

Thermodynamics of nonconvergent cation ordering in minerals: I. An alternative approach

MICHAEL A. CARPENTER

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K.

ROGER POWELL

Department of Geology, University of Melbourne, Parkville, Victoria 3052, Australia

EKHARD K. H. SALJE

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K.

ABSTRACT

A general expression for the free energy of ordering, based on Landau theory, is proposed for describing the thermodynamics of nonconvergent cation ordering in minerals. The energy due to fundamental structural differences between crystallographic sites over which ordering occurs is accounted for by adding a term that is linear in the order parameter, Q , to an expansion of the form frequently used to describe phase transitions, giving

$$G = -hQ + \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{n}e_nQ^n$$

where h , a , T_c , and e_n are constants and $n = 3, 4$, or 6 . Normal Landau symmetry rules are relaxed, with the result that all spontaneous strains are expected to vary linearly with Q . The excess entropy is shown to vary approximately linearly with Q^2 , except at $Q \gtrsim 0.9$, where higher order terms are required to account adequately for purely configurational effects. If the Landau coefficients are allowed to vary with composition, nonconvergent ordering in solid solutions can, in principle, also be described. Some advantages of the proposed approach are that (1) it is quite general and does not depend on any structure-specific model, (2) a wide variety of patterns of structural behavior can be produced by selecting values for only a limited number of parameters, (3) the problem of identifying and determining the magnitudes of different entropy contributions is avoided, and (4) the simple form of the expansion can be accommodated readily into wider thermodynamics-based computer models of mineral stabilities.

INTRODUCTION

Atomic ordering processes in minerals influence both the stability limits of individual minerals and the partitioning of elements between different minerals. Their pressure and temperature dependencies have attracted attention largely for the geobarometric and geothermometric information that they might yield. Following Thompson (1969) a distinction is usually drawn between convergent and nonconvergent ordering. In the former, two or more crystallographic sites can become related by symmetry when their average occupancy by different atoms becomes the same. The ordering characteristically gives rise to a reduction in symmetry at a discrete phase transition. In contrast, the sites over which nonconvergent ordering occurs can never become related by symmetry even if their occupancies are identical—a degree of site preference by different atoms is retained at all temperatures and pressures because of some fundamental differences in local coordination or bonding.

Progressively more sophisticated models have been de-

veloped for describing the thermodynamics of nonconvergent cation ordering in such minerals as spinels (recent reviews: Navrotsky, 1987; Ghiorso and Sack, 1991; Wood et al., 1991; Della Giusta and Ottonello, 1993), orthopyroxenes (Sack and Ghiorso, 1989; Davidson and Lindsley, 1989; Shi et al., 1992, and references therein), and olivines (e.g., Sack and Ghiorso, 1989). At the same time, advances have been made in the quantitative treatment of convergent cation ordering (e.g., Cohen, 1986a, 1986b; Salje, 1990; Carpenter, 1988, 1992a, 1992b; Carpenter et al., 1990a). The purpose of the present paper is to present a new method of analyzing nonconvergent processes, which makes use of recent developments of Landau theory for describing the thermodynamics of phase transitions. By setting both convergent and nonconvergent processes under the same theoretical framework, a significant step toward a unified treatment of all order-disorder phenomena in minerals may be achieved. In two companion papers (Carpenter and Salje, 1994a, 1994b) some practical applications of the approach are presented, making use of experimental data for NiAl_2O_4 and

MgAl₂O₄ spinels, the (Mg,Fe)SiO₃ orthopyroxene solid solution, and potassium feldspar, to illustrate its strengths and weaknesses.

Landau free energy expansions appear to provide useful thermodynamic descriptions of phase transitions in minerals with both displacive and order-disorder character (recent reviews: Salje, 1990, 1991, 1992a; Carpenter 1988, 1992a). Salje and Kroll (1991) have shown that the same formal approach can be applied to nonconvergent ordering, in which no phase transition is involved, if an additional term that is linear in the order parameter, Q , is included (see also Salje, 1992b). The physical basis of this extension of the theory can be understood by analogy with magnetic ordering processes occurring in an externally applied magnetic field. A magnetic ordering transition occurs by the spontaneous alignment of magnetic dipoles. Above a critical temperature the dipoles may be aligned spin-up or spin-down at random, whereas below this temperature they will have some degree of preferred orientation. If the crystals are held in a magnetic field, one orientation of the magnetic dipoles becomes energetically favored at all temperatures; there is then no phase transition, and the disordered state no longer has an equilibrium stability field. Thus, in the presence of an applied field, the magnetic ordering becomes nonconvergent. The importance of this analogy is that the methodology for describing the macroscopic effect of applied fields on phase transitions has been thoroughly investigated for a variety of materials (see Bruce and Cowley, 1981, for example). The effects of a field on materials that are expected to conform to Landau theory (e.g., with large spontaneous strains) appear to be quite well reproduced by normal expansions in Q when a linear term is added.

Harris et al. (1989) and Salje and Kroll (1991) argued, in effect, that the energy associated with structural differences between two crystallographic sites over which nonconvergent ordering occurs can be represented in the same way as energy differences arising from the application of an external field. The field term is sometimes referred to as being a symmetry-breaking term because its existence stabilizes the low symmetry state and ensures that crystals with $Q = 0$ cannot have an equilibrium stability field. One implication of that, however, is that the normal symmetry rules for determining which terms are allowed in Landau expansions no longer apply. Odd order terms cannot be automatically excluded, and so the form of expansion that would be expected to apply to a general case of nonconvergent ordering might be

$$G = -hQ + \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{3}bQ^3 + \frac{1}{4}cQ^4 + \dots \quad (1)$$

Here, a , b , c , ... are standard Landau coefficients, T_c is some critical temperature, and h refers to the effective field. This equation provides the basis for the present analysis. It bears qualitative similarities to the series expansions introduced into the geological literature by Thompson (1969, 1970), though its origin derives from

the group theoretical treatment of phase transitions by Landau and Lifshitz (Landau, 1937; Lifshitz, 1942a, 1942b; Landau and Lifshitz, 1980). In particular, the treatment of entropy is rather different from that of Thompson and many subsequent workers.

The paper is divided into four main sections. Firstly, since many readers may not be familiar with the approach, the consequences of adding a field term to a normal Landau expansion are illustrated schematically. A theoretical justification, with some analysis of the physical origin of the terms in Equation 1, is then offered. Comparison is also made with Boltzmann and Bragg-Williams type solutions and with some of the models currently used for minerals. In the following section, a few intimations of the possibilities for describing thermodynamic effects due to nonconvergent ordering in mineral solid solutions are offered. Finally, the way in which the basic ideas may be applied in practice is outlined.

LANDAU THEORY

Convergent ordering

For a material containing atoms of A and B that order between sites s and s' , the order parameter is usually defined as

$$Q = |X_A^s - X_A^{s'}| = |X_B^s - X_B^{s'}| \quad (2)$$

where X_A^s is the proportion (between 0 and 1) of A atoms on s sites, etc. $Q = 0$ represents fully disordered states, and $Q = 1$ represents the fully ordered state of a crystal with equal proportions of A and B atoms. For phase transitions that, for symmetry reasons, have odd order terms that must be strictly zero, the familiar form of the Landau free energy expansion (without degeneracies, coupling, etc.) is

$$G = \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{4}bQ^4 + \frac{1}{6}cQ^6 + \dots \quad (3)$$

The free energy, G , is, as usual, defined as the excess due to the transition with respect to the fully disordered state. It is commonly found that the expansion can be truncated after the fourth-order term to describe observed excess properties (second-order transitions). In some systems the fourth-order term is found to be negligibly small, and the series can be truncated after the sixth-order term (tricritical transitions). In both these cases, T_c is the equilibrium transition temperature. If the fourth-order term is negative, the sixth-order term must be positive for stability (first-order transitions).

Experimental data are rarely of adequate precision to allow the determination of coefficients for more than three terms of a Landau expansion in one order parameter. For nonconvergent ordering that would include the term linear in Q , and so, for comparative purposes, it is convenient to consider only two terms in Equation 3, which may be rewritten as

$$G = \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{n}e_nQ^n. \quad (4)$$

Values of n that are going to be of principal interest are 3, 4, and 6 ($n = 4$ is the second-order case, $n = 6$ the tricritical case, and $n = 3$ would give a truncated expansion describing a transition in which odd order terms are not constrained to be strictly zero). Also for comparative purposes, it is convenient to reduce the number of variables. By dividing by aT_c , Equation 4 becomes

$$g \equiv \frac{G}{aT_c} = \frac{1}{2}(T' - 1)Q^2 + \frac{1}{n}e'_n Q^n \quad (5)$$

where $T' = (T/T_c)$ and $e'_n = (e_n/aT_c)$.

The equilibrium value of Q is found from the minimum in g , i.e., from

$$\frac{\partial g}{\partial Q} = 0 = (T' - 1)Q + e'_n Q^{n-1}. \quad (6)$$

In the limit of $T' = 0$, Q attains a limiting value Q_0 , which gives

$$e'_n = \frac{1}{Q_0^{n-2}}. \quad (7)$$

This, substituted into Equation 6, gives

$$\frac{\partial g'}{\partial Q'} = 0 = (T' - 1)Q' + Q'^{(n-1)} \quad (8)$$

and, hence

$$Q'^{(n-2)} = T' - 1 \quad (9)$$

where $g' = (g/Q_0^2)$ and $Q' = (Q/Q_0)$. The form of Q' as a function of T' that results for $n = 3, 4,$ and 6 is shown in Figure 1.

