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Thermodynamics of order-disorder in minerals: I. Symmetric formalism applied to minerals of fixed composition

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ABSTRACT

Thermodynamics of order-disorder in minerals may be approached by treating the mineral as a solid solution between an independent set of end-members with which the range of possible states of ordering of the phase can be represented. Thus, a mineral of fixed composition (a one-component phase), requiring s independent order parameters to represent the state of order in the mineral, involves an independent set of $s + 1$ end-members. This approach is applied by means of symmetric formalism, with the entropy part of the Gibbs energy taken to be the ideal configurational entropy of mixing using a mixing-on-sites formulation, and the enthalpy part taken to be that of a regular solution between the $s + 1$ end-members. Symmetric formalism is shown to be formally identical to the generalized Bragg-Williams or point approximation, and its treatment of convergent and nonconvergent cation ordering is compared with that of the Landau theory. Its flexibility in describing a wide range of order-disorder behavior is illustrated with applications to sillimanite, spinel, albite, and potassium feldspar, the latter two involving order-parameter coupling.

INTRODUCTION

Without knowledge of the activity-composition ($a - X$) relationships for minerals, the reliable calculation of the conditions of formation of rocks and the calculation of geologic phase diagrams is impossible. As discussed in Wood and Nicholls (1978), Wood (1987), Ghiorso (1990), and Powell and Holland (1993), for example, the task is not straightforward. As a consequence, for all the models normally used (regular, subregular, reciprocal), thermodynamic mole fractions are written in terms of ideal mixing, with the activity-coefficient terms written separately. In Powell and Holland (1993), it was shown that for nonideality formulated with symmetric enthalpic interactions involving all sites, including same-site (regular) and cross-site (reciprocal) interactions, an important simplification of a-X relationships is possible, termed symmetric formalism. The application of the approach to complex phases, which, however, do not involve intermediate states of long-range order, was demonstrated.

The purpose of this paper is to extend symmetric formalism to minerals in which the state of order varies with, for example, temperature and composition. The result is formally identical to the well-known generalized Bragg-Williams or point approximation (e.g., Thompson 1969, 1970; Sack 1980; Davidson and Burton 1987; Ghiorso 1990; Sack and Ghiorso 1991), but because it is derived macroscopically the representation of the thermodynamics of even complex minerals is straightforward. In addition, the form allows ready comparison with Landau theory, a model being increasingly applied to problems of order-disorder (e.g., Salje et al. 1985; Carpenter 1992; Carpenter et al. 1994).

SYMMETRIC FORMALISM AS A MACROSCOPIC BRAGG-WILLIAMS MODEL

In a mineral showing cation order-disorder, there are, in general, s independent order parameters needed to describe the state of order. These order parameters are functions of the site distributions describing this state. Such a mineral in an n-component system can be treated as a solid solution between a set of $n + s$ end-members representing the range of composition and order-disorder (see also, e.g., Nell and Wood 1989; Ghiorso 1990; Sack and Ghiorso 1991). For a mineral of fixed composition, this set involves $1 + s$ end-members. This representation can be illustrated using sillimanite.

Sillimanite is a phase of fixed composition, $^{[6]}\mathrm{Al}\text{-}\mathrm{Al}^{t1}\mathrm{Si}^{t2}\mathrm{O}_5$, with Al and Si capable of disorder between the two tetrahedral sites, t1 and t2. One order parameter is necessary and can be defined as $Q = X_{\mathrm{Al}}^{t1} - X_{\mathrm{Al}}^{t2}$, with values ranging from zero (for complete disorder) to unity (for complete order). Sillimanite is considered to be a binary solid solution between two end-members, ordered sillimanite (osil) and disordered sillimanite (dsil), the tetrahedral site distributions of which are shown in Figure 1. The proportion, or mole fraction, of the ordered end-member, osil, is given by $p_{\mathrm{osil}} = Q$, and the proportion of the disordered end-member, dsil, by $p_{\mathrm{dsil}} = 1 - Q$, with the proportions depending on temperature. The site distributions are given by

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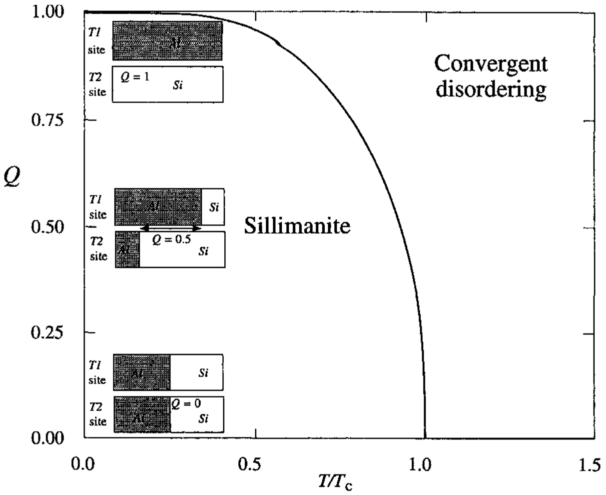

FIGURE 1. The order parameter Q and site distributions for the osil and dsil end-members of sillimanite as a function of changing temperature.

$$X_{\mathrm{Al}}^{\mathrm{t1}} = \frac{1+Q}{2}$$

$$X_{\mathrm{Al}}^{\mathrm{t2}} = \frac{1-Q}{2}$$

$$X_{\mathrm{Si}}^{\mathrm{t1}} = \frac{1-Q}{2}$$

$$X_{\mathrm{Si}}^{\mathrm{t2}} = \frac{1+Q}{2}. \qquad (1)$$

The ideal parts of the activities of the end-members are formulated in terms of ideal mixing-on-sites (e.g., Wood and Banno 1973; Powell 1978; Anderson and Crerar 1993) and are given by

$$a_{\mathrm{osil}}^{\mathrm{ideal}} = X_{\mathrm{Al}}^{\mathrm{t1}} X_{\mathrm{Si}}^{\mathrm{t2}} = \frac{1}{4}(1+Q)^2$$

$$a_{\mathrm{dsil}}^{\mathrm{ideal}} = 4(X_{\mathrm{Al}}^{\mathrm{t1}} X_{\mathrm{Si}}^{\mathrm{t1}} X_{\mathrm{Al}}^{\mathrm{t2}} X_{\mathrm{Si}}^{\mathrm{t2}})^{1/2} = (1+Q)(1-Q) \qquad (2)$$

where the factor of 4 is a normalization constant to ensure unit activity of dsil in completely disordered sillimanite, and the power of one-half is used because Al and Si half occupy each site in this end-member. The activity coefficients are given by the usual expressions for a regular solution (Thompson 1967; Powell 1978; Anderson and Crerar 1993):

$$\mathrm{R}T \ln \gamma_{\mathrm{osil}} = W(1 - p_{\mathrm{osil}})^2 = W(1-Q)^2$$

$$\mathrm{R}T \ln \gamma_{\mathrm{dsil}} = W(1 - p_{\mathrm{dsil}})^2 = WQ^2 \qquad (3)$$

in which W is the macroscopic interaction energy for the binary osil-dsil and includes individual t1 and t2 site-interaction energies and the t1-t2 cross-site (or reciprocal) energy (Powell and Holland 1993, p. 1178, Eq. 20).

