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Isosymmetric Structural Phase Transitions: Phenomenology and Examples

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Abstract

Structural phase transitions ('type 0') in which there is no change of space group or of the occupied Wyckoff sites contrast with others in which diffusionless transformation can occur in a single step between higher- and lower-symmetry space groups (type I), through a low-symmetry transition state between relatively higher-symmetry initial and final structures (type II), and those where the mechanism is necessarily more complex (type III). A phenomenological model shows that type 0 transitions are necessarily first order, and may terminate at a critical point. The corresponding supercritical behaviour is a 'crossover' or 'diffuse transition' in which there is no discontinuity in any free-energy derivative. However, the location of the crossover is precisely defined at a minimum in the second derivative of the free energy with respect to a suitable order parameter. Isosymmetric transitions and/or crossovers occur in important mineralogical systems (pyroxenes, feldspars and carbonates) and non-linear optic materials ($KTiOPO_4$). Non-monotonic variation of free-energy derivatives around the crossover can have a serious effect on the locations and slopes of phase equilibria in pressure–temperature space. Interaction between non-symmetry-breaking and symmetry-breaking order parameters appears to play a major rôle in stabilizing low-symmetry clinopyroxene and anorthite feldspar phases.

1. Introduction

This paper presents an extension of an approach to the classification of phase transitions that has been outlined previously (Christy, 1993). In that work, three types of transition were rigorously distinguished on symmetry criteria:

(1) Transitions in which a low-symmetry (LS) phase is obtained from a high-symmetry (HS) phase by atomic displacements which are consistent with a unique non-identity irreducible representation of the higher symmetry. These type I transitions can be modelled phenomenologically using Landau theory, and can be first or second order thermodynamically.

(2) 'Type II' transitions in which two different HS structures share a common LS phase and can be regarded as having special cases of the LS structure which arise when a structural parameter of the LS structure takes special values. The initial and final structures (HS) and transition state (LS) of a 'martensitic' transition are examples. The free energy of such systems may be expressed as a Fourier series in the appropriate order parameter. Examples are reviewed in Tolédano & Dmitriev (1993) and described in more detail in papers cited therein.

(3) 'Type III' transitions, where the atomic rearrangements involved are more complex. These can be decomposed into multiple type I and type II steps, which link various transition states of specific symmetry.

Christy (1993) showed that the minimum number of steps needed for several important transitions is quite small (3–5), and that there is experimental evidence for the utilization of such short diffusionless routes in some 'reconstructive' transitions.

Transitions between phases which have the same space group, and have corresponding atoms on the same Wyckoff sites, do not fall into any of these categories. An additional type 0 is proposed to incorporate these into the scheme. Although isosymmetric transitions are well known for amorphous systems (e.g. the liquid–gas transition) and electronic transitions (metal–insulator, valence transitions), only a few examples are currently known where the transformation is predominantly structural, i.e. where a change in the atomic coordination environment appears to be the driving force. It will be apparent from the examples discussed below that a change in unconstrained axial ratios or atomic coordinates does indeed result in distinctively different coordination environments and energetics without a change in symmetry for some systems. Intimately associated with isosymmetric transitions are supercritical 'crossovers' in which thermal expansivity and/or compressibility vary non-monotonically with temperature or pressure. These may be more widespread than discontinuous isosymmetric transitions, but the causative factors are similar.

First, a Landau-type free-energy expansion is constructed, from which the phase equilibrium topology for these materials is predicted. Initially, the thermodynamics are considered of a hypothetical model system which exhibits the possibility of an isosymmetric transition. In the final section, the behaviour of real systems will be interpreted in the light of that predicted by the model.

2. Phenomenology

Suppose a structure has an unconstrained parameter (atomic coordinate axial parameter or ratio) Q. There is no special significance to the zero value of Q, which may be chosen arbitrarily. The free energy G may be assumed to vary as a polynomial in Q. Since Q and all its powers transform as the identity representation, and there is no requirement for G to be symmetrical about $Q = 0$, we write

$$G = aQ + bQ^2 + cQ^3 + dQ^4 \text{ (+ higher-order terms).}$$

$$(1)$$

We assume that this equation provides a fair approximation to the free energy over some finite Q range of interest. Stable or metastable phases have Q values corresponding to the minima of G. Inclusion of fourth-order terms in (1) allows up to two such minima. There may be more if higher-order terms are significantly negative. Materials that do not show isosymmetric transitions have one free-energy minimum only.