Nonconvergent ordering

The important step in adapting conventional Landau theory to describe nonconvergent processes is the assumption that the factors that ensure that crystallographic sites in a structure are invariably distinct can be treated as being equivalent to an applied field. By following the argument that only three terms are likely to be of practical use, Equation 1 may be written in the form of Equation 4 as

$$G = -hQ + \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{n}e_n Q^n. \quad (10)$$

Reducing the number of variables as before gives a simplified condition for equilibrium:

$$\frac{\partial g'}{\partial Q'} = 0 = -h' + (T' - 1)Q' + (h' + 1)Q'^{(n-1)} \quad (11)$$

where $h' = (h/aT_c Q_0)$. This has two adjustable parameters, h' and n . The T' dependence of Q' for $n = 3, 4,$ and 6 is illustrated for different values of h' , i.e., for different field strengths, in Figure 2. The most important consequences of introducing the linear field term are that there is no longer any phase transition and that a degree of order (finite Q) is retained at all temperatures. At $T' \gg 1$, the order parameter becomes small, giving $Q' \gg Q'^{(n-1)}$ for $n > 3$. In the high-temperature limit the solution for

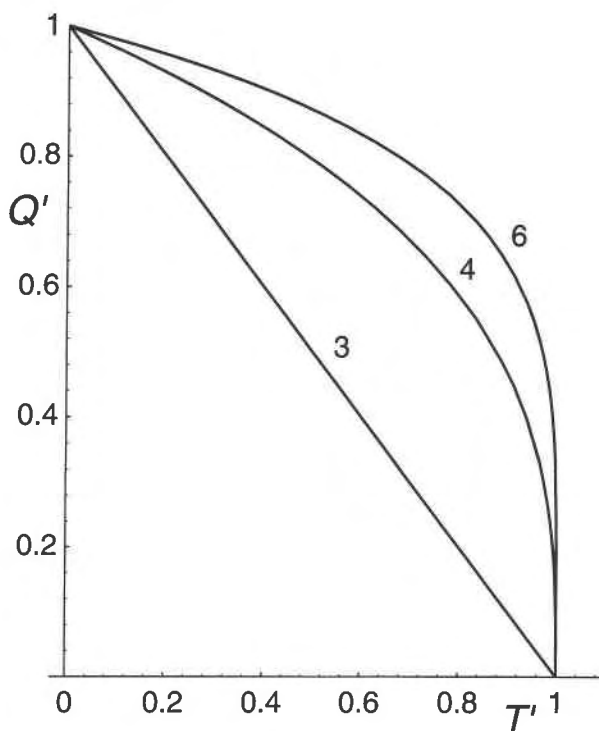


Fig. 1. The variation of $Q' = Q/Q_0$ as a function of $T' = T/T_c$ for convergent processes, obtained by solving Equation 8 with values of $n = 3, 4,$ and 6 .

Q' becomes

$$Q' = \frac{h'}{(T' - 1)} \approx \frac{h'}{T'} \quad (12)$$

which is independent of the details of the model.

A wide range of equilibrium behavior can be reproduced using equations with the form of Equation 10 by adjusting only a small number of parameters. The field term can be positive or negative, for example favoring A atoms ordering onto s sites or A atoms ordering onto s' sites. Similarly, the order parameter can itself be positive or negative if it is expressed as $Q = (X_A^s - X_A^{s'})$. The concept of a first-order transition becomes of limited importance in this context because, in the absence of any phase transition, discontinuities are not expected in the variation of Q with temperature. However, there is an advantage in deriving the equation from Landau theory in this way because it then becomes possible to draw on the substantial experience gained in the study of phase transitions as to the likely importance of high-order terms. Thus, for example, Q^3 terms can be small even when they are allowed by symmetry (Devarajan and Salje, 1984; Palmer et al., 1990; Hatch et al., 1990; de Dombal and Carpenter, 1993), and Q^4 terms can be small in systems with order-disorder transitions (Redfern et al., 1989; Carpenter et al., 1990a).

The linear field term has been added to account for intrinsic energetic differences between the crystallograph-

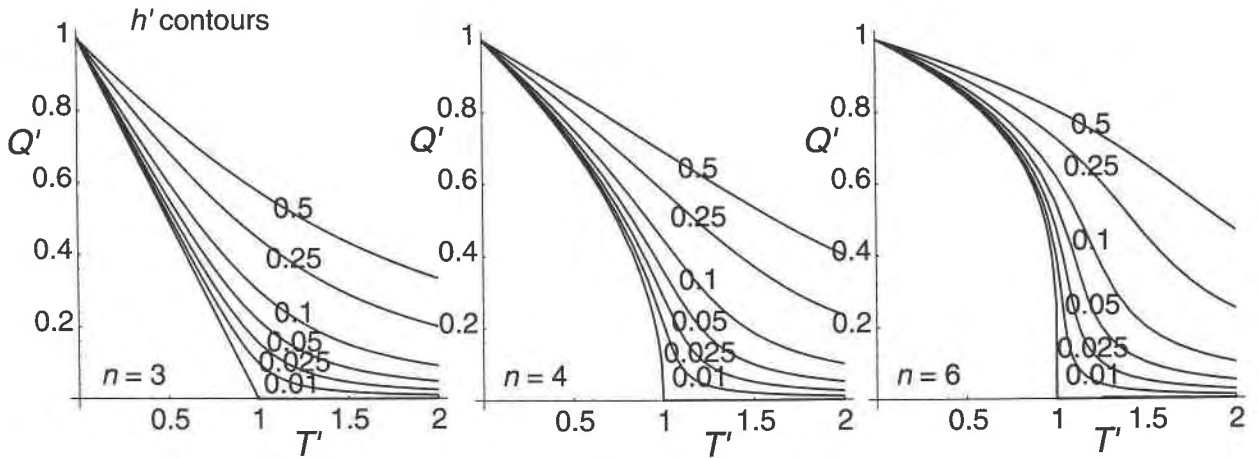


Fig. 2. The variation of $Q' = Q/Q_0$ as a function of $T' = T/T_c$ for nonconvergent processes, obtained by solving Equation 11. The contours are for different values of h' ($= h/aT_cQ_0$).

ic sites on which nonconvergent ordering occurs. It might reasonably be expected to be at least weakly temperature dependent, and the assumption of a linear temperature dependence for h' in Equation 11 allows this possibility to be explored. If h' decreases with increasing temperature there should be some extrapolated value of T' , T'_{lim} , at which it goes to zero. At $T' < T'_{lim}$ and $T'_{lim} > 1$, this variation can be described as

$$h' = h'_0 \left(\frac{T'_{lim} - T'}{T'_{lim} - 1} \right) \quad (13)$$

where h'_0 is the value of h' at $T' = 1$. Equation 11 then becomes

$$\frac{\partial g'}{\partial Q'} = 0 = -h'_0 \left(\frac{T'_{lim} - T'}{T'_{lim} - 1} \right) + (T' - 1)Q' + \left[h'_0 \left(\frac{T'_{lim} - T'}{T'_{lim} - 1} \right) + 1 \right] Q'^{(n-1)}. \quad (14)$$

The variation of Q' has been calculated as a function of T' for $T'_{lim} = 2$ and $T'_{lim} = 4$, and the results are shown in Figure 3. The temperature dependence of h' certainly causes changes in the detailed evolution of Q' but does not give distinctly different patterns. The same variation of Q' could probably be reproduced quite closely by assuming h' to be constant and allowing its temperature dependence to be accommodated in the selection of alternative (but constant) values of n , a , T_c and e_n . For the present, therefore, a pragmatic approach is maintained, and it is assumed that any temperature dependence of the effective field can be ignored.

THEORETICAL JUSTIFICATION

In using qualitatively similar types of expansion to describe thermodynamic changes in minerals, it is sometimes assumed that the coefficients are merely fit parameters that have little or no physical meaning. This is not the case in Landau theory, for it is known that the mac-

roscopic Landau coefficients can be understood in terms of specific microscopic origins (e.g., Salje, 1992a; Salje and Marais, 1992; Dove et al., 1992; Heine et al., 1992). Moreover, the predicted variations of Q and of other excess properties extrapolated over temperature intervals of hundreds of degrees are consistent with observed variations in many systems (see reviews by Carpenter, 1988, 1992a; Salje, 1990, 1991, 1992a, 1992b). To explain why that is so and to examine some of the assumptions involved, it is helpful to compare the physical origin of terms in the Landau expression with comparable terms in models of ordering processes that are likely to be more familiar to mineralogists. The methods of accounting for entropy and enthalpy, the roles of symmetry and lattice distortions, and possible behavior at low temperatures as $Q \rightarrow 1$ are discussed here.

Configurational and nonconfigurational entropy

The excess entropy, S , due to ordering with respect to a fully disordered state, as derived from both Equation 4 (convergent ordering) and Equation 10 (nonconvergent ordering), is given by

$$S = -\frac{dG}{dT} = -\frac{1}{2}aQ^2. \quad (15)$$

This is, in reality, a series expansion truncated after the second-order term. For phase transitions that are purely displacive in character, the excess entropy is nonconfigurational, and the higher order terms can be shown to be small (Salje et al., 1991).