To find the equilibrium value of Q at any temperature, either the Gibbs energy of the solid solution may be differentiated with respect to Q, setting the result to zero, or, equivalently, the equilibrium condition for the intracrystalline reaction may be used:

$$\underset{\text{osil}}{\mathrm{Al(Al)^{t1}(Si)^{t2}O_5}} = \underset{\text{dsil}}{\mathrm{Al(Al_{1/2}Si_{1/2})^{t1}(Al_{1/2}Si_{1/2})^{t2}O_5}}. \qquad (4)$$

Substituting the activities from above into the equilibrium condition $0 = \Delta G^0 + \mathrm{R}T \ln K$ gives

$$\begin{aligned} 0 &= \Delta H_{\mathrm{R}} - T\Delta S_{\mathrm{R}} + P\Delta V_{\mathrm{R}} + \mathrm{R}T \ln\left(\frac{1-Q}{1+Q}\right) \\ &\quad + \mathrm{R}T \ln(4) + (2Q-1)W \\ &= A + BQ + \mathrm{R}T \ln\left(\frac{1-Q}{1+Q}\right) \end{aligned} \qquad (5)$$

where $A = \Delta H_{\mathrm{R}} - W + P\Delta V_{\mathrm{R}}$ and $B = 2W$. In these expressions ΔH_{R} is the standard enthalpy of the reaction osil = dsil as written above, representing the enthalpy difference between completely disordered and completely ordered sillimanite. Note that the factor ¼ from the activity of osil, which contributes $\mathrm{R}T \ln(4)$ above, does not appear in the final equilibrium relation because it is exactly canceled by the $-T\Delta S_{\mathrm{R}}$ term stemming from the difference in entropy between disordered and ordered sillimanite. In the remaining discussion, it is assumed that $\Delta V_{\mathrm{R}} = 0$ unless there is specific reference to a nonzero ΔV_{R}. Equation 5 is used to determine the equilibrium value for Q at any desired temperature.

Two situations are represented in Equation 5. When the term $B = 0$, it reduces to the nonconvergent, simple disordering model commonly found in the literature (e.g., for sillimanite, by Navrotsky et al. 1973). This simple theory, however, is not applicable to sillimanite because sillimanite undergoes a symmetry change at a critical temperature above 1700 °C (Holland and Carpenter 1986) and therefore shows convergent disordering. Such behavior, in which a rapid decrease in Q to zero occurs at a critical temperature, T_{c}, can be handled by setting $A = 0$ (i.e., when $W = \Delta H_{\mathrm{R}}$), in which case Equation 5 reduces to the classical, convergent Bragg-Williams model also used for sillimanite by Greenwood (1972).

Considering the sillimanite energetics, the model values $W = 17$ kJ and $\Delta H_{\mathrm{R}} = 17$ kJ give convergent behavior with T_{c} at 2044 K (1772 °C). These energies, obtained as averages from the Bragg-Williams parameters derived by Bertram et al. (1990), yield critical temperatures in agreement with those suggested by Holland and Carpenter (1986) from their experimental study. Sillimanite is predicted to be almost fully ordered at all geologically significant temperatures, in agreement with the phase-equilibrium studies used to generate thermodynamic data sets (e.g., Berman 1988; Holland and Powell 1990).

Symmetric formalism has a form that is identical overall to the generalized Bragg-Williams models (e.g., Thompson 1969, 1970; Sack 1980; Davidson and Burton 1987; Nell and Wood 1989; Ghiorso 1990; Sack and Ghiorso 1991). In such microscopic approaches sillimanite would be treated energetically in terms of regular solutions on the t1 and t2 sites (w^{t1}, w^{t2}) with a reciprocal (or cross-site) interaction energy ($\Delta G_{\mathrm{recip}} = w^{t1\,t2}_{\mathrm{rec}}$) and an enthalpy of exchange (ΔH_{ex}) for the internal reaction $\mathrm{Si^{t1}Al^{t2}} = \mathrm{Al^{t1}Si^{t2}}$. The equilibrium condition for this internal exchange reaction would be written by substitution of the individual terms into the equation $0 = \Delta G^0 + \mathrm{R}T \ln K$:

$$0 = \frac{\Delta H_{\mathrm{ex}}}{2} + \mathrm{R}T \ln\left(\frac{1+Q}{1-Q}\right) + \frac{(w^{t1\,t2}_{\mathrm{rec}} - w^{t1} - w^{t2})}{2}Q$$
$$= A + BQ + \mathrm{R}T \ln\left(\frac{1+Q}{1-Q}\right) \tag{6}$$

which is identical in form to Equation 5. In a comparison of terms, the parameters W and ΔH_{R} are equivalent to combinations of the microscopic model values:

$$W = \frac{(w^{t1} + w^{t2} - w^{t1\,t2}_{\mathrm{rec}})}{4}$$
$$\Delta H_{\mathrm{R}} = -\frac{\Delta H_{\mathrm{ex}}}{2} + \frac{(w^{t1} + w^{t2} - w^{t1\,t2}_{\mathrm{rec}})}{4}. \tag{7}$$

Although the equations have the same final form as those of the generalized Bragg-Williams models, symmetric formalism is not motivated by pairwise atomic interactions; it assumes only that the enthalpy of disordering is a simple (e.g., regular) macroscopic function of Q and may result as much from lattice strains or ionic size mismatch as it does from assumed pairwise interaction energies. The equivalence of final form arises because pairwise interactions yield a symmetric result. However, the ΔH_{R} term in this formalism does represent the difference in enthalpies between ordered and disordered end-members, whatever the origins of that difference.

THERMODYNAMIC BEHAVIOR AND LANDAU THEORY

In Landau theory different types of ordering behavior (see below) are distinguished by careful measurement of physical quantities such as heat capacity or order parameter over a range of temperature. The basic similarities between symmetric formalism and Landau approaches to ordering are outlined before comparing the way each describes the behavior of heat capacity and order parameter. The enthalpies of the disordering process may be illustrated by considering the binary osil-dsil as in Figure 2, where it can be seen that the enthalpy of sillimanite is given by $H_{\mathrm{sil}} = H_{\mathrm{dsil}} - Q\Delta H_{\mathrm{R}} + WQ(1 - Q)$. The enthalpy and entropy of ordering, relative to a disordered state, depend on the degree of order, Q, and are given by

$$\Delta H^{\mathrm{ordering}}_{\mathrm{SF}} = Q(W - \Delta H_{\mathrm{R}}) - Q^2 W$$
$$\Delta S^{\mathrm{ordering}}_{\mathrm{SF}} = S^{\mathrm{ordering}}_{\mathrm{config}}. \tag{8}$$

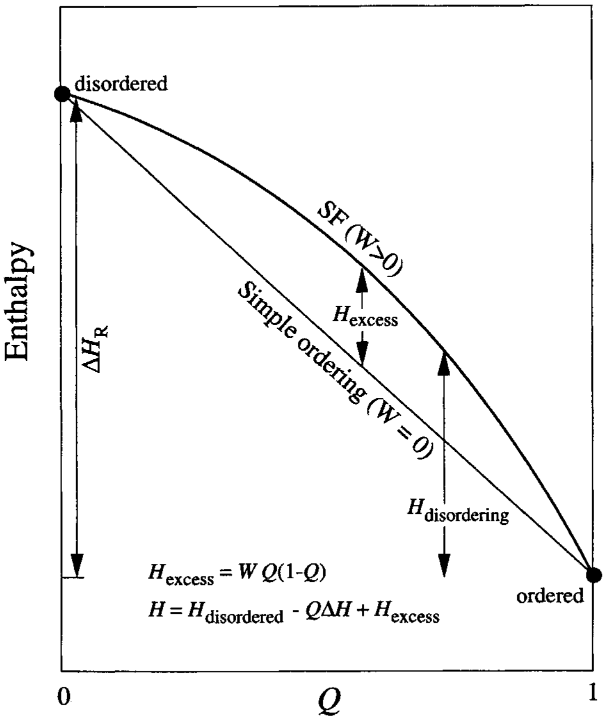

FIGURE 2. Enthalpy–order parameter relationships for a regular solution between ordered and disordered end-members. The ΔH_{R} is the maximum enthalpy of ordering from the disordered state, and W is the regular-solution parameter.