The origin of Q could be shifted so as to eliminate the first-order term in (1), but one stationary point of G would then be constrained to be at $Q = 0$. It will be seen below that this obscures the nature of the supercritical behaviour in this model system. However, 2–3–4 potentials have been used in phenomenological studies of first-order and isosymmetric transitions (Krumhansl & Gooding, 1989; Kerr & Rave, 1993).

Consider the variation in the shape of $G(Q)$ as the coefficients a and b are varied (as may occur in response to a change in temperature or pressure). Six distinct thermodynamic régimes may be distinguished, as shown in Figs. 1(a) and (b). Those labelled 'R' have the most stable minimum in G on the right (high Q), those labelled 'L' have the most stable state for low Q. The régimes labelled '1' have only a single energy minimum and no regions of instability. Those labelled '3' have a stable minimum, a metastable minimum and a distinct energy maximum separating the two. The intermediate régimes, labelled '2', have only one minimum, but there is a region to one side of it where there is spinodal instability with respect to fluctuations in Q. The curve shapes 1–3 can be defined in terms of the behaviour of the derivatives dG/dQ and d^2G/dQ^2 as follows.

(1) In regions $R1$ and $L1$, the first derivative has three roots and the second derivative has two over the Q range of interest.

(2) In $R2$ and $L2$, the first derivative has three roots but the second derivative has none.

(3) In $R3$ and $L3$, the first derivative has only one root and the second has none.

Variation in the coefficient a does not affect the shape of the dG/dQ curve. An increase in a will result in progression through the régimes $R2$–$R3$–$L3$–$L2$ or $R1$–$L1$. Conversely, changing b does affect the shape of the dG/dQ curves. An increase in b causes the curve shape to change to $R2$–$R1$ or $R2$–$R3$–$L3$–$L2$–$L1$.

Examination of the derivatives of G with respect to Q allows the régime boundaries to be defined more quantitatively in terms of the coefficients a–d.

(1) The dG/dQ cubic derived from (1) has the form

$$dG/dQ = a + 2bQ + 3cQ^2 + 4dQ^3; \qquad (2)$$

this cubic has a distinct maximum and minimum only if real roots exist for

$$d^2G/dQ^2 = 2b + 6cQ + 12dQ^2 = 0, \qquad (3a)$$

that is

$$b < 3c^2/8d. \qquad (3b)$$

This value of b delineates the $(R1, L1)/(R2.L2)$ boundary.

(2) All six curve types meet when the roots of the dG/dQ cubic are coincident. This occurs when

$$b = 3c^2/8d \text{ and } a = c^3/64d^3. \qquad (4)$$

For constant (c, d), this implies the existence of a critical point in (a, b) space, at which all boundary lines between fields of different curve shape converge.

(3) A third differentiation of G with respect to Q gives

$$\mathrm{d}^3/\mathrm{d}Q^3 = 6c + 24dQ, \tag{5}$$

so the position of the inflexion in the $\mathrm{d}G/\mathrm{d}Q$ cubic is at $Q = -c/4d$, independent of a and b.

The conditions (1) and (2) above are summarized in the qualitative phase diagram shown in Fig. 2. Topologically, this is identical to the gas–liquid diagram obtained from consideration of the van der Waals's equation of state. If a and b are approximately monotonic functions of intensive variables such as pressure or temperature, this phase diagram topology would be preserved.

Thermodynamically, the changes in curve shape may be described as follows.

(1) The $R2$–$R3$–$L3$–$L2$ progression corresponds to a first-order transition. The $R2/R3$ and $L2/L3$ boundaries are limits of metastability for the less stable phases on each side. The transition occurs when the central root of the $\mathrm{d}G/\mathrm{d}Q$ cubic (corresponding to the local energy maximum between phases) crosses the inflexion point at $Q = -c/4d$. This is depicted in Fig. 3(a).

(2) $R2$–$R1$ (or $L1$–$L1$) corresponds to closure of the spinodal instability, but not a phase transition (Fig. 3b).

