. Replacement of (2) in F and minimization of F with respect to the shifts ξ, yields the equation of state:

$$[\sin f(\xi)-\tfrac{1}{2}]\cos f(\xi)\{2a_1+3b[\sin f(\xi)-\tfrac{1}{2}]+4a_2[\sin f(\xi)-\tfrac{1}{2}]^2\}=0, \quad (3)$$

with $f(\xi)=4\pi\xi/a\sqrt{3}+\pi/6$. It leads to three possible stable states: the β and hexagonal ω phases for, respectively, $\sin f(\xi)=\frac{1}{2}$ (i.e., for $\xi=0,1,2,3,\ldots$) and $\cos f(\xi)=0$ (i.e., for $\xi=\frac{1}{6},\frac{7}{6},\frac{13}{6},\frac{19}{6},\ldots$), namely for *constant values of the order parameter.* For

$$\sin f(\xi)=\frac{1}{2}+\frac{-3b+(9b^2-32a_1a_2)^{1/2}}{8a_2},$$

one gets the rhombohedral ω phase as a stable state. It is easy to show that this latter phase coincides with the *Landau solution*, obtained by our minimizing F with respect to the order parameter η, which depends on the coefficients in F, in agreement with the phenomenological model of Cook and Pardee.[11] Let us stress that the *non*-Landau hexagonal ω phase is obtained only by a minimization of F with respect to the shifts. Besides, the h phase, which corresponds to $\cos f(\xi)=0$, represents an unstable configuration of the atoms with respect to the α structure discussed here below.

A similar scheme applies to the β-α transition[12,13] also reported in Ti, Zr, and Hf. In the hexagonal closed-packed α modification, the angle between the threefold axes, which is about 70° in the β phase, becomes 60°. The basic vectors of the hexagonal α unit cell can be expressed in functions of the primitive cubic lattice vectors as

$$\mathbf{a}_\alpha=\mathbf{a}_\beta+\mathbf{b}_\beta+\mathbf{c}_\beta,\quad \mathbf{b}_\alpha=-\mathbf{c}_\beta,\quad \mathbf{c}_\alpha=\mathbf{a}_\beta-\mathbf{b}_\beta\ . \quad (4)$$

The wave vector corresponding to (4) is $\mathbf{k}_2=\frac{1}{2}(\mathbf{a}_\beta^*+\mathbf{b}_\beta^*)$, located at the N point of the bcc Brillouin zone. The star of $\mathbf{k}_2$ has six arms,[10] and the shifts of the atoms at the β-α transition, which take place along the cubic [110] direction,[12] are connected with a single six-dimensional IR, denoted by τ_4 in Ref. 10. From the symmetries induced by the preceding IR,[14] one can infer the following scheme for the β-α transition: when the atoms are shifted along [110], the system exhibits the symmetries D_{2h}^{17} $(Z=2)$ for general shifts and D_{6h}^{4} $(Z=2)$ for the high-symmetric shifts of magnitude $a\sqrt{2}/12,7a\sqrt{2}/12,\ldots$. *This latter space group coincides with the symmetry reported for the α phase.* The form of the order-parameter modulus ζ as function of the average shifts ξ is given for the β-α transition by

$$\zeta=\zeta_0\left[\sin\left(\frac{4\pi\xi}{a\sqrt{2}}+\frac{\pi}{2}\right)-\frac{1}{2}\right], \quad (5)$$

which is represented in Fig. 2(b). Thus, one can see that for the high-symmetric shifts $a\sqrt{2}/4,3a\sqrt{2}/4,\ldots$, one gets the h phase of symmetry D_{6h}^{1} $(Z=1)$ already found in the β-ω mechanism. Accordingly, the unstable h phase provides the link between the β-ω and β-α transitions, the ω-α transition[15] appearing in our model as a *transition between two low-symmetry phases* associated with different IR's (and different wave vectors) of the parent β phase.

As another illustration of our approach, we will examine the bcc-to-fcc and bcc-to-hcp transition, which both occur in Ba, Tl, Fe, and Yb.[3] In iron, for example, the phase sequence $\delta(O_h^9)$-$\gamma(O_h^5)$-$\alpha(O_h^9)$ is reported at atmospheric pressure and decreasing temperature,[3] while a triple point is found at $P_t\simeq97$ kbar and $T_t\simeq450$ °C, at which the α and γ phases merge with the hcp ϵ phase.[3] For all phases, $Z=1$, except ϵ for which $Z=2$.

The periodic character of the bcc-to-fcc Bain deformation of the unit cell in iron can be viewed by our considering the angle ξ between the diagonals in the (110) cubic plane (Fig. 3). One can see that the δ-γ and γ-α transitions both correspond to an increase of ξ by about 19°. Such a deformation is accounted by the two-dimensional IR of the parent O_h^9 space group (i.e., the δ phase) at $\mathbf{k}=0$, denoted by τ_3 in Ref. 10, which is spanned[14] by the two combinations of the strain-tensor components: $\eta_1=\frac{1}{2}(e_{xx}-e_{yy})$ and $\eta_2=\frac{1}{6}(e_{xx}+e_{yy}-2e_{zz})$. It induces[14] for $\eta_1=0$, $\eta_2=\eta\neq0$, the symmetry D_{4h}^{17}. However, as when going from the δ to the γ phase ξ varies from $\simeq71°$ to 90°, the preceding tetragonal symmetry *transforms into the cubic symmetry* O_h^5 (the γ structure). A subsequent variation of ξ by 19° restores the O_h^9 symmetry (the α phase).

The dependence of the δ-γ transition order-parameter η as a function of the angle ξ is given here by

$$\eta = \eta_0[\sin(6\xi - \pi/2) - \cos(6\arccos\tfrac{1}{3})] \quad (6)$$

and is represented in Fig. 2(c). The unobserved tetragonal D_{4h}^{17} phases labeled ϵ' and ϵ'' in Fig. 3, correspond to a deviation of about 11° from the δ and α phases, respectively. ϵ' and ϵ'' are obtained one from another by a rotation of 90° around [110]. Their pseudohexagonal character prefigures the hcp ϵ phase, which is induced by the same IR of the O_h^9 space group (the α phase), at the N point of the bcc Brillouin zone, which has been shown here above to be associated with the β-α transition in Ti, Zr, and Hf. Consequently, the same dependence, given by (5), is verified for the α-ϵ transition order parameter as a function of the angle ξ. An experimental confirmation of this analysis is provided by the phonon spectrum of lithium,[16] *which reveals the softening of an optical mode at the N point* of the bcc Brillouin zone for its bcc-hcp 78-K transition, as predicted in our approach.

Although the generalization of the Landau's theory presented in this Letter applies in a general manner to reconstructive transitions, we have chosen to illustrate its applicability to the restricted case of some groups of elements, because the simplicity of their structures allows concrete considerations on the shifts of the atoms. The existence of a small number of sublattices is indeed an important necessary condition for one of the more essential mechanisms assumed in our approach to take place, namely, the increase of symmetry of one phase due to specific high-symmetric shifts of the atoms. The existence of a complex set of sublattices would be unfavorable for such a mechanism, as the increase of symmetry associated with one type of sublattice should be compensated by the nonsymmetric shifts associated with the other sublattices, and the group-subgroup relationship between the phases should be preserved as noted by Cahn in the case of metallic alloys.[17]

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