In contrast, in Landau theory, the Gibbs energy of ordering from a disordered starting point is given by a series expansion in the order parameter Q, such that its enthalpy and entropy are given by

$$\Delta H^{\mathrm{ordering}}_{\mathrm{Landau}} = -HQ - \frac{1}{2}aT_{\mathrm{c}}Q^2 + \frac{1}{4}bQ^4 + \frac{1}{6}cQ^6 + \ldots$$
$$\Delta S^{\mathrm{ordering}}_{\mathrm{Landau}} = -\frac{1}{2}aQ^2. \tag{9}$$

The field term H allows nonconvergent ordering, in which no phase transition occurs (Carpenter et al. 1994). For convergent ordering, in which $H = 0$, Landau theory usually distinguishes among three types of ordering behavior. Second-order phase transitions, in which Q approaches zero as T approaches T_{c} (Fig. 3), have $c = 0$, and hence no sixth-order term in Q occurs. The heat capacity in second-order transitions increases linearly with temperature and falls abruptly to zero at T_{c}. Tricritical phase transitions, in which Q approaches zero as T approaches T_{c} rather more catastrophically than in second-order transitions (Fig. 3), have $b = 0$, and hence no fourth-order term in Q occurs. The heat capacity in tricritical transitions increases dramatically toward an infinite value as T_{c} is approached, whereupon it then drops to zero. First-order behavior, in which Q jumps discontinuously to zero at the temperature of the phase transition, can occur when b becomes slightly negative, with the variation of heat capacity being similar to the tricritical case. Further details of these cases may be found in Carpenter (1992).

The variation of Q with temperature in symmetric formalism is shown in Figure 4 for various combinations of

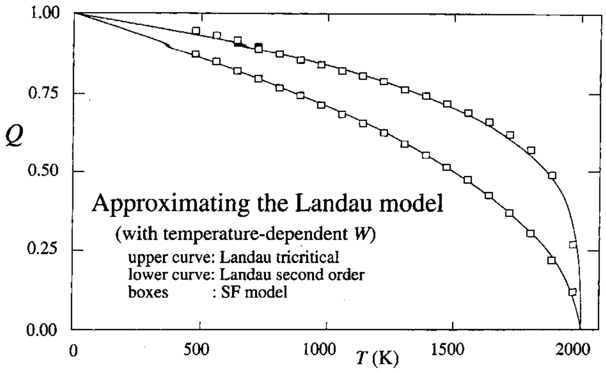

FIGURE 3. Modeling Landau tricritical and second-order behavior with the use of symmetric formalism. Curves = Landau variation of Q with temperature. Boxes = symmetric formalism fit to the Landau behavior (W allowed to be a linear function of temperature). Model values (lower curve) Al_2Si_2 ($n = 1$): Landau second-order model with $T_c = 2000$ K, $S_{max} = 23.05$ J/K, and $H_{max} = 23.05$ kJ, and symmetric formalism with $\Delta H_R = 27.5$ kJ and $W = -18.50 + 0.0227T$ kJ; (upper curve) $AlSi_3$ ($n = 3$): Landau tricritical model with $T_c = 2000$ K, $S_{max} = 18.70$ J/K, and $H_{max} = 24.93$ kJ, and symmetric formalism with $\Delta H_R = 29.0$ kJ and $W = -19.97 + 0.0242T$ kJ. In both cases the excess (nonconfigurational) entropy is modest, $S_{ex} = -[(\partial W)/(\partial T)]Q(1 - Q)$, reaching maximal values of about 5–6 J/K at $Q = 0.5$.

values of the parameters W and ΔH_R. As can be seen, if W is zero or small in comparison with ΔH_R, then the result is a typical nonconvergent situation with Q decreasing continuously with increasing temperature. In this case there is no phase transformation, merely a continuously changing cation distribution. If $W = \Delta H_R$ (classical Bragg-Williams behavior), then Q falls off dramatically with temperature, reaching zero at the critical temperature, T_c. The critical temperature for a 1:1 compound like sillimanite occurs at $T_c = W/R$ (see Appendix 2). If ΔH_R is a little larger than W, this behavior is modified such that Q "tails off" above T_c (Fig. 4). Thus, the relative magnitudes of these parameters determine the size of the field term and hence the degree of nonconvergence of the disordering behavior. The condition $W > \Delta H_R$ is not appropriate because it implies that the anti-ordered state is more stable than the ordered one. For minerals in which there is not an equal proportion of sites, i.e., for $n > 1$, the phase transition in the case $W = \Delta H_R$ does not occur at the T_c predicted above but becomes first order in character with a transition temperature just above T_c, as seen in Figure 5. However, if ΔH_R is a little greater than W, the transition can be made to become continuous with a small tail to Q above T_c. Figure 5 illustrates the effect on Q of varying the ratio $\Delta H_R : W$ slightly from unity.

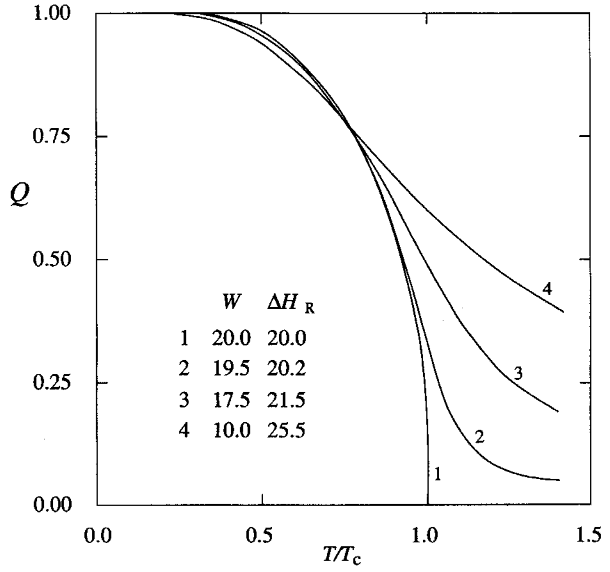

FIGURE 4. Variation of order parameter Q with temperature for a 1:1 compound (e.g., sillimanite) as a function of the relative magnitudes of the parameters (ΔH_R and W in kilojoules). T_c is the critical temperature if $Q \to 0$ when $\Delta H_R = W$.

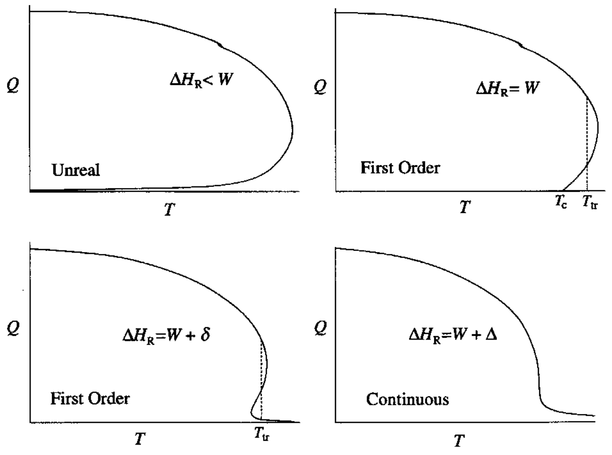

FIGURE 5. Variation of the behavior of Q with temperature for relative values of ΔH_R and W for a 1:3 compound. The situation $\Delta H_R < W$ (**top left**) is inappropriate because it implies that the anti-ordered state is most stable; if $\Delta H_R = W$ (**top right**), there is a first-order transformation with a transition temperature, T_{tr}, a little higher than T_c. Although when $(\partial Q)/(\partial T)$ is negative the phase is unstable with a meaningless negative heat capacity, the transition temperature does not occur at the point where $(\partial Q)/(\partial T)$ changes sign but must be determined from Gibbs energy criteria (see Fig. 8). If ΔH_R is marginally larger than W (**bottom left**), there is a first-order transition and Q drops to a small but nonzero value, which then tails off with temperature. If ΔH_R is significantly larger than W (**bottom right**), the transition is continuous and nonconvergent.