(3) $R1$–$L1$ is more interesting in that a root of the $\mathrm{d}G/\mathrm{d}Q$ cubic crosses the inflexion line. At the crossover point, $\mathrm{d}^2G/\mathrm{d}Q^2$ is at a minimum, and Q changes fast from a value typical for the 'right-hand' phase to a value more appropriate for the 'left-hand' phase. A 'diffuse' or 'crossover' transition occurs. Although there are no thermodynamic discontinuities, the location of the crossover as a function of intensive variables such as pressure and temperature can be precisely specified at the zero in $\mathrm{d}^3G/\mathrm{d}Q^3$ (Fig. 3c).
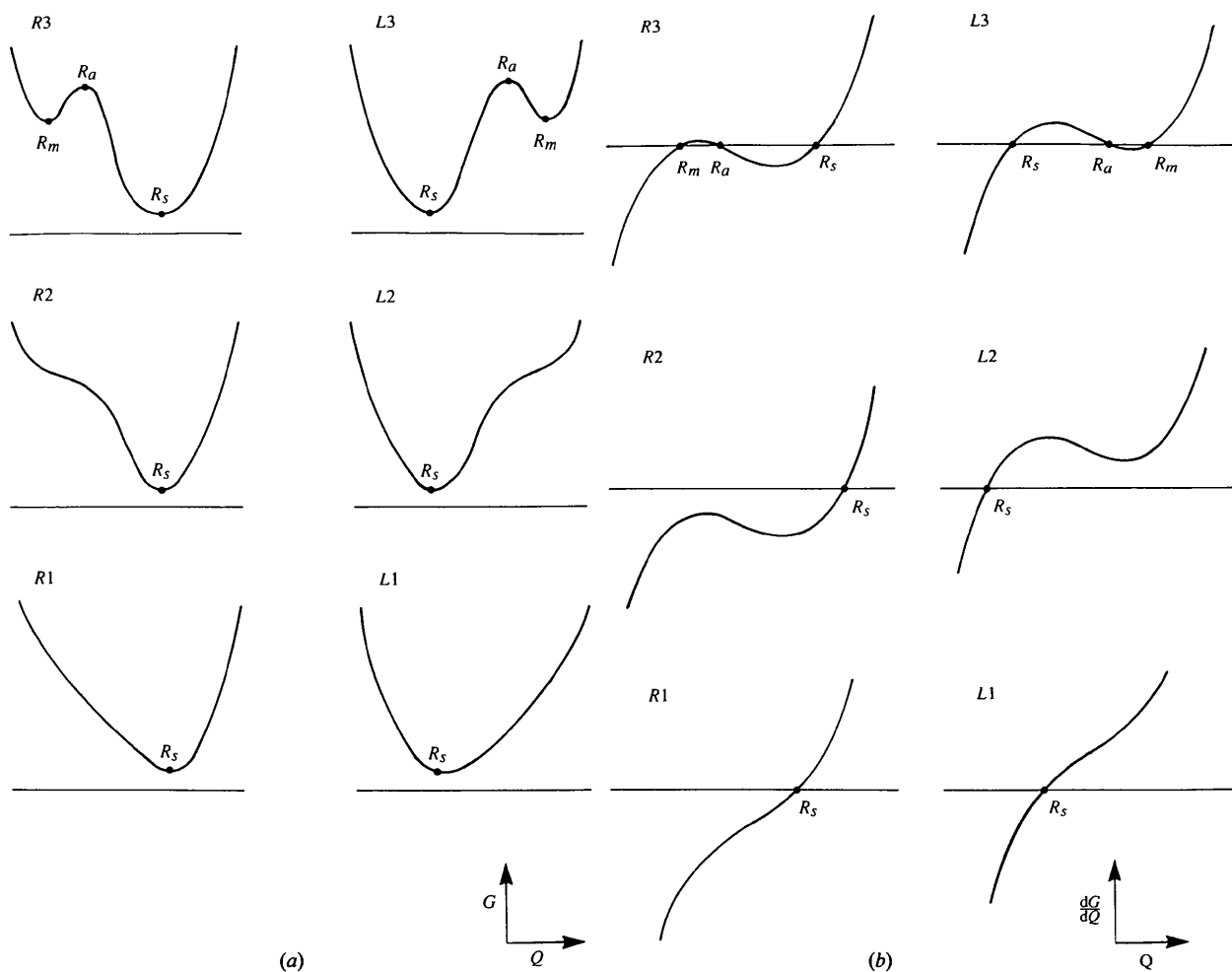

Fig. 1. (a) Variation of G with Q for six distinct geometries of the free-energy quartic. Stationary points are labelled R_s (stable minimum), R_m (metastable minimum) and R_a (unstable energy maximum). (b) Variation of $\mathrm{d}G/\mathrm{d}Q$ with Q for the six different curves of (a).