For atomic ordering processes, the configurational entropy would usually be calculated from an expression of the form $-R(X'_A \ln X'_A + X'_B \ln X'_B + X'_A \ln X'_A + X'_B \ln X'_B)$, for a crystal with equal numbers of s and s' sites. Rewriting this in terms of Q and defining the excess configurational entropy, S_{config} , as being relative to the disordered state gives

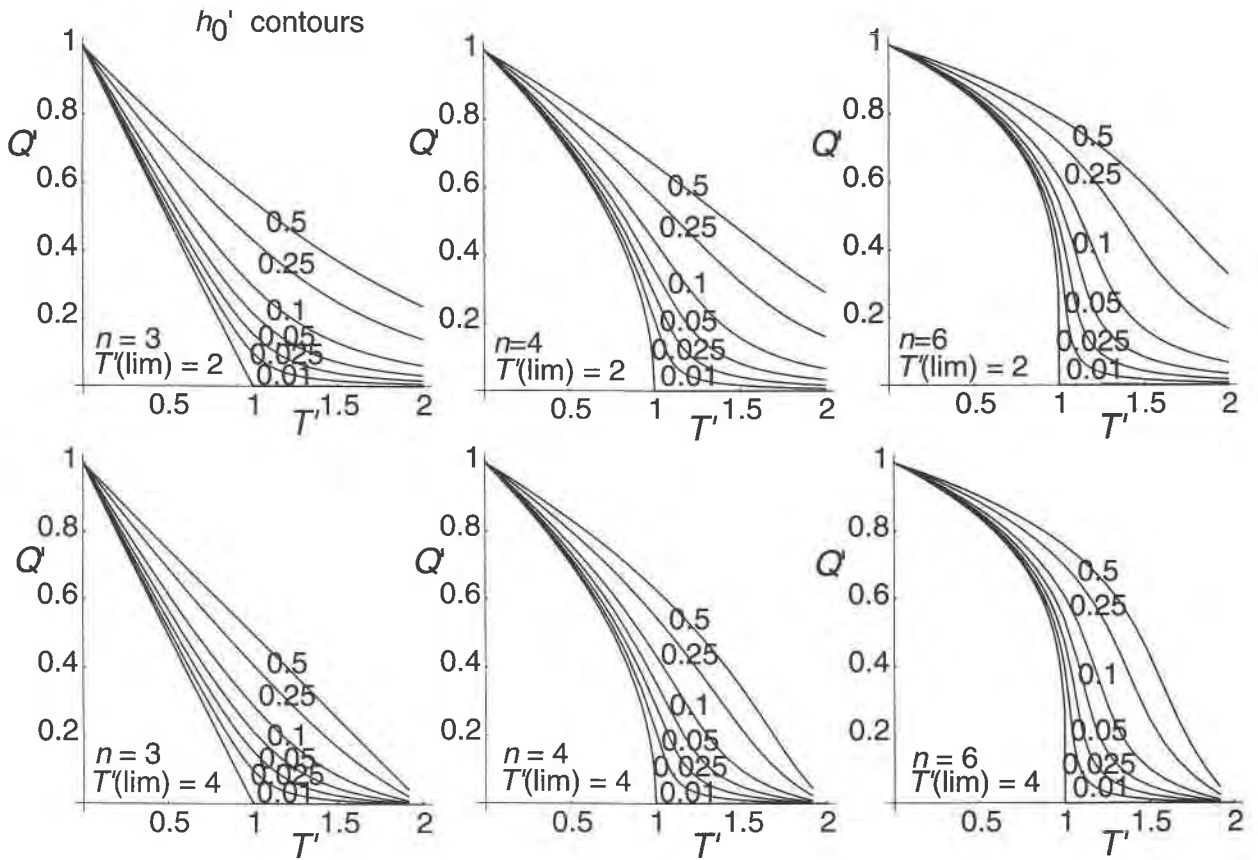


Fig. 3. Variation of Q' as a function of T' as in Fig. 2, but with h' a linear function of temperature. Contours are for constant h'_0 , which is related to h' in the manner expressed by Equation 13. Different temperature dependencies are given by setting $T'_{lim} = 2$ (top) or $T'_{lim} = 4$ (bottom) in Equation 13.

$$S_{config} = -\frac{nR}{2}[(1 + Q)\ln(1 + Q) + (1 - Q)\ln(1 - Q)] \quad (16)$$

where n is the number of sites per formula unit over which the ordering occurs, and R is the gas constant. Expanding each of $(1 + Q)\ln(1 + Q)$ and $(1 - Q)\ln(1 - Q)$ then gives

$$S_{config} = -\frac{nR}{2}\left(Q^2 + \frac{1}{6}Q^4 + \frac{1}{15}Q^6 + \frac{1}{28}Q^8 + \dots\right). \quad (17)$$

In this case the series expansion converges relatively slowly, but for values of Q less than ~ 0.9 , S_{config} is still close to being a linear function of Q^2 , as shown in Figure 4.

Equation 15 is known to account for nonconfigurational contributions to the total excess entropy of phase transitions that might be predominantly order-disorder in character (Salje, 1990, 1992a). The origin of these contributions might be understood as arising from so-called hard phonon modes, for example (Bismayer, 1990; Salje, 1990, 1992b). Any extra configurational effects due to

local short-range ordering are expected to be consistent with an expression based on summations of the form $\sum X \ln X$, and therefore also with a series expansion of the same general form as Equation 17. Real systems may not necessarily be purely displacive or purely order-disorder in character, and so the most accurate representation of the excess entropy would be by some appropriately scaled combination of equations with the forms of Equations 15 and 17. In practice it is rarely possible to separate and account explicitly for the different contributions, and the important question is then, to what extent will the normal Landau description of entropy (Eq. 15) be valid for the total excess entropy? As already pointed out, a linear relationship between S_{config} and Q^2 is a reasonable approximation, at least up to $Q \approx 0.9$ (Fig. 4). Adding some nonconfigurational entropy to this would then improve the linearity. For a considerable range of values of Q , therefore, Equation 15 should indeed provide a good description of all the entropy changes accompanying an atomic ordering process, if an empirically derived value of the a coefficient is used. It should be emphasized that, because the derivative dG/dT is the same for both Equations 3 and 10, these arguments apply equally to conver-

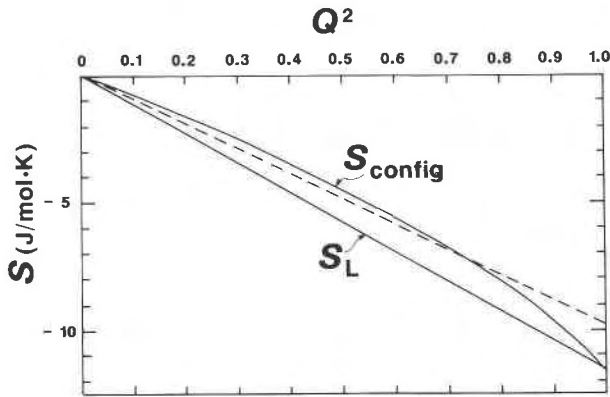


Fig. 4. Comparison of purely configurational excess entropy, S_{config} , from Equation 15, with a Landau excess entropy, S_L ($= aQ^2/2$), obtained by setting $S_L = S_{\text{config}}$ (J/mol·K) at $Q = 1$. The calculations were made for ordering equal proportions of A and B atoms between two crystallographic sites per formula unit. The dashed line shows a linear representation of the excess entropy as a function of Q^2 , which would be approximately valid up to $Q \approx 0.9$.

gent and nonconvergent ordering processes. Also, it is self-evident that the purely configurational entropy could be given in its standard form and an excess entropy term in Q^2 expressed separately. As discussed at length by Cohen (1986a), however, the formal description of configurational entropy for systems with ions whose configurations may be constrained by charge balancing requirements is not so straightforward. Such a division of entropy contributions results in a loss of generality and may not always be helpful.

The direct relationship between excess entropy and Q^2 has been demonstrated experimentally for phase transitions in which equilibration at each temperature is sufficiently rapid that heat capacity changes due to all the structural effects involved can be measured in a scanning calorimeter. Some examples of this are provided by the transitions in $\text{K}_2\text{Cd}_2(\text{SO}_4)_3$ (Devarajan and Salje, 1984), $\text{Pb}_3(\text{PO}_4)_2$ (Salje and Wruck, 1983), and NaNO_3 (Reeder et al., 1988). The transition in NaNO_3 is predominantly of an order-disorder character. If a direct experimental method for determining the excess heat capacity (and, hence, the excess entropy) is not feasible, some indirect means of obtaining a value for the a coefficient must be used. As discussed in the following section, the term aT_cQ^2 contributes directly to the excess enthalpy in such a way that, in principle, measurements of enthalpy differences between samples with different states of order can provide a means of quantifying the associated entropy variations.

The most significant points here are, firstly, that the empirical a coefficient can account, to a good approximation, for all the entropy contributions due to ordering even if details of all the atomic processes involved, such as thermal vibrations, charge balancing, or positional dis-

order, are only poorly understood. Secondly, assigning the excess entropy to a single coefficient of the expansion in this way means that its value can be determined experimentally from measurements of excess enthalpy. If the total excess entropy is assigned separately to ideal configurational and other terms, this aspect of the approach is lost.

Enthalpy and the meaning of T_c

Since $H = G + TS$, the excess enthalpy, H , due to convergent ordering is given in the usual way from Equation 4 as

$$H = -\frac{1}{2}aT_cQ^2 + \frac{1}{n}e_nQ^n. \quad (18)$$

The excess enthalpy due to nonconvergent ordering, from Equation 10, is given (for h independent of T) by

$$H = -hQ - \frac{1}{2}aT_cQ^2 + \frac{1}{n}e_nQ^n. \quad (19)$$

In the case of convergent processes, T_c can have an obvious physical meaning as the equilibrium transition temperature when the phase transition is second order or tricritical in character. More fundamentally, the product aT_c defines an energy whose origin may be understood in terms of interaction effects of the nearest neighbor type (A-A, A-B, B-B, etc.). This is illustrated most clearly by taking two of the general results from the Bragg-Williams model of atomic ordering in AB alloys. If enthalpy is assumed to be equivalent to internal energy, the Bragg-Williams excess enthalpy, H_{BW} , defined with respect to a fully disordered state is

$$H_{\text{BW}} = -\frac{N}{4}W_{\text{BW}}Q^2 \quad (20)$$

where N is the number of sites per formula unit over which the ordering occurs. The interaction parameter, W_{BW} , is taken to be a constant and depends linearly on A-A, A-B, and B-B nearest neighbor interaction energies. The equilibrium transition temperature, T_c , is given by

$$T_c = \frac{W_{\text{BW}}}{2R} \quad (21)$$

and, hence,

$$H_{\text{BW}} = -\frac{N}{2}RT_cQ^2. \quad (22)$$

This is not quite identical to a truncated Landau expansion for the excess enthalpy but makes a direct connection between the coefficient for the Q^2 term, nearest neighbor interaction energies, and a critical temperature. The geometrical origin of this relationship arises from the fact that, for a structure with equal proportions of A and B atoms, the total number of A-A, A-B, and B-B linkages is proportional to Q^2 . If some constant enthalpy is assigned to each linkage, the net enthalpy must also be proportional to Q^2 . The value of T_c then represents a scaling of this energy. Or course, real mineral structures have more complex topologies and bonding than simple AB

alloys, but that fact does not prevent an effective interaction parameter relating to nearest neighbor cation sites from being determined in terms of T_c in each case. An almost identical result emerges from the regular solution model for binary solid solutions, in which the nearest neighbor interaction energies and a different critical temperature, the solvus crest, are linearly related (e.g., Carmichael et al., 1974; Christian, 1975). Thus, in the Landau expansion, T_c scales a measure of configuration, a (J/mol·K), into an energy, aT_c (J/mol), whether the ordering is convergent or nonconvergent, and association with the Q^2 term implies a microscopic origin of the pairwise nearest neighbor type. A large value of T_c would signify a strong driving force for ordering because of this energy contribution, whereas a small value of T_c would imply a relatively small driving force.