The temperature variation of the heat capacity, C_P, in symmetric formalism is shown in Figure 6 for various combinations of values of the parameters W and ΔH_R. If $W = \Delta H_R$, the heat capacity increases to a maximum and then drops to zero at T_c, as is typical of convergent behavior. If W is a little less than ΔH_R, the peak in the heat capacity becomes rounded, and the small nonconvergent contribution to the disordering causes a tail to develop

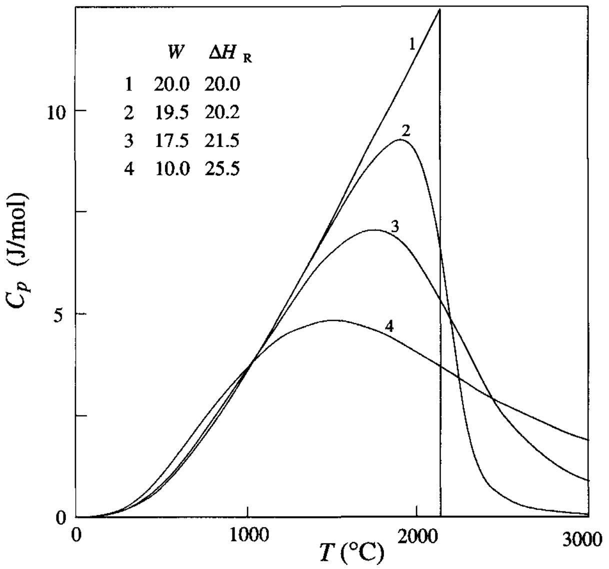

Figure 6. Variation of heat capacity with temperature for a 1:1 compound as a function of the relative magnitudes of the parameters (ΔH_R and W in kilojoules) in symmetric formalism. If $\Delta H_R = W$, the heat capacity reaches a peak and drops abruptly to 0, whereas if $\Delta H_R > W$, the peak becomes rounded with a tail above T_c.

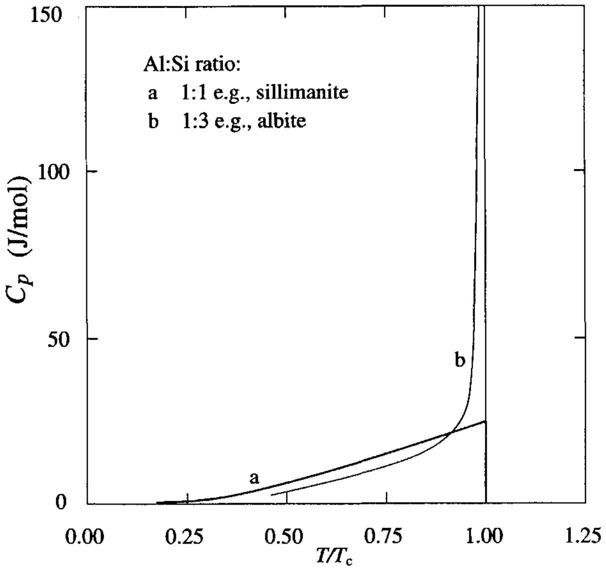

Figure 7. Comparison of the 1:1 and 1:3 behavior of heat capacity. The heat capacity of the 1:1 compound is nearly linear, reaches a peak of finite size, and is like that of a Landau second-order transition. The heat capacity of the 1:3 compound becomes infinite [where $(\partial Q)/(\partial T)$ in Fig. 5, top left, becomes infinite] and resembles that of the Landau tricritical transition.

above T_c. The heat capacity of the 1:1 compound is almost linear with temperature after an initial nonlinear increase and therefore closely resembles the second-order behavior in Landau theory, whereas the 1:3 compound has an ever-increasing heat capacity up to the critical point, much resembling the tricritical behavior in Landau theory (Fig. 7).

An interesting feature of this approach is that 1:1 phases cannot undergo first-order transitions because of the symmetry imposed by the regular-solution enthalpy assumption: If there are to be two minima in Gibbs energy, symmetric formalism forces them to be at identical positive and negative values of Q (Fig. 8). Within the general framework of this approach, 1:1 phases can undergo a first-order transition if the enthalpy is made asymmetric, and this is most easily achieved by replacing the regular solution by a subregular solution between the endmembers (see the Discussion section below).

The differences in heat-capacity behavior in Landau theory result from varying the higher order terms in enthalpy (the Q^4 term in Eq. 9), which linearly increases heat capacity in the second-order model, and the Q^6 term, which accounts for the increasingly sharp rise in heat capacity in the tricritical model). In contrast, it is the differences in configurational entropy resulting from the different ratio of Al:Si that result in the two forms of heat-capacity behavior in symmetric formalism, the 1:1 ratio giving the linear increase and the 1:2 and 1:3 ratios giving the rapidly increasing heat capacities. The first three terms in the series expansion for configurational entropy of ordering for 1:n materials are

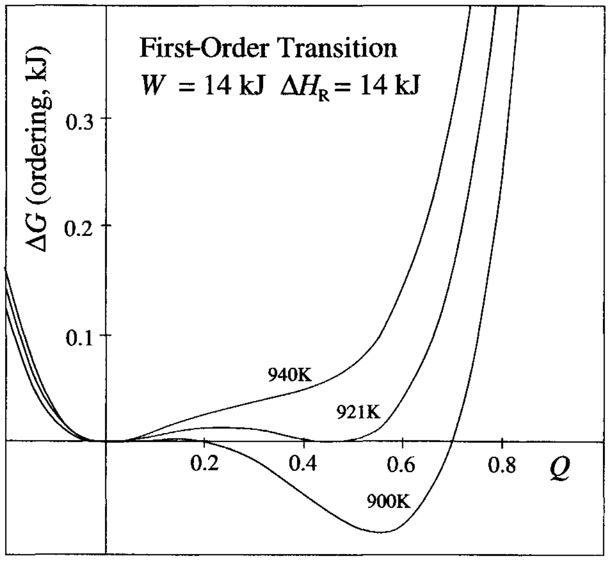

Figure 8. Plot of Gibbs energy of ordering against Q for temperatures above, below, and at the transition temperature for a first-order transition at T_{tr}. The transition temperature occurs where the minimums at $Q = 0$ and $Q \geq 0$ are at the same (zero) free energy.

$$S_{\mathrm{ord}} = -\frac{\mathrm{R}}{2}(1 + n)\left[Q^2 - \frac{1}{3n}(1 - n)^2Q^3 + \frac{1}{6n}(1 - n + n^2)^2Q^4 \ldots\right]. \quad (10)$$

Thus, if $n = 1$, there are only even terms in the expansion and the entropy of ordering is symmetric about $Q = 0$; whereas, if $n > 1$, odd-order terms appear and the entropy at negative Q is not the mirror image of its value at positive Q. The Landau entropy ($-\tfrac{1}{2}aQ^2$) does not take this asymmetry (and heat capacity) stemming from configurational terms into account but deals with them through different higher order terms in enthalpy. Kroll et al. (1994) also compared Landau theory with Bragg-Williams models but from a somewhat different perspective.

Pressure dependence of the disordering behavior is incorporated by allowing the two (or more) end-members to have different molar volumes. In rare cases it could be important to allow different thermal expansions and compressibilities as well. Changing the value of ΔV_{R} between end-members can also cause the type of phase transition to change with pressure; for example, a first-order transition in a 1:3 compound with $\Delta H_{\mathrm{R}} = W$ can become nonconvergent as pressure increases because of the increase in Gibbs energy from the additional $\Delta V_{\mathrm{R}}(P - 1)$ term. To preserve the nature of the transition with pressure, while allowing the transition temperature to change, requires the pressure dependence of W to be equal to $\Delta V_{\mathrm{R}}(W_V = \Delta V_{\mathrm{R}}$, where $W = W_H + W_VP)$.