Note that a second-order transition cannot occur without coalescing the $R1/R2/R3/L3/L2/L1$ boundaries into a single line, which requires $c = 0$. Since there is no change in symmetry in this model system, there is no symmetry constraint that forces this condition. Therefore, truly continuous transitions will not be observed although (a, b) paths that go through the critical point will result in *apparent* second-order behaviour (Fig. 3d).

3. Discussion and examples

It is apparent that isosymmetric phase transitions are necessarily first order. When plotted against two intensive state variables such as pressure and temperature, the equilibrium line terminates at a critical point but extrapolates into a crossover line. Physical properties change rapidly but continuously at the crossover, whose location is given by a minimum in d^2G/dQ^2.

Electronic transitions provide familiar examples of first-order transitions and critical points (*e.g.* Ce metal: Jayaraman, 1965) and crossover [the 'diffuse valence transition' in $EuPd_2Si_2$ (Adams, Heath, Jhans, Norman & Leonard, 1991)]. In the case of Ce, the crossover behaviour is still abrupt enough to cause a change in the slope of the melting curve 1.55 GPa and 385 K above the α/γ critical point. A contrasting example is provided by the change in slope of the helically ordered–disordered phase boundary in $CsCuCl_3$, a compound in which the Jahn–Teller distorted $CuCl_6$ octahedra may each adopt one of three different orientations. This may be related to a (presumably isosymmetric) static-dynamic disorder transition in the high-symmetry phase (Christy, Angel, Haines & Clark, 1994). Atomic displacements are unimportant in all these cases. Below,

systems are considered where the transition is primarily 'structural', *i.e.* changes in atomic coordinates and environments play a vital rôle in the transition.

Christy (1993) stressed the need for atomic displacements at a type I or II phase transition to be consistent with the symmetry of an extant phonon. For the intermediate steps of a type III transition, the phonon is not required to soften to zero velocity between transition states since these states are of ephemeral existence. Krumhansl & Gooding (1989) have pointed out that full phonon softening is not observed in most phase transitions. For isosymmetric type 0 transitions, the only atomic coordinates that change are those unconstrained by the current symmetry. Therefore, the existence is guaranteed of a corresponding identity-representation phonon.

The likelihood of isosymmetric structural transitions was recognized by Cowley (1980), who cited as a possible example $KHPO_4$ (Eberhard & Horn, 1975). In the last few years, a number of examples have been found. These are loosely classified below.

(1) Transitions dominated by coordination change. The volume change at the 0.3 GPa II–IV transition in KNO_3 is 11.5%, although diffraction and spectroscopic
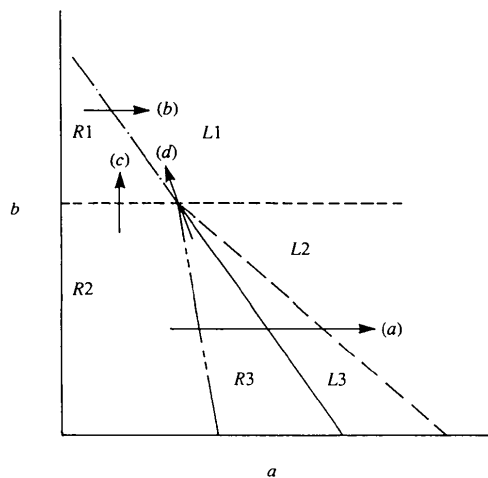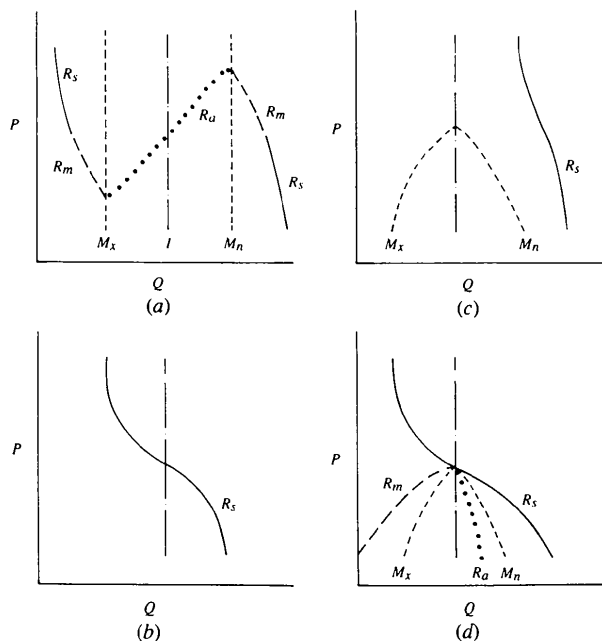