Higher order terms in the Landau expansion should allow the effects of more distant neighbor interactions or many-body interactions to be expressed. Furthermore, both long-range and short-range ordering are incorporated in Equations 18 and 19, if the coefficients are extracted from experimental measurements of H as a function of Q . In some cases, there may be sufficient evidence from other sources, such as nuclear magnetic resonance spectroscopy, to separate the coefficients into long-range and short-range contributions. For example, the expected relationship $\sigma \propto Q^2$, where σ is a short-range order parameter, appears to describe the degree of short-range Al-Si ordering in anorthite (Carpenter, 1991; Phillips et al., 1992).

The physical origin of the linear term in Equation 19 and, hence, of the effective field coefficient, h , lies in the difference in site energies between the crystallographically distinct sites involved in nonconvergent ordering. When complete, exchanging all A atoms from s sites to s' sites and all B atoms from s' sites to s sites is equivalent to changing Q from $+1$ (fully ordered) to -1 (antiorordered). The enthalpy for that would be $2h$ if n is even.

Symmetry constraints

As discussed in the introduction, adding the symmetry-breaking linear term to a Landau expansion ensures that only the low symmetry (ordered) state of a crystal can have an equilibrium stability field. The normal symmetry rules governing whether odd order terms (in Q^3 , Q^5 , etc.) must be strictly zero no longer apply. In the first instance, it might therefore be reasonable to choose $n = 3$ when fitting Equation 10 to experimental data. However, experience with some phase transitions suggests that the third-order term tends to be small even when it is not required by symmetry to be zero. Some examples of this are the cubic = tetragonal transition in leucite (Palmer et al., 1990; Hatch et al., 1990), the cubic = orthorhombic transition in $K_2Cd_2(SO_4)_3$ (Devarajan and Salje, 1984) and the hexagonal = orthorhombic transition in tridymite (de Dombal and Carpenter, 1993). This is presumably a reflection of the microscopic physical origin of the Q^3 term, along the lines discussed above for the Q and

Q^2 terms. No explanation is offered here as to why this term might in general be small, but the immediate implication is that a more appropriate initial choice for describing data from some real nonconvergent system may be $n = 4$. A choice of $n = 6$ might be equally appropriate in that the single high-order term might provide an adequate approximation for several physically real high-order terms that could not be distinguished on the basis of available experimental data.

The role of strain

Lattice distortions accompanying structural changes can be described formally in terms of spontaneous strains (see recent reviews by Carpenter, 1988, 1992a; Salje, 1990, 1991). The analysis for nonconvergent ordering parallels exactly that for convergent processes. The spontaneous strain, ϵ , can be accounted for explicitly, rather than implicitly as in Equation 10, by rewriting the Landau expansion as

$$G = -hQ + \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{n}e_nQ^n + p\epsilon Q + q\epsilon Q^2 + \dots + r\epsilon^2. \quad (23)$$

The coefficients p and q are strain-order parameter coupling constants, and the term in $r\epsilon^2$ is the (Hooke's law) elastic energy. The coefficient r consists of an appropriate combination of elastic constants that can be written out in full for individual cases, as necessary.

At equilibrium a crystal must be at a free energy minimum with respect to strain, so that

$$\frac{\partial G}{\partial \epsilon} = 0 = pQ + qQ^2 + \dots + 2r\epsilon \quad (24)$$

and, hence

$$\epsilon = -\left(\frac{pQ + qQ^2 + \dots}{2r}\right). \quad (25)$$

Because there are no symmetry constraints determining which terms are strictly zero in the free energy expansion, the term in $p\epsilon Q$ is always allowed. Experience derived from strain measurements in many materials that undergo phase transitions indicates that more than one term may only very rarely be required to account for observed relationships between Q and ϵ . It is likely, therefore, that the $q\epsilon Q^2$ term (and higher order terms) will be small with respect to $p\epsilon Q$ and can be ignored. Equation 25 then gives an expected relationship of the form

$$\epsilon = -\left(\frac{p}{2r}\right)Q \quad (26)$$

for nonconvergent ordering in this approximation.

The spontaneous strain is a second-rank tensor property, and ϵ consists of six components. Each of the components is defined in terms of differences in lattice parameters of crystals with a specified degree of order at some temperature, relative to the lattice parameters of the same crystals at the same temperature but with $Q = 0$. For example, in the simple case of nonconvergent ordering in

crystals with orthogonal crystallographic axes, the three nonzero spontaneous strain tensor components would be

$$e_{11} = \frac{a - a_0}{a_0} \quad (27)$$

$$e_{22} = \frac{b - b_0}{b_0} \quad (28)$$

$$e_{33} = \frac{c - c_0}{c_0} \quad (29)$$

where a , b , and c are lattice parameters for the crystals and a_0 , b_0 , and c_0 are the lattice parameters for fully disordered crystals at the same temperature. The volume strain, V_s , is given by:

$$V_s = \frac{V - V_0}{V_0} \quad (30)$$

where the subscript has the same meaning as before. V_s is also given by the sum of the diagonalized components of the spontaneous strain matrix (for small volume strains), and, in the case of orthogonal axes to which Equations 27–29 refer, this implies

$$V_s = e_{11} + e_{22} + e_{33}. \quad (31)$$

Strictly speaking, the lattice parameters should be measured at the equilibration temperature of the sample, to give a , b , c , α , β , γ , V , or extrapolated from high-temperature measurements from disordered crystals, to give a_0 , b_0 , c_0 , α_0 , β_0 , γ_0 , and V_0 . In practice, measurements at room temperature on crystals with degrees of order quenched in from higher temperatures can be adequate (e.g., Carpenter et al., 1990b; Carpenter and Salje, 1994a, 1994b). Given that $Q = 0$ is a stable solution for crystals of a nonconvergent ordering material only at infinite temperature, values of a_0 , b_0 , etc., have to be obtained by extrapolation. In many cases the individual lattice parameters may vary linearly with Q , though, formally, the expected relationship between lattice strains and the degree of order for nonconvergent processes is expected to be

$$e_{ik} \propto V_s \propto Q \quad (32)$$

where $i, k = 1-6$. Expressions for the six strain components, e_{ik} , in terms of lattice parameters of ordered ($Q \neq 0$) and disordered ($Q = 0$) forms are given by Redfern and Salje (1987). As with linear strain-order parameter coupling in convergent systems, the strain and elastic energy terms can be eliminated from the Landau expansion by substituting Equation 26 into Equation 23 to give a renormalized value of $T_{c,ren} = T_c + (p^2/2ar)$ (e.g., see Salje and Devarajan, 1986, or Carpenter, 1992a). $T_{c,ren}$ would refer to a crystal that is allowed to deform freely in response to changes in the degree of order, and T_c would refer to a crystal that is clamped in such a way as to prevent such deformation. The coupling may account for a substantial proportion of the total energy reduction associated with the ordering.

The observation that a given material with nonconvergent ordering showed spontaneous strains of greater than ~ 0.001 would, of itself, have significant thermodynamic implications. Since the strain arises by coupling with the order parameter, the effective interaction length of Q becomes large (see references and discussion of minerals in Carpenter and Salje, 1989; Salje, 1990). This causes any fluctuations in the local degree of order, which can cause deviations from the simple predictions of Landau theory, to be reduced or entirely suppressed (see Salje, 1992a, for example). In addition, if there are lattice distortions, it necessarily follows that there will be changes in phonon frequencies (e.g., see Bismayer, 1990; Güttler, 1990; Salje, 1992b) and, hence, also in the excess entropy. The system will become increasingly of a displacive rather than a pure order-disorder character (in the sense used by physicists, cf. Bruce and Cowley, 1981), and is increasingly likely to conform to the thermodynamic description generated from a Landau free energy expansion.

Order parameter saturation and behavior as $Q \rightarrow 1$

Conventional Landau expansions give invalid results for the variation of Q with temperature at very low temperatures in that they incorrectly predict $dQ/dT \neq 0$ at $T = 0$ K. Additional terms must be included to correct for this, and Salje et al. (1991) have shown how order parameter saturation can be accounted for. This saturation, which is observed as a leveling off of Q to some constant value and is due to quantum effects, appears to be significant only below a few hundred kelvins, however. It need not be considered when the ordering processes of interest occur at normal geological temperatures.

Of more serious concern for the treatment of nonconvergent ordering in minerals is the progressively less reliable approximation of excess entropy as $Q \rightarrow 1$ for pure order-disorder systems and the substantially enhanced degrees of order promoted by large effective fields. This issue was evaded in Figures 2 and 3 by scaling Q with respect to Q_0 , the (unspecified) degree of order at 0 K. Taking Equation 10 as it stands, with h as a positive quantity, could lead to values of $Q_0 > 1$, unless the relative values of the coefficients are constrained. The predicted variation in Q in relation to the true variation might be as represented in Figure 5. Three solutions are possible for this problem. Firstly, higher order terms might be added or the coefficients of the high-order terms made temperature dependent to ensure $Q \rightarrow 1$ as $T \rightarrow 0$ K. As already pointed out, however, experimental data for minerals are unlikely to be sufficiently accurate to allow the extra coefficients to be determined uniquely. Alternatively, fixing $Q = 1$ at 0 K (for a crystal with equal proportions of A and B atoms) gives, from the equilibrium condition derived for Equation 10,

$$h = e_n - aT_c. \quad (33)$$

In the fitting procedure to extract values of coefficients from experimental data it may be just as convenient to incorporate this constraint by using $Q = 1$ at 0 K as an

additional data point. Finally, the question of what happens as $Q \rightarrow 1$ can be ignored when the equilibrium values of Q in a temperature interval of interest are relatively small. Each of the terms h , a , T_c , and e_n could be assumed to be independent.