MINERAL EXAMPLES

Spinel

Magnesium spinel, $^{[4]}\mathrm{Mg}^{[6]}\mathrm{Al_2O_4}$, is an example of a normal spinel in which Mg is ordered onto the tetrahedral site and Al onto the octahedral sites at low temperature. This is a 1:2 compound, with site distributions given by (see Appendix 2)

$$X^{\mathrm{t}}_{\mathrm{Al}} = \frac{2 - 2Q}{3}$$

$$X^{\mathrm{t}}_{\mathrm{Mg}} = \frac{1 + 2Q}{3}$$

$$X^{\mathrm{o}}_{\mathrm{Al}} = \frac{2 + Q}{3}$$

$$X^{\mathrm{o}}_{\mathrm{Mg}} = \frac{1 - Q}{3} \quad (11)$$

where, with Q defined as $X^{\mathrm{o}}_{\mathrm{Al}} - X^{\mathrm{t}}_{\mathrm{Al}}$, $Q = 1$ for normal spinel, $Q = 0$ for disordered (random) spinel, and $Q = -0.5$ for a completely inverse spinel. The disordering is continuous with increasing temperature and nonconvergent in behavior. The equilibrium condition (see Appendix 2) is

$$0 = \Delta H_{\mathrm{R}} + \frac{2}{3}\mathrm{R}T\ln\frac{(2 - 2Q)(1 - Q)}{(1 + 2Q)(2 + Q)} + (2Q - 1)W \quad (12)$$

and this expression fits well the site-distribution data of Peterson et al. (1991), with $W = 2.4$ kJ and $\Delta H_{\mathrm{R}} = 16.0$ kJ providing as good a fit to the data as the Landau model of Carpenter and Salje (1994a). Equation 12 is formally identical to the expressions in Sack and Ghiorso (1991) and O'Neill and Navrotsky (1984), the parameter equivalences being $\alpha = \tfrac{3}{2}(\Delta H_{\mathrm{R}} + W)$ and $\beta = -\tfrac{9}{4}W$ in the terminology of O'Neill and Navrotsky.

Recent measurements of the solubility of spinel in palladium alloys by Chamberlin et al. (1995) have endorsed the suggestion of Carpenter and Salje (1994a) that the ordering entropy (and enthalpy) is very much less than the configurational estimate. The advantage claimed for the Landau model over the classical models is that the entropy is adjustable and not forced to take configurational values. Carpenter and Salje (1994a) used the calorimetric enthalpy of ordering to scale their entropy to a value that is approximately one-half the configurational value. Symmetric formalism can be similarly modified by scaling the entropy and also the enthalpy. If the configurational entropy of ordering is halved, then the term $\tfrac{2}{3}\mathrm{R}$ in the equilibrium condition (Eq. 12) becomes $\tfrac{1}{3}\mathrm{R}$ and the values for W and ΔH_{R} must be halved. This modification then reproduces the Landau-predicted enthalpy behavior in Carpenter and Salje (1994a, Fig. 5).

Order-parameter coupling in alkali feldspar end-members

It has been suggested that order-parameter coupling, as implied for the alkali feldspar end-members (Salje et al. 1985; Carpenter and Salje 1994a), using Landau theory cannot be modeled by classical (Bragg-Williams–type) approaches (Kroll et al. 1994). However (see Thompson et al. 1974), order-parameter coupling is possible with classical models if neither order parameter refers solely to displacive transitions.

In potassium feldspar, $\mathrm{KAlSi_3O_8}$, there are four tetrahedral sites on which one Al and three Si atoms are distributed. The ordering process can be envisaged as occurring in two stages with decreasing temperature. In the first stage the Al and Si atoms are distributed over two t1 and two t2 sites within the monoclinic structure. The order parameter for this process, designated Q_{t}, following Carpenter and Salje (1994b), is defined as

$$Q_{\mathrm{t}} = \frac{X^{\mathrm{t1}}_{\mathrm{Al}} - X^{\mathrm{t2}}_{\mathrm{Al}}}{X^{\mathrm{t1}}_{\mathrm{Al}} + X^{\mathrm{t2}}_{\mathrm{Al}}} \quad (13)$$

and varies smoothly with decreasing temperature (nonconvergent ordering). Below a critical temperature near 475 °C, a second stage in ordering occurs in which the t1 site splits into t1o and t1m sites and the structure becomes triclinic. It has been a matter of some debate as to whether this symmetry change accompanies a first-order (Kroll and Voll, in Ribbe 1983; Carpenter and Salje 1994b) or a continuous (Brown and Parsons 1989) phase transformation. A second-order parameter, Q_{od}, is required to monitor this further ordering behavior and is defined as

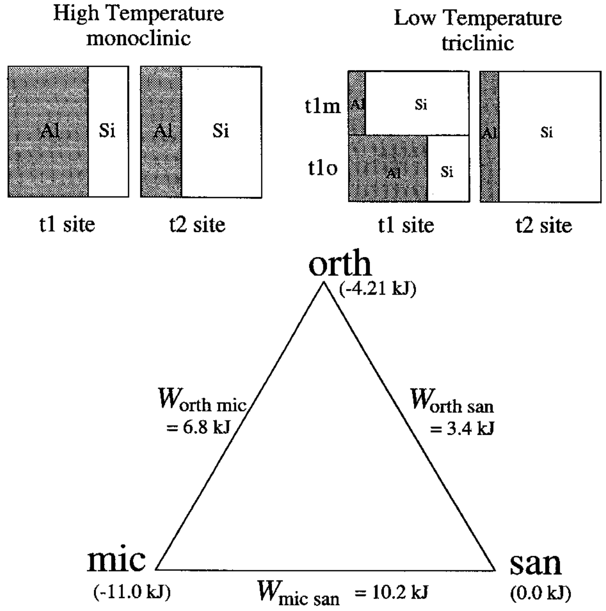

FIGURE 9. Site distributions and pseudoternary model for potassium feldspar. The boxes show the unequal distribution of Al and Si between t1 and t2 sites in the monoclinic form and the further ordering of Al onto t1o in the triclinic state. On the ternary plot are shown the enthalpies of each end-member relative to disordered sanidine and the magnitudes of the interaction energies along each join.

$$Q_{\text{od}} = \frac{X_{\text{Al}}^{\text{t1o}} - X_{\text{Al}}^{\text{t1m}}}{X_{\text{Al}}^{\text{t1o}} + X_{\text{Al}}^{\text{t1m}}}. \tag{14}$$

At temperatures above the triclinic-monoclinic inversion, Q_{od} is zero and only the Q_{t} order parameter operates, whereas below the transition both order parameters are defined but do not operate independently; clearly as Q_{od} increases, the value of Q_{t} must also increase because more Al is being transferred from the t2 site to the two t1 sites, leading to coupling of order parameters.