Fig. 3. Trajectories of stationary points in P–Q space, where P is an intensive variable such as pressure or temperature, and is taken to be a locally monotonic function of a and b. Corresponding values of a and b for cases (a)–(d) are shown in Fig. 2. Loci are labelled as follows. I = inflexion in dG/dQ cubic; M_n/M_x = minimum and maximum of cubic; others as in Fig. 1. The stable equilibrium value of Q is shown by the solid line, metastable by dashes, unstable by heavy dots. The four cases are: (a) first-order phase transition (a increases with P, less positive b); (b) crossover (a increases with P, more positive b); (c) closure of spinodal (b increases with P); (d) continuous transition through a critical point.

Fig. 2. Generalized phase diagram topology. Metastability limits for phases L and R are the boundaries between regions labelled '2' and '3'. The crossover is between $R1$ and $L1$, and the spinodal line follows the 1–2 boundaries. Arrows (a)–(d) are the trajectories in (ab) space of Fig. 3.

studies indicate that space group and Wyckoff sites are identical for both phases (Worlton, Decker, Jorgensen & Keb, 1986; Adams, Hatton, Heath & Russell, 1988). However, the coordination number of K increases from 9 to 11.

(2) Transitions due to framework collapse. The 5.5 GPa transition in $KTiOPO_4$ involves crumpling of the Ti—O—P framework and a relative slip of its constituent chains. The transition is strongly first order, with a volume decrease of 4.2% (Allan, Loveday, Nelmes & Thomas, 1992; Allan & Nelmes, 1992). Framework collapse also leads to distinctive structural parameters for the high-pressure and high-temperature forms of $I\bar{1}$ anorthite feldspar, $CaAl_2Si_2O_8$, although these appear to be separated by a crossover rather than a first-order transition over the pressure–temperature range examined to date. This would account for the observation that the equilibrium line separating the body-centred phase from the low-pressure, low-temperature $P\bar{1}$ phase is strongly curved (Redfern & Salje, 1992); Hackwell & Angel, 1993).

(3) Transitions arising due to the existence of two competing order parameters, which can independently cause the same descent from a higher symmetry. Each type of order predominates over the other in a distinct pressure–temperature regime. An example of crossover driven in this fashion is provided by the behaviour of the spontaneous strain and cation ordering of albite feldpar, $NaAlSi_3O_8$, as a function of temperature (Salje, Kuscholke, Wruck & Kroll, 1985). The phases of $KTiOPO_4$ are both $Pna2_1$ in symmetry, but show a common $Pnan$ pseudo-symmetry. This suggests that there are two distinct structural mechanisms for breaking the higher symmetry in this system also.

(4) High-pressure transitions and crossovers arising from a change in dominant compression mechanism. These have been documented for $MgSiO_3$ orthopyroxene (Hugh-Jones & Angel, 1994) and the carbonate minerals magnesite, $MgCO_3$, and dolomite, $CaMg(CO_3)_2$ (Fiquet, Guyot & Itié, 1994).

In all the above examples, distinct phases can be distinguished only along pressure–temperature paths which cross the first-order transition line. Maxima in compressibility or thermal expansivity indicate a crossover, which does *not* separate thermodynamically distinct phases but *may* extrapolate into a first-order transition line. Therefore, a crossover indicates an incipient isosymmetric transition which may be observed experimentally under different pressure–temperature conditions if the structure does not undergo transitions

of types I–III first. Careful characterization of the crossover behaviour in $I\bar{1}$ anorthite is important in order to define a reference $I\bar{1}$ structural state in the stability field of the $P\bar{1}$ phase, so as to describe the type I $I\bar{1}$–$P\bar{1}$ transition properly (Hackwell & Angel, 1995). Crossover in a phase may have a marked influence on the rest of the phase diagram. For instance, it has recently been shown (Christy & Angel, 1995) that the low-pressure/low-temperature $P\bar{1}$ phase of anorthite and pigeonite phase of clinopyroxene may in fact be stabilized relative to the corresponding high-symmetry phases due to coupling of the non-symmetry-breaking order parameter with a cell-doubling order parameter near the crossover in the high-symmetry phase.

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