COMPARISON WITH OTHER MODELS

So far, the use of an effective field for describing nonconvergent ordering has been discussed only in the context of Landau free energy expansions. It is instructive to compare the resulting solutions with those from more familiar approaches. Here it is shown that, for high temperatures and small fields at least, Landau, Boltzmann, and Bragg-Williams models predict identical variations for the equilibrium order parameter. Rather similar expressions for the energetics are also obtained by treating the ordering in terms of independent mixing of atoms on separate sites.

Boltzmann distribution for noninteracting sites

If there are no interactions between cations on different crystallographic sites, there will not be an order-disorder phase transition. Some ordering occurs if there are energetic differences between the sites, however. Again, with the effective field, h , representing these energetic differences and with the earlier formalism for A and B atoms distributed between s and s' sites maintained, the Boltzmann probabilities for the s and s' sites being occupied by an A atom become

$$X_A^s = \exp\left(\frac{+h}{kT}\right) \tag{34}$$

and

$$X_A^{s'} = \exp\left(\frac{-h}{kT}\right) \tag{35}$$

where k is the Boltzmann constant. Substituting these equations into Equation 2 and normalizing to express the ordering in terms of Q instead of X_A^s and $X_A^{s'}$ gives

$$Q = \frac{\exp\left(\frac{h}{kT}\right) - \exp\left(\frac{-h}{kT}\right)}{\exp\left(\frac{h}{kT}\right) + \exp\left(\frac{-h}{kT}\right)} = \tanh\left(\frac{h}{kT}\right) \tag{36}$$

$$\approx \frac{h}{kT} - \frac{1}{3}\left(\frac{h}{kT}\right)^3 + \frac{2}{15}\left(\frac{h}{kT}\right)^5 - \dots$$

(for $\left|\frac{h}{kT}\right| < \frac{\pi}{2}$). (37)

For the limiting case of $|h| \gg kT$, the solution is simply $Q = \pm 1$, where the sign depends on the orientation of the field. This means that the crystal would be fully ordered. The situation relevant for nonconvergent ordering corresponds to $|h| \lesssim kT$, in which case the equilibrium degree of order would be much lower. For $|h| \ll kT$, i.e., for small effective fields, only the first term in

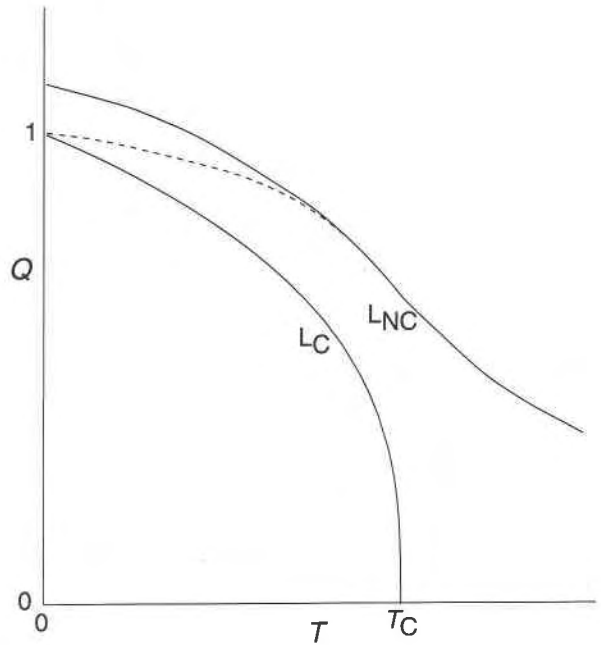


Fig. 5. Variation of Q as a function of T , illustrating schematically the effect of adding a field term to a normal Landau expansion. The predicted variation of Q for a Landau second-order transition is indicated by L_C . Addition of only a field term gives L_{NC} , which has $Q > 1$ at 0 K. The real behavior at low temperatures is represented by a broken line and could be reproduced by a Landau expansion if further constraints concerning the relative values of the coefficients were assumed, or if extra terms were added.

Equation 37 is significant, and the solution is identical in form to Equation 12.

Bragg-Williams theory

The enthalpy change associated with ordering in the Bragg-Williams model can be given in the form of Equation 20. An inherent assumption is that interactions between cations on different sites occur in a pairwise and harmonic manner. With the strength of these interactions being kT_c [i.e., $W_{BW}/(2 \times \text{Avogadro's number})$], the same result is obtained by asserting that there is a mean field of strength $kT_c Q$ favoring ordering (see, for example, Becker, 1978, and the discussion of the Bragg-Williams model in Christian, 1975). For nonconvergent ordering, this field, due to the pairwise interactions, is additional to the effective field, h , and Equation 36 for the order parameter then becomes

$$Q = \tanh\left(\frac{h + kT_c Q}{kT}\right). \tag{38}$$

For $h = 0$, this is the traditional Bragg-Williams result:

$$Q = \tanh\left(\frac{T_c Q}{T}\right). \tag{39}$$

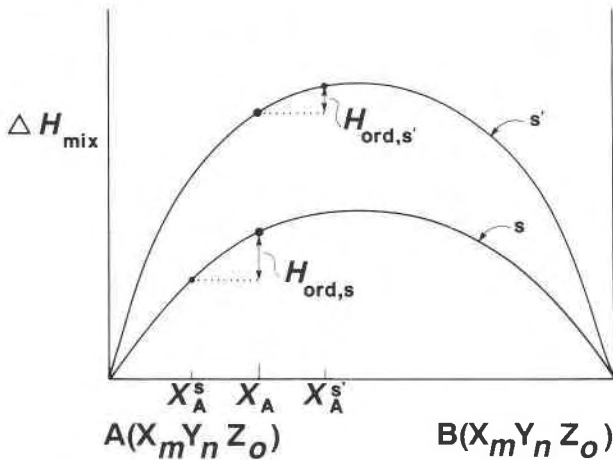


Fig. 6. In a solid solution of the form $(A,B)(X_m Y_n Z_o)$, the mixing of A and B atoms on s and s' sites can be described in terms of two separate solutions. Each site has its own excess enthalpy of mixing, ΔH_{mix} . In crystals with bulk composition, X_A , preferential ordering of A atoms onto s sites and B atoms onto s' sites to give site occupancies of X_A^s and $X_A^{s'}$, respectively, gives a net change of enthalpy of $H_{ord,s} + H_{ord,s'}$.

Thus, the Boltzmann solution (Eq. 36) is only a special case of Equation 38, namely for $T_c = 0$.

The quantitative temperature dependence of Q for $T \gg T_c$ follows from the same series expansion as in Equation 37, extended by the interaction term $T_c Q/T$:

$$Q = \frac{h}{kT} + \frac{T_c Q}{T} - \frac{1}{3} \left(\frac{h}{kT} + \frac{T_c Q}{T} \right)^3 + \dots \quad (40)$$

For small values of Q and at $T \gg T_c$ this can be rewritten as

$$Q = \frac{h}{k(T - T_c)} - \frac{1}{3} \left(\frac{T}{T - T_c} \right) \left[\left(\frac{h}{kT} \right)^3 + 3 \left(\frac{h}{kT} \right)^2 \left(\frac{T_c Q}{T} \right) + 3 \left(\frac{h}{kT} \right) \left(\frac{T_c Q}{T} \right)^2 + \left(\frac{T_c Q}{T} \right)^3 \right] + \dots \quad (41)$$

Temperature, T , in the leading term is now replaced by $T - T_c$. For $|h| \ll kT$, terms in $(h/kT)^2$, $(h/kT)^3$ are irrelevant, and higher order terms depend on Q^2 and Q^3 in a manner that is not dissimilar to the high-order terms in a Landau solution (Eq. 11). The main difference is that in Equation 41 the higher order terms disappear more quickly because of prefactors in $(T_c/T)^2$ or $(T_c/T)^3$.

Independent mixing on sites

The starting point for many models of nonconvergent ordering in mineral solid solutions is the assumption that a substantial part of the stabilization energy for ordering can be identified as arising from nonideal mixing of at-

oms on independent crystallographic sites. As has already been discussed with respect to the Bragg-Williams model for ordering, pairwise symmetric interactions between cations on equivalent crystallographic sites and between cations on nonequivalent crystallographic sites are quadratic in the site occupancies and so are also quadratic in Q (see, for example, Powell, 1977, 1983; Wood and Nicholls, 1978). To illustrate the implications of this, consider a solid solution of the form $A(X_m Y_n Z_o) - B(X_m Y_n Z_o)$ where the A and B atoms spread between crystallographically distinct s and s' sites in some structure containing proportions of X, Y, and Z atoms. The two sites may be treated as independent solutions with their own associated excess enthalpies of mixing due to the substitution $A = B$. From the regular solution model, the excess enthalpy of mixing, ΔH_{mix} , on each site would be

$$\Delta H_{mix,s} = W_s X_A^s X_B^s \quad (42)$$

$$\Delta H_{mix,s'} = W_{s'} X_A^{s'} X_B^{s'} \quad (43)$$

where the subscripts s and s' identify the separate sites, X_A^s , X_B^s , etc., are the mole fractions of A and B atoms occupying these sites, as before, and W_s , $W_{s'}$ are standard regular solution mixing parameters.