In the simplest coupled representation, potassium feldspar is treated as a ternary regular solution involving three end-members: ordered triclinic microcline (mic), disordered monoclinic sanidine (san), and a hypothetical t1–t2–ordered monoclinic orthoclase (orth) end-member. In mic the configuration is Al on the t1o site and Si on the t1m site and two t2 sites; in san the Al and Si are disordered over all four sites; and in orth all Al is randomly distributed on the two t1 sites, whereas the t2 sites contain only Si. These relationships are shown in Figure 9. For practical calculations the mole fractions of two of the end-members, p_{mic} and p_{san}, are used to describe the site ordering. The site fractions are derived by considering that during t1-t2 ordering the proportion of Al on t2 decreases by m, and that on t1 increases by m; and that during t1o-t1m ordering, the proportion of Al on t1m decreases by n, and that on t1o increases by n:

$$\begin{aligned}
X_{\text{Al}}^{\text{t2}} &= \frac{1}{4} - m &&= \frac{1}{4}p_{\text{san}} \\
X_{\text{Si}}^{\text{t2}} &= \frac{3}{4} + m &&= \frac{1}{4}(4 - p_{\text{san}}) \\
X_{\text{Al}}^{\text{t1o}} &= \frac{1}{4} + m + n &&= \frac{1}{4}(2 - p_{\text{san}} + 2p_{\text{mic}}) \\
X_{\text{Si}}^{\text{t1o}} &= \frac{3}{4} - m - n &&= \frac{1}{4}(2 + p_{\text{san}} - 2p_{\text{mic}}) \\
X_{\text{Al}}^{\text{t1m}} &= \frac{1}{4} + m - n &&= \frac{1}{4}(2 - p_{\text{san}} - 2p_{\text{mic}}) \\
X_{\text{SI}}^{\text{t1m}} &= \frac{3}{4} - m + n &&= \frac{1}{4}(2 + p_{\text{san}} + 2p_{\text{mic}}).
\end{aligned} \tag{15}$$

The conventional order parameters may be found from $Q_{\text{t}} = 1 - p_{\text{san}}$ and $Q_{\text{od}} = (2p_{\text{mic}})/(1 + Q_{\text{t}}) = (2p_{\text{mic}})/(2 - p_{\text{san}})$.

To determine the equilibrium site distribution, two conditions of equilibrium must be solved, corresponding to an independent set of two reactions among the three end-members, which necessitates setting up the ideal mixing-on-sites activities and activity coefficients for mic, orth, and san:

$$a_{\text{mic}}^{\text{ideal}} = \frac{1}{256}(2 - p_{\text{san}} + 2p_{\text{mic}})(2 + p_{\text{san}} + 2p_{\text{mic}})(4 - p_{\text{san}})^2$$

$$\begin{aligned}
a_{\text{san}}^{\text{ideal}} = \frac{1}{27}&(2 - p_{\text{san}} + 2p_{\text{mic}})^{1/4}(2 + p_{\text{san}} - 2p_{\text{mic}})^{3/4} \\
&\cdot(2 - p_{\text{san}} - 2p_{\text{mic}})^{1/4}(2 + p_{\text{san}} + 2p_{\text{mic}})^{3/4} \\
&\cdot(p_{\text{san}})^{1/2}(4 - p_{\text{san}})^{3/2}
\end{aligned}$$

$$\begin{aligned}
a_{\text{orth}}^{\text{ideal}} = \frac{1}{64}&(2 - p_{\text{san}} + 2p_{\text{mic}})^{1/2}(2 + p_{\text{san}} - 2p_{\text{mic}})^{1/2} \\
&\cdot(2 - p_{\text{san}} - 2p_{\text{mic}})^{1/2}(2 + p_{\text{san}} + 2p_{\text{mic}})^{1/2}(4 - p_{\text{san}})^2
\end{aligned}$$

and, from the ternary regular solution formulation,

$$\begin{aligned}
RT\ln\gamma_{\text{mic}} &= p_{\text{orth}}(1 - p_{\text{mic}})W_{\text{orth mic}} + (1 - p_{\text{mic}})p_{\text{san}}W_{\text{mic san}} \\
&\quad - p_{\text{orth}}p_{\text{san}}W_{\text{orth san}} \\
RT\ln\gamma_{\text{orth}} &= (1 - p_{\text{orth}})p_{\text{mic}}W_{\text{orth mic}} - p_{\text{mic}}p_{\text{san}}W_{\text{mic san}} \\
&\quad + (1 - p_{\text{orth}})p_{\text{san}}W_{\text{orth san}} \\
RT\ln\gamma_{\text{san}} &= -p_{\text{orth}}\,p_{\text{mic}}W_{\text{orth mic}} + p_{\text{mic}}(1 - p_{\text{san}})W_{\text{mic san}} \\
&\quad + p_{\text{orth}}(1 - p_{\text{san}})W_{\text{orth san}}.
\end{aligned} \tag{16}$$

In these equations p_{orth} can be replaced by $1 - p_{\text{san}} - p_{\text{mic}}$.

The energetic consequences of order-parameter coupling may be seen by writing the enthalpy of ordering first in terms of the end-member proportions and their enthalpies,

$$\begin{aligned}
H_{\text{mechanical}} &= H_{\text{san}}p_{\text{san}} + H_{\text{orth}}p_{\text{orth}} + H_{\text{mic}}p_{\text{mic}} \\
H_{\text{excess}} &= p_{\text{mic}}p_{\text{san}}W_{\text{mic san}} + p_{\text{orth}}p_{\text{san}}W_{\text{orth san}} \\
&\quad + p_{\text{orth}}p_{\text{mic}}W_{\text{orth mic}} \\
H_{\text{ordering}} &= H_{\text{san}} - H_{\text{mechanical}} - H_{\text{excess}}
\end{aligned} \tag{17}$$

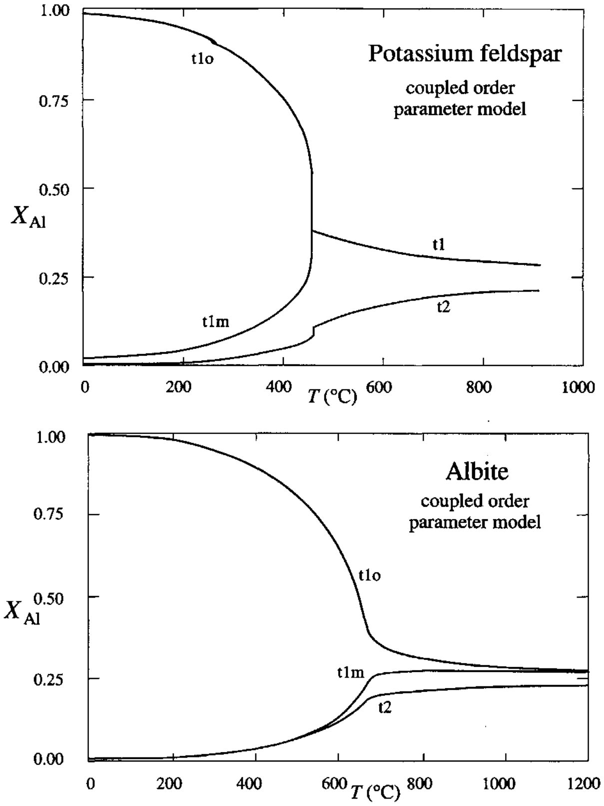

FIGURE 10. Calculated distribution of Al among the various sites in potassium feldspar (**top**) and albite (**bottom**) as a function of temperature. Note the first-order step at 470 °C in potassium feldspar in contrast to the continuous ordering of albite.

and then rewriting in terms of the two conventional order parameters, Q_{od} and Q_t, and the enthalpies of reaction of the two independent reactions mic = san(ΔH_1) and orth = san(ΔH_2):

$$
\begin{aligned}
H_{\text{ordering}} = {} & Q_{od}\frac{1}{2}(\Delta H_1 - \Delta H_2 - W_{\text{mic san}} + W_{\text{orth san}}) \\
& + Q_t(\Delta H_2 - W_{\text{orth san}}) + Q_{od}^2\frac{1}{4}(W_{\text{orth mic}}) \\
& + Q_t^2(W_{\text{orth san}}) + Q_{od}Q_t\frac{1}{2}(\Delta H_1 - \Delta H_2 - W_{\text{orth mic}}) \\
& + Q_{od}Q_t^2\frac{1}{2}(W_{\text{mic san}} - W_{\text{orth mic}} - W_{\text{orth san}}) \\
& + Q_{od}^2 Q_t\frac{1}{2}(W_{\text{orth mic}}) \\
& + Q_{od}^2 Q_t^2\frac{1}{4}(W_{\text{orth mic}}).
\end{aligned}
$$

Thus, the ordering enthalpy for potassium feldspar is equivalent (see also Thompson et al. 1974) to a series expansion to second order in the two order parameters (all bracketed terms above ≥0). Because Q_{od} monitors the monoclinic-triclinic phase transformation, and must go to zero at and above T_c, no terms linear in Q_{od} (field terms) are allowed in this expansion. This allows simplification and constrains some of the terms involved:

$$\Delta H_1 - \Delta H_2 - W_{\text{orth mic}} = 0$$

$$W_{\text{mic san}} - W_{\text{orth mic}} - W_{\text{orth san}} = 0$$

and

$$\Delta H_1 + W_{\text{orth san}} = \Delta H_2 + W_{\text{mic san}}. \qquad (18)$$

The experimental values for Q_t as a function of temperature in the monoclinic phase determined by Kroll and Knitter (1991) allow derivation of values for ΔH_2 and $W_{\text{orth san}}$. With these two parameters known, the two expressions above and the known disordering temperature (T_c) can be used to determine $W_{\text{mic san}}$, ΔH_1, and $W_{\text{orth mic}}$. The final values for the parameters are given in Figure 9, and the calculated site distributions are displayed in Figure 10, top. The model results suggest that the phase transition has a first-order step, in agreement with the conclusion of Carpenter and Salje (1994b).

Albite ($NaAlSi_3O_8$) behaves similarly to potassium feldspar, but the ordering processes operate entirely in the triclinic state because albite undergoes a triclinic → monoclinic displacive transition at much higher temperatures. Thus, all the equations developed above may be used to describe the t1-t2 ordering and the t1o-t1m ordering but with no symmetry constraints on the parameter values. However, there are calorimetric constraints on the total enthalpy of ordering, and the studies of Salje et al. (1985) and Goldsmith and Jenkins (1985) indicated a sharp decrease in Q_{od} at temperatures close to 900 K. A provisional set of parameters, which accounts for these observations and for the pressure-temperature location of the heterogeneous reaction jadeite + quartz = albite (see below), using the three end-members low albite (abl), t1-t2 ordered albite (abt), and high albite (abh) is as follows: $W_{\text{abl abh}} = 12.7$ kJ, $W_{\text{abt abh}} = 3.4$ kJ, and $W_{\text{abl abt}} = 8.3$ kJ, with $\Delta H_R = 13.5$ kJ and $\Delta V_R = 0.042$ kJ/kbar for abl = abh, and $\Delta H_R = 4.2$ kJ and $\Delta V_R = 0$ for abt = abh. The calculated site distributions are displayed in Figure 10, bottom, where the nonconvergent behavior in albite is compared with first-order behavior in potassium feldspar (Fig. 10, top). In comparison with the Landau theoretical treatment of Salje et al. (1985), this model differs in that the effects of the displacive transition in albite (which accounts for only a few percent of the energetics) have been ignored; however, the effects of the t1-t2 ordering ignored by Salje et al. (1985) have been included.

In many practical situations a single order-parameter treatment, involving only two end-members, may suffice in approximating the more complex coupled order-parameter model. For example, a single order-parameter treatment of both potassium feldspar and albite can represent the overall energetics reasonably closely. In both cases, the bulk of the disordering (t1o-t1m) is accomplished, in this simplified treatment, by the convergent behavior im-

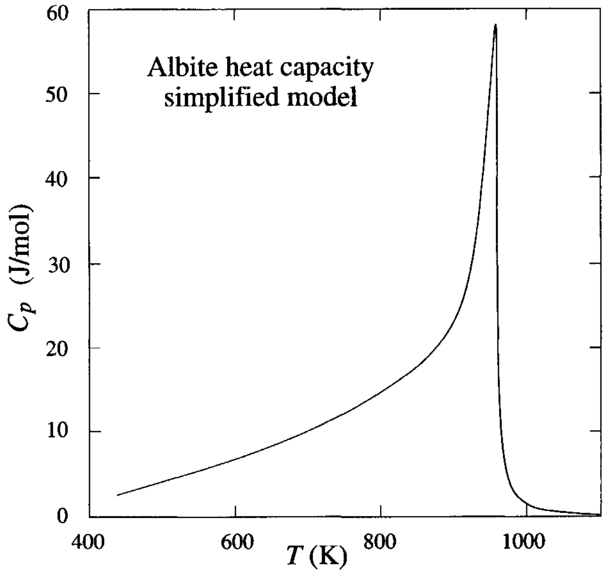

Figure 11. Heat capacity of albite in the simplified, symmetric formalism approximation. Note that the peak is rounded at the top [Q behavior as in Fig. 12, where $(\partial Q)/(\partial T)$ never becomes infinite].

parted by W, whereas the nonconvergent component (t1-t2) of the disordering is modeled by the field term ΔH_R. This simplified symmetric formalism for albite, using only one order parameter, predicts a heat capacity (Fig. 11) that is remarkably similar to that of the coupled order-parameter Landau model of Salje et al. (1985) and that is also in good agreement with the measured enthalpy of disorder and the temperature of transition of albite as tabulated in Salje et al. (1985). The variation of enthalpy (ΔH_R) and order parameter (Q) with temperature for this simple $n = 3$ albite model is illustrated in Figure 12. The superposition of a small nonconvergent field onto the convergent behavior of albite has the effect of smearing the phase transition and producing the rounded top of the heat-capacity spike.

In this simplified albite model, there are two end-members, low albite and high albite, in which Al is assumed to order onto just one of the four tetrahedral sites. For this model $\Delta H_R = 14.0$ kJ and $\Delta V_R = 0.042$ kJ/kbar for the reaction ordered albite = disordered albite and W (kJ) $= 13.6 + 0.042P$. Likewise, in the simplified potassium feldspar model, there are also only two end-members, microcline and sanidine, in which Al orders onto just the one tetrahedral site. For this model $\Delta H_R = 10.8$ kJ and $\Delta V_R = 0.010$ kJ/kbar for the reaction microcline = sanidine and $W = 10.6$ kJ. These values closely approximate the free energy of potassium feldspar ordering described by Carpenter and Salje (1994b).

DISCUSSION

Two principal objections to symmetric formalism might be raised, in comparison with the Landau approach.

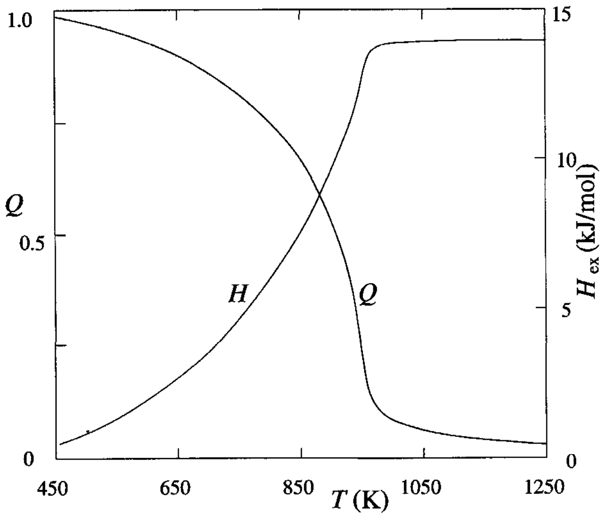

Figure 12. Variation of Q and enthalpy with temperature for the simplified (single-order parameter) albite model.