If both W_s and $W_{s'}$ are positive, there can be a net reduction in enthalpy, H_{ord} , if the proportion of A atoms on s sites is increased and the proportion on s' sites decreased (Fig. 6). For a bulk composition X_A , ordering to give the occupancies X_A^s and $X_A^{s'}$ shown in Figure 6 gives a net enthalpy of ordering of

$$H_{ord} = H_{ord,s} + H_{ord,s'} \quad (44)$$

The enthalpy changes $H_{ord,s}$ and $H_{ord,s'}$, caused by the change in occupancy of the two sites, are themselves derived from Equations 42 and 43 as

$$H_{ord,s} = W_s [X_A^s (1 - X_A^s) - X_A (1 - X_A)] \quad (45)$$

and

$$H_{ord,s'} = W_{s'} [X_A^{s'} (1 - X_A^{s'}) - X_A (1 - X_A)]. \quad (46)$$

These may be written in terms of the bulk composition, X_A , and the degree of order, Q , by substituting

$$X_A = \frac{X_A^s + X_A^{s'}}{2} \quad (47)$$

and

$$X_A^s = X_A + \frac{Q}{2} \quad (48)$$

$$X_A^{s'} = X_A - \frac{Q}{2}. \quad (49)$$

Equation 44 for the total enthalpy change due to ordering becomes

$$H_{ord} = (W_s - W_{s'}) \left(\frac{1}{2} - X_A \right) Q - \left(\frac{W_s + W_{s'}}{4} \right) Q^2. \quad (50)$$

To this must be added the direct energy advantage,

often referred to as the site preference energy, of ordering the A and B atoms onto their preferred sites. This may be taken as a linear function of Q and amounts to $2h$ for the complete exchange $Q = +1 \rightarrow Q = -1$. Equation 50 then becomes

$$H_{\text{ord}} = -hQ + (W_s - W_{s'})\left(\frac{1}{2} - X_A\right)Q - \left(\frac{W_s + W_{s'}}{4}\right)Q^2. \quad (51)$$

Finally, the coefficient for the quadratic term may be corrected to account for the non-coplanarity of the standard enthalpies, H_{AA}^0 , H_{BB}^0 , etc., of the pure end-member phases, $A^sA^s(X_mY_nZ_o)_2$, $B^sB^s(X_mY_nZ_o)_2$, $A^sB^s(X_mY_nZ_o)_2$, $B^sA^s(X_mY_nZ_o)_2$, where A^s represents an A atom on an s site, etc. (Sack, 1980; Sack and Ghiorso, 1989). The correction term, ΔH_{rec}^0 , is the enthalpy for the reciprocal reaction where

$$\Delta H_{\text{rec}}^0 = H_{A^sB^s}^0 + H_{B^sA^s}^0 - H_{A^sA^s}^0 - H_{B^sB^s}^0 \quad (52)$$

and is incorporated into Equation 51 as

$$H_{\text{ord}} = -hQ + (W_s - W_{s'})\left(\frac{1}{2} - X_A\right)Q - \left(\frac{W_s + W_{s'} + \Delta H_{\text{rec}}^0}{4}\right)Q^2. \quad (53)$$

The form of the enthalpy of ordering is now identical to that used by Sack and Ghiorso (1989). For the 1:1 composition, $AB(X_mY_nZ_o)_2$, it becomes

$$H_{\text{ord}} = -hQ - \left(\frac{W_s + W_{s'} - \Delta H_{\text{rec}}^0}{4}\right)Q^2 \quad (54)$$

which differs from the Landau excess enthalpy by the absence of a higher order term. The term ΔH_{rec}^0 is equivalent to the Bragg-Williams term W_{BW} in Equation 20 (also discussed by Sack, 1980), and so the coefficient for the quadratic term ($1/2aT_c$ in Eq. 20) is seen to contain contributions both from pairwise nearest neighbor interactions between atoms on s sites and between atoms on s' sites (intrasite, from the regular solution origin of W_s and $W_{s'}$) and from pairwise interactions between atoms on different sites (intersite).

Configurational and nonconfigurational entropy contributions to the free energy of ordering can be accounted for either by assuming the latter to be negligible (Sack and Ghiorso, 1989), or by allowing all or some of the coefficients to be temperature dependent (Davidson and Lindsley, 1989; Shi et al., 1992). This contrasts with the Landau entropy, which incorporates all the configurational and nonconfigurational contributions in the coefficient of the second-order term.

The significant conclusion, here, is that the Landau free energy expansion has the characteristics of a generalized version of more specific models of nonconvergent ordering. Even the semiempirical approach of O'Neill and Navrotsky (1983) gives enthalpy changes in a form that is

essentially the same as Equation 54. All the models are likely to give rather similar patterns for the equilibrium variation of Q as a function of temperature. They may differ in the detailed variations of G , H , and S that they predict, however.

EXTENSION TO SOLID SOLUTIONS

In most mineral systems showing nonconvergent atomic ordering, the variations of thermodynamic properties with changing composition are as important as the variations with changing temperature. Landau expansions can, in principle, be used to describe the excess energies due to ordering in a solid solution by allowing the coefficients to become composition dependent. Two different approaches might be adopted: either a microscopic model of atomic interactions is built up to predict a theoretical form for the composition dependence, or a macroscopic and empirical course is followed. The latter is of more immediate practical value, and in this section the possibilities of both linear and nonlinear composition dependencies for the coefficients are briefly outlined.

Linear composition dependence for Landau coefficients

As a first approximation, the Landau coefficients might be treated as linear functions of the mole fraction, X , of a second component added to some solid solution. In the case of the monoclinic \rightarrow triclinic transition in alkali feldspars with complete Al-Si disorder, available thermodynamic data can be reproduced by allowing T_c to vary linearly with composition (Carpenter, 1988). This is a transition that is probably close to the displacive limit, however, and may not necessarily typify the behavior at order-disorder transitions. For a limited composition range in Na-rich pyroxenes, the cation ordering transition in omphacite appears to be described by a tricritical expansion with only T_c as a linear function of jadeite content (Carpenter et al., 1990a). On the other hand, the Al-Si ordering transition in anorthite-rich plagioclase feldspars appears to require that the coefficients for the Q^4 and Q^6 terms, as well as T_c , should vary with albite content (Carpenter, 1992b).

The basic constraints of composition as a variable can be illustrated by allowing T_c to be linearly dependent on X in Equation 10. The coefficients h , a , and e_n are assumed to be constant. Q is defined with respect to complete order ($Q = 1$) at the composition $A_{0.5}B_{0.5}(X_mY_nZ_o)$ and is taken as being equal to $X_A^s - X_A^s$ irrespective of bulk composition. For the composition range $0 < X_B < 0.5$, T_c may be replaced by T_c^* where

$$T_c^* = T_c[1 - u(0.5 - X_B)] \quad (55)$$

with u as a constant. Substituting $T_c^{*'} = T/T_c^*$ for T' ($= T/T_c$) in Equations 10 and 11 then allows the equilibrium value of Q as a function of X_B to be examined for selected values of u and n . The value of Q_0 is taken to be unity for $A_{0.5}B_{0.5}(X_mY_nZ_o)$ at 0 K and, because of the definition of Q chosen above, does not vary with composition. Two

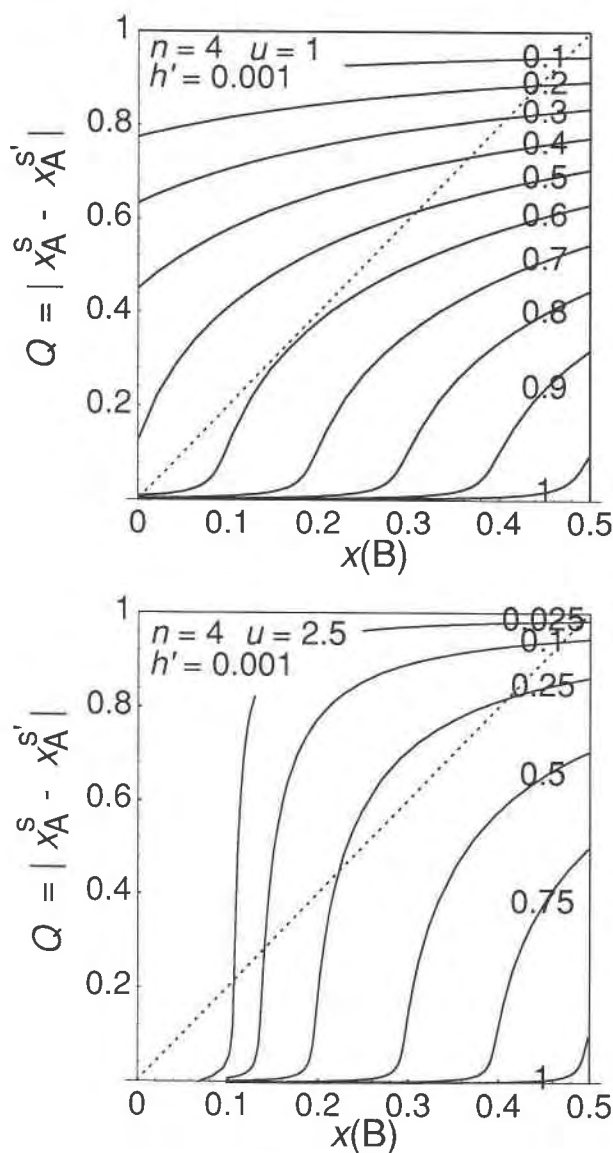


Fig. 7. Variation of Q as a function of composition, X_B , for nonconvergent ordering with T_c as a linear function of X_B , from Equation 55. The contours are for constant T (normalized with respect to the value of T_c at $X_B = 0.5$). (top) In Equation 55 $u = 1$, and so T_c^* remains positive at all compositions; (bottom) $u = 2.5$, and so T_c^* becomes negative with decreasing X_B . Note that in each case some physically impossible values of Q , i.e., values above the dotted line, are predicted.

sets of solution, with $n = 4$, $h' = 0.001$, and $u = 1$ or $u = 2.5$, are shown in Figure 7. The contours are for different values of T renormalized with respect to T_c at the composition $X_B = 0.5$. If $u = 1$ (Fig. 7 top), T_c^* remains positive over the complete composition range, and if $u = 2.5$ (Fig. 7 bottom), T_c^* becomes negative as X_B decreases.

Solutions of the forms shown in Figure 7 might give reasonable approximations for small deviations of X_B from 0.5, but they both give the unreal result $Q > 2X_B$ at some

compositions. A crystal cannot have a value of Q representing a state with more than all the available B atoms located on the s' site. Furthermore, $Q \neq 0$ is physically invalid at $X_B = 0$ (Fig. 7 top), since there are no B atoms available to become ordered in the pure end-member. Thus, although there may be solid solutions for which linear changes of the coefficients with composition are not unreasonable, nonlinear behavior must also be anticipated.

Nonlinear composition dependence for Landau coefficients

Once a linear solution is excluded, the variety of possible compositional relationships that may be tried becomes almost infinite. There is at present no theoretical basis for choosing a unique compositional dependence, and an empirical approach of fitting trial expressions to observed data for real systems has to be adopted. The most fundamental constraint is that $Q = 0$ for all temperatures in pure end-member phases where there are no atoms of a second component to be ordered. Such a singularity can be incorporated by making the coefficients a and e , diverge as $X_B \rightarrow 0$. T_c can be chosen to be constant or allowed to vary. One suitable expression for a as a function of composition might be

$$a(X) - a(X = 0.5) = v \left(\frac{\Delta X}{0.5 - \Delta X} \right)^w \quad (56)$$

where $a(X = 0.5)$ is the value of the a coefficient at $X_A = X_B = 0.5$ and ΔX is the deviation from this composition; v and w are constants. An alternative form with the same characteristics might be

$$\frac{a(X)}{a(X = 0.5)} = \left(\frac{0.5}{0.5 - \Delta X} \right)^w \quad (57)$$

Some rationalization of why such expansions provide useful approximations for the effect of composition is derived from a consideration of purely configurational effects. If it is assumed that the equilibrium value of Q at 0 K, Q_0 , represents the maximum degree of order possible for a given stoichiometry and that the associated excess configurational entropy is $S_{o,\text{config}}$, Equation 15 yields

$$a_{\text{config}}(X) = \frac{2S_{o,\text{config}}(X)}{[Q_0(X)]^2} \quad (58)$$

Here $a_{\text{config}}(X)$ represents the Landau coefficient defining configurational entropy changes in a crystal with composition X . $S_{o,\text{config}}(X)$ can be calculated for different compositions in the conventional way, and $Q_0 = 1$ may be set for $X_A = X_B = 0.5$, with $Q = 0$ in the pure end-member phases ($X_A = 1, X_B = 0$ or $X_A = 0, X_B = 1$). At intermediate compositions the maximum possible degree of order corresponds to one site being filled entirely by atoms of A or atoms of B, and Q_0 is given by

$$Q_0 = 2X_A \quad (\text{for } 0 \leq X_A \leq 0.5) \quad (59)$$

$$Q_0 = 2X_B \quad (\text{for } 0 \leq X_B \leq 0.5). \quad (60)$$

Rearranging terms and making substitutions in Equation 58 gives, for $0 \leq X_B \leq 0.5$,

$$\begin{aligned} a_{\text{config}}(X) - a_{\text{config}}(X = 0.5) \\ = \frac{2S_{\text{o,config}}(X)}{4X_B^2} - 2S_{\text{o,config}}(X = 0.5). \end{aligned} \quad (61)$$

The question is, then, to what extent does the right side of Equation 56 provide an adequate representation of the right side of Equation 61? The relationship is not easy to demonstrate analytically, but numerically it is found to be close to linearity (see Fig. 10d of Carpenter and Salje, 1994a). A similarly linear relationship is found numerically using the right side of Equation 57.

Nonconfigurational contributions to the excess entropy in order-disorder systems result in deviations from these relationships but are accounted for, to a first approximation, by fitting values for the coefficients v and w using a coefficients extracted from experimental data. Thus, although no rigorous justification is offered here, equations such as 56 and 57 are seen to provide a convenient means of expressing smooth variations of $a(X)$ with the required divergence as $X_A \rightarrow 0$ or $X_B \rightarrow 0$.

The value of the coefficient e_n in Equation 4 must also diverge as the pure end-members are approached. Once the value of Q at 0 K is specified, however, it is no longer an independent parameter and can be determined from the values of the other coefficients. If h and T_c are constant or vary only slightly with X , e_n diverges more strongly than a , independently of temperature, such that $Q \rightarrow 0$ as $X_A \rightarrow 0$ or as $X_B \rightarrow 0$, and the same basic form of Landau expansion is retained at all compositions.

Landau expansions of the form used here account for the energy changes due to ordering with respect to the fully disordered state ($Q = 0$). For a complete mixing model it is therefore necessary to add terms for mixing of the disordered solid solution.

AN EMPIRICAL APPROACH FOR REAL SYSTEMS

A variety of arguments have been presented to justify the use of a Landau expansion to describe nonconvergent processes. At the very least, it can be seen as a generalized form of many more specific models. Once the basis for including an effective field term and for accounting for excess entropies in terms of $S \propto Q^2$ are accepted, the application to real systems is quite straightforward. First, experimental data for the variation of Q as a function of T are required. The condition for equilibrium from Equation 10 is

$$\frac{\partial G}{\partial Q} = 0 = -h + a(T - T_c)Q + e_n Q^{n-1}. \quad (62)$$

Dividing by h gives

$$0 = -1 + \frac{a}{h}(T - T_c)Q + \frac{e_n}{h}Q^{n-1}. \quad (63)$$

An initial choice of $n = 4$ or $n = 6$ is sensible, and values of $Q > 1$ can be excluded by incorporating $Q = 1$ at 0 K

as a data point. Values of a/h , T_c , and e_n/h can then be determined from the observed values of Q at different T , using some convenient fitting procedure.

A second set of observations is required to determine absolute values of a , h , and e_n from their ratios. One of the most useful properties to measure is enthalpy, both because appropriate calorimetric techniques are often available and because the expression for excess enthalpy has a form (Eq. 19) that is nonlinear with Equation 63. The tightest constraints on values of the coefficients are obtained if the enthalpy data refer to crystals with the widest possible range of states of order.

If the system of interest forms an extensive solid solution, the procedure must, at present, be repeated for crystals with different compositions. An asymmetry in the compositional dependence of Q might be used as an argument for allowing the value of h to vary with X . On the other hand, the assumption of constant h , equal to the value extracted, say, for $X_A = X_B = 0.5$, allows values of $a(X)$, $T_c(X)$, and $e_n(X)$ to be determined from measurements of Q as a function of X and T . Additional enthalpy data would not necessarily be needed, though they would provide further indications of the validity of the model. Some empirical expression similar to Equation 56 could then be used to extrapolate between values at different compositions, and the final free energy expansion used to back-calculate Q for all temperatures and compositions.

Physical insights into the mechanisms of nonconvergent ordering processes are likely to result from such analyses. In particular, the importance of any nonconfigurational contribution to the excess entropy should emerge. If it is found that the value of $a/2$, which would be the total excess entropy for crystals with a maximum degree of order, is similar in magnitude to the total expected configurational entropy change for these crystals, it is likely that the excess entropy is mainly configurational. In this case it may be appropriate to return to the more standard description of configurational entropy. On the other hand, a much larger value of $a/2$ would signify the contribution of substantial nonconfigurational effects, whereas a smaller value of $a/2$ might signify substantial local ordering. The latter could arise, for example, from local charge-balancing requirements. Given the nature of the approximation for the excess entropy, as illustrated in Figure 4, $a/2$ is unlikely to correspond exactly to S_{config} . It is important to reemphasize, however, that prior assumptions concerning the relative magnitudes of different entropy contributions are not required when this overall approach is followed; the real excess entropy of a system under investigation can be extracted from experimental data for Q and H alone.

CONCLUSIONS

The main advantages in using a Landau expansion to describe nonconvergent ordering in minerals are, firstly, that the approach is general and, secondly, that the sometimes difficult problem of determining different entropy

contributions directly can be avoided. Only four parameters need to be extracted from measurements of Q , H , or of some other physical property related to Q . The form of the expansion is also such that it can reproduce a great variety of thermal or compositional behavior by the adjustment of relatively few parameters, and that it can be incorporated into computer programs for wider thermodynamics-based petrological calculations.

Further theoretical analysis of solid solutions is clearly necessary, possibly through the development of microscopic models. The behavior at high degrees of order may also need to be examined but, as is demonstrated for nonconvergent cation ordering in spinels, orthopyroxene, and potassium feldspar in companion papers (Carpenter and Salje, 1994a, 1994b), the overall approach appears to be practical and can be convenient. Through the use of the Ginzburg-Landau equation (e.g., Carpenter and Salje, 1989; Salje and Kroll, 1991; Salje, 1992a), the kinetics of nonconvergent order-disorder processes might also be analyzed.

ACKNOWLEDGMENTS

M.A.C. is grateful to the Royal Society of Great Britain for financial support in association with a period of study leave spent in Melbourne and to the Department of Geology, University of Melbourne, for generous hospitality during that period. The need for derivations of free energy functions to describe nonconvergent ordering has also been stimulated by a grant from the Natural Environment Research Council of Great Britain (GR3/8220 to M.A.C. and E.K.H.S.) to investigate the kinetics of cation ordering, which is gratefully acknowledged. R.P. acknowledges Australian Research Council funding of his research on the thermodynamics of minerals. H. Kroll is thanked for his critical comments on the manuscript. We are also particularly grateful to W.J. Carey and a second, anonymous reviewer for their meticulous care in reviewing all three of the manuscripts in this series. Cambridge Earth Sciences contribution no. ES3577.

REFERENCES CITED

- Becker, R. (1978) *Theorie der Wärme*, 336 p. Springer-Verlag, Berlin.
- Bismayer, U. (1990) Hard mode Raman spectroscopy and its application to ferroelastic and ferroelectric phase transitions. *Phase Transitions*, 27, 211–267.
- Bruce, A.D., and Cowley, R.A. (1981) *Structural phase transitions*, 326 p. Taylor and Francis, London.
- Carmichael, I.S.E., Turner, F.J., and Verhoogen, J. (1974) *Igneous petrology*, 739 p. McGraw-Hill, New York.
- Carpenter, M.A. (1988) Thermochemistry of aluminium/silicon ordering in feldspar minerals. In E.K.H. Salje, Ed., *Physical properties and thermodynamic behaviour of minerals*. NATO ASI series C, vol. 225, p. 265–323. Reidel, Dordrecht, The Netherlands.
- (1991) Mechanisms and kinetics of Al-Si ordering in anorthite: II. Energetics and a Ginzburg-Landau rate law. *American Mineralogist*, 76, 1120–1133.
- (1992a) Thermodynamics of phase transitions in minerals: A macroscopic approach. In G.D. Price and N.L. Ross, Eds., *The stability of minerals*, p. 172–215. Chapman and Hall, London.
- (1992b) Equilibrium thermodynamics of Al/Si ordering in anorthite. *Physics and Chemistry of Minerals*, 19, 1–24.
- Carpenter, M.A., and Salje, E.K.H. (1989) Time-dependent Landau theory for order/disorder processes in minerals. *Mineralogical Magazine*, 53, 483–504.
- (1994a) Thermodynamics of nonconvergent cation ordering in minerals: II. Spinel and the orthopyroxene solid solution. *American Mineralogist*, 79, 1068–1083.
- (1994b) Thermodynamics of nonconvergent cation ordering in minerals: III. Order parameter coupling in potassium feldspar. *American Mineralogist*, 79, 1084–1098.
- Carpenter, M.A., Domeneghetti, M.-C., and Tazzoli, V. (1990a) Application of Landau theory to cation ordering in omphacite: I. Equilibrium behaviour. *European Journal of Mineralogy*, 2, 7–18.
- Carpenter, M.A., Angel, R.J., and Finger, L.W. (1990b) Calibration of Al/Si order variations in anorthite. *Contributions to Mineralogy and Petrology*, 104, 471–480.
- Christian, J.W. (1975) *The theory of transformations in metals and alloys: An advanced textbook in physical metallurgy* (2nd edition), 586 p. Pergamon, Oxford, U.K.
- Cohen, R.E. (1986a) Configurational thermodynamics of aluminous pyroxenes: A generalised pair approximation. *Physics and Chemistry of Minerals*, 13, 183–197.
- (1986b) Thermodynamic solution properties of aluminous clinopyroxenes: Nonlinear least squares refinements. *Geochimica et Cosmochimica Acta*, 50, 563–575.
- Davidson, P.M., and Lindsley, D.H. (1989) Thermodynamic analysis of pyroxene-olivine-quartz equilibria in the system CaO-MgO-FeO-SiO₂. *American Mineralogist*, 74, 18–30.
- de Dombal, R.F., and Carpenter, M.A. (1993) High temperature phase transitions in Steinbach tridymite. *European Journal of Mineralogy*, 5, 607–622.
- Della Giusta, A., and Ottonello, G. (1993) Energy and long range disorder in simple spinels. *Physics and Chemistry of Minerals*, 20, 228–241.
- Devarajan, V., and Salje, E. (1984) Phase transitions in K₂Cd₂(SO₄)₂: Investigation of the nonlinear dependence of spontaneous strain and morphic birefringence on order parameter as determined from excess entropy measurements. *Journal of Physics C*, 17, 5525–5537.
- Dove, M.T., Giddy, A.P., and Heine, V. (1992) On the application of mean-field and Landau theory to displacive phase transitions. *Ferroelectrics*, 136, 33–49.
- Ghiorso, M.S., and Sack, R.O. (1991) Thermochemistry of the oxide minerals. In *Mineralogical Society of America Reviews in Mineralogy*, 25, 221–264.
- Güttler, B. (1990) Elastic phase transitions in minerals and hard mode infrared spectroscopy: Some examples. In E.K.H. Salje, Ed., *Phase transitions in ferroelastic and co-elastic crystals*, p. 230–252. Cambridge University Press, Cambridge, U.K.
- Harris, M.J., Salje, E.K.H., Güttler, B.K., and Carpenter, M.A. (1989) Structural states of natural potassium feldspar: An infrared spectroscopic study. *Physics and Chemistry of Minerals*, 16, 649–658.
- Hatch, D.M., Ghose, S., and Stokes, H.T. (1990) Phase transitions in leucite, KAlSi₃O₈: I. Symmetry analysis with order parameter treatment and the resulting microscopic distortions. *Physics and Chemistry of Minerals*, 17, 220–227.
- Heine, V., Chen, X., Dattagupta, S., Dove, M.T., Evans, A., Giddy, A.P., Marais, S., Padlewski, S., Salje, E., and Tautz, F.S. (1992) Landau theory revisited. *Ferroelectrics*, 128, 255–264.
- Landau, L.D. (1937) On the theory of phase transitions, part I. *Soviet Physics JETP*, 7, 19ff. (not seen; extracted from *Collected papers of L.D. Landau*, p. 193–209. Pergamon, Oxford, U.K., 1965).
- Landau, L.D., and Lifshitz, E.M. (1980) *Statistical Physics*, part 1 (3rd edition), 544 p. Pergamon, Oxford, U.K.
- Lifshitz, E.M. (1942a) On the theory of phase transitions of the second order: I. Changes of the elementary cell of a crystal in phase transitions of the second order. *Journal of Physics*, 6, 61–74.
- (1942b) On the theory of phase transitions of the second order: II. Phase transitions of the second order in alloys. *Journal of Physics*, 6, 251–263.
- Navrotsky, A. (1987) Models of crystalline solutions. In *Mineralogical Society of America Reviews in Mineralogy*, 17, 35–69.
- O'Neill, H.St.C., and Navrotsky, A. (1983) Simple spinels: Crystallographic parameters, cation radii, lattice energies, and cation distribution. *American Mineralogist*, 68, 181–194.
- Palmer, D.C., Bismayer, U., and Salje, E.K.H. (1990) Phase transitions in leucite: Order parameter behaviour and the Landau potential deduced from Raman spectroscopy and birefringence studies. *Physics and Chemistry of Minerals*, 17, 259–265.

- Phillips, B.L., Kirkpatrick, R.J., and Carpenter, M.A. (1992) Investigation of short-range Al,Si order in synthetic anorthite by ^{29}Si MAS NMR spectroscopy. *American Mineralogist*, 77, 484–494.
- Powell, R. (1977) Activity-composition relationships for crystalline solutions. In D.G. Fraser, Ed., *Thermodynamics in geology*, p. 57–65. Reidel, Dordrecht, The Netherlands.
- (1983) Thermodynamics of complex phases. In S.K. Saxena, Ed., *Advances in physical geochemistry*, vol. 3, p. 241–266. Springer-Verlag, New York.
- Redfern, S.A.T., and Salje, E.K.H. (1987) Thermodynamics of plagioclase: II. Temperature evolution of the spontaneous strain at the $\text{II} \leftrightarrow \text{PI}$ phase transition in anorthite. *Physics and Chemistry of Minerals*, 14, 189–195.
- Redfern, S.A.T., Salje, E.K.H., and Navrotsky, A. (1989) High-temperature enthalpy at the orientational order-disorder transition in calcite: Implications for the calcite/aragonite phase equilibrium. *Contributions to Mineralogy and Petrology*, 101, 479–484.
- Reeder, R.J., Redfern, S.A.T., and Salje, E.K.H. (1988) Spontaneous strain at the structural phase transition in NaNO_3 . *Physics and Chemistry of Minerals*, 15, 605–611.
- Sack, R.O. (1980) Some constraints on the thermodynamic mixing properties of Fe-Mg orthopyroxenes and olivines. *Contributions to Mineralogy and Petrology*, 71, 257–269.
- Sack, R.O., and Ghiorso, M.S. (1989) Importance of considerations of mixing properties in establishing an internally consistent thermodynamic database: Thermochemistry of minerals in the system $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4\text{-SiO}_2$. *Contributions to Mineralogy and Petrology*, 102, 41–68.
- Salje, E.K.H. (1990) Phase transitions in ferroelastic and co-elastic crystals, 366 p. Cambridge University Press, Cambridge, U.K.
- (1991) Crystallography and structural phase transitions: An introduction. *Acta Crystallographica*, A47, 453–469.
- (1992a) Application of Landau theory for the analysis of phase transitions in minerals. *Physics Reports*, 215, 49–99.
- (1992b) Hard mode spectroscopy: Experimental studies of structural phase transitions. *Phase Transitions*, 37, 83–110.
- Salje, E.K.H., and Devarajan, V. (1986) Phase transitions in systems with strain-induced coupling between two order parameters. *Phase Transitions*, 6, 235–248.
- Salje, E.K.H., and Kroll, H. (1991) Kinetic rate laws derived from order parameter theory: III. Al,Si ordering in sanidine. *Physics and Chemistry of Minerals*, 17, 563–568.
- Salje, E.K.H., and Marais, S. (1992) On the correlation between local potentials and thermodynamic/kinetic behaviour of ferroelectrics. *Ferroelectrics*, 136, 1–13.
- Salje, E.K.H., and Wruck, B. (1983) Specific-heat measurements and critical exponents of the ferroelastic phase transition in $\text{Pb}_3(\text{PO}_4)_2$ and $\text{Pb}_3(\text{P}_{1-x}\text{As}_x\text{O}_4)_2$. *Physical Review*, B28, 6510–6518.
- Salje, E.K.H., Wruck, B., and Thomas, H. (1991) Order-parameter saturation and low-temperature extension of Landau theory. *Zeitschrift für Physik*, B82, 399–404.
- Shi, P., Saxena, S.K., and Sundman, B. (1992) Sublattice solid solution model and its application to orthopyroxene (Mg,Fe) $_2\text{Si}_2\text{O}_6$. *Physics and Chemistry of Minerals*, 18, 393–405.
- Thompson, J.B., Jr. (1969) Chemical reactions in crystals. *American Mineralogist*, 54, 341–375.
- (1970) Chemical reactions in crystals: Corrections and clarification. *American Mineralogist*, 55, 528–532.
- Wood, B.J., and Nicholls, J. (1978) The thermodynamic properties of reciprocal solid solutions. *Contributions to Mineralogy and Petrology*, 66, 389–400.
- Wood, B.J., Nell, J., and Woodland, A.B. (1991) Macroscopic and microscopic thermodynamic properties of oxides. In *Mineralogical Society of America Reviews in Mineralogy*, 25, 265–302.

MANUSCRIPT RECEIVED JUNE 10, 1993

MANUSCRIPT ACCEPTED JULY 19, 1994