The first is that the enthalpy of ordering might, if more accurate calorimetric data were to become available in the future, require higher order terms in Q, and the second is that nonconfigurational entropy contributions cannot be properly taken into account. The first objection can be removed by relaxing the restriction of symmetric (regular-solution) interactions and allowing subregular or higher order Margules terms in the enthalpy of mixing. For example, if the ordered and disordered end-members mix according to a subregular solution, the enthalpy of ordering becomes cubic in Q,

$$H^{\text{ordering}}_{\text{subreg}} = Q(W_1 - \Delta H_R) + (W_2 - 2W_1)Q^2 + (W_1 - W_2)Q^3 \quad (19)$$

and higher order Margules mixing models can provide higher order terms in the enthalpy of ordering if needed. On the other hand, the higher order term in the Landau description may lead to questionable kinetic consequences at low temperatures (Kroll et al. 1994).

A response to the second objection requires provision of a nonconfigurational entropy in symmetric formalism to account for temperature-dependent lattice distortions and similar effects of displacive phase transformations. There are two simple ways of introducing such an entropy contribution: first, by making W a linear function of temperature such that $W = W_H - TW_S$; and second, by altering the entropy of the disordered end-member. The first method adds a temperature-dependent term linear in Q^2 to the free energy, as in the Landau model, whereas the second method adds a temperature dependence to the field term and corresponds to the approach of O'Neill and Navrotsky (1984). In this context, in dealing with cation ordering in which the entropy is likely to be dominated by configurational effects, it may be noted that the usual Landau expression may not be completely satisfactory. Kroll et al. (1994) addressed this point and suggested

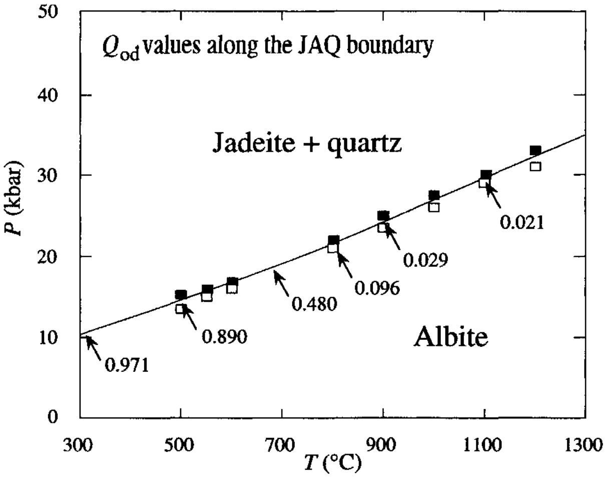

Figure 13. Calculated location of the jadeite + quartz = albite equilibrium, using an updated version of the thermodynamic data of Holland and Powell (1990) and the program Thermocalc. The curvature of the boundary is a consequence of the disordering of albite with temperature, with the values for the order parameter Q_{od} indicated. The experimental brackets are from Newton and Smith (1967) and Holland (1980).

adding the term $-T\Delta S_{config}$ to the Landau free-energy expansion. This has the advantage of allowing symmetric formalism to handle the configurational part of the entropy of ordering and the Landau entropy to handle the displacive and other nonconfigurational contributions to the total entropy.

Regardless of these concerns, and given the recognized ability of Landau theory to represent a range of order-disorder behavior, the flexibility of symmetric formalism is apparent in its simulation of the *Q*-*T* and free-energy behavior of the Landau tricritical and second-order models (Fig. 3). It is not surprising that nonconfigurational entropy is required for the Landau-type behavior to be reproduced closely over a large temperature range.

Calculations of heterogeneous equilibria, involving phases that undergo disordering, are particularly simple to perform with symmetric formalism and an internally consistent thermodynamic data set. All that is required are the thermodynamic data for each end-member of interest and the mixing properties of each solid solution (remembering that ordered and disordered end-members are treated as a solid solution). For example, the reaction of jadeite + quartz to albite in *P*-*T* space is considered. At an arbitrarily fixed temperature, *T*, three unknown parameters, the pressure (*P*) of the equilibrium boundary and the values for the two order parameters in albite (p_{abh} and p_{abl}) must be determined; these may be found from the following three equilibrium constraints:

$$\underset{\text{jadeite}}{NaAlSi_2O_6} + \underset{\text{quartz}}{SiO_2} = \underset{\text{abh}}{NaAlSi_3O_8} \tag{20}$$

$$\underset{\text{abl}}{NaAlSi_3O_8} = \underset{\text{abh}}{NaAlSi_3O_8} \tag{21}$$

and

$$\underset{\text{abt}}{NaAlSi_3O_8} = \underset{\text{abh}}{NaAlSi_3O_8} \tag{22}$$

where abl, abh, and abt refer to fully ordered low albite, fully disordered high albite, and a fictive t1-t2 ordered albite, respectively.

The equilibrium relation for each reaction may be written, using the activities and activity coefficients for the three albite end-members (the expressions for mic, orth, and san discussed earlier may be used directly for abl, abt, and abh albite, respectively) and the three nonlinear equations solved by numerical methods for the values for *P*, p_{abh}, and p_{abl}. The values for Q_t and Q_{od} can then be substituted if desired. The calculated *P*-*T* curve generated using the thermodynamic data of Holland and Powell (1990) is displayed in Figure 13, in which the curvature introduced by the progressive disordering is clearly visible.

In conclusion, symmetric formalism provides a simple and powerful way of handling the thermodynamics of cation-dominated order-disorder in minerals. As discussed in the companion paper (Holland and Powell 1996), such classical models are much easier than Landau models to extend to multicomponent solid solutions.

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APPENDIX 1

The purpose of this Appendix is to consider a thermodynamic treatment of an s order-parameter phase of fixed composition in terms of the mixing of its $1 + s$ end-members. Each end-member was chosen to have the stoichiometry of the phase. The Gibbs energy describing nonequilibrium as well as equilibrium states, known as the virtual Gibbs energy, G^*, is a function of the s order parameters, Q (Kroger et al. 1959; Powell 1983). The equilibrium state of the phase, Q_{equil}, can be found by solving

$$\left(\frac{\partial G^*}{\partial Q_k}\right)_{Q_{j(j\neq k)}} = 0 \qquad \text{for } k = 1, 2, \ldots, s. \tag{A1-1}$$

The Gibbs energy for the equilibrium state of the phase, G, is found by substituting Q_{equil} into the expression for G^*, so the $G = \{G^*\}_{Q=Q_{\text{equil}}}$. The equilibrium state may also be found from equilibrium relationships using the virtual chemical potentials of the end-members, denoted μ_k^*, formed from the virtual Gibbs energy, G^*:

$$\mu_k^* = \left(\frac{\partial nG^*}{\partial n_k}\right)_{n_{j(j\neq k)}} \tag{A1-2}$$

in which n_k is the number of moles of the end-member, k, in the phase, and G^* is taken to be a molar quantity so that in Equation A1-2 it is multiplied by n, with $n = \Sigma_{i=1}^{1+s} n_i$. From the form of Equation A1-2, these chemical potentials are defined identically to chemical potentials in phases without order parameters, so they can be formulated in any consistent way by, for example, symmetric formalism. Thus, the virtual chemical potentials can usually be written directly without recourse to Equation A1-2.

To use the virtual chemical potentials to generate equilibrium relationships, note that

$$G^* = \sum_{j=1}^{1+s} p_j \mu_j^* \tag{A1-3}$$

because the virtual Gibbs energy is a first-degree homogeneous function of the number of moles of the end-members. The proportion of j in the phase is given by $p_j = n_j/n$. Differentiating Equation A1-3 with respect to Q_k gives

$$\left(\frac{\partial G^*}{\partial Q_k}\right)_{Q_{j(j\neq k)}} = \sum_{j=1}^{1+s}\left(\frac{\partial p_j}{\partial Q_j}\right)_{Q_{l(l\neq j)}}\mu_j^* + \sum_{j=1}^{1+s} p_j\left(\frac{\partial \mu_j^*}{\partial Q_k}\right)_{Q_{l(l\neq j)}} = 0 \tag{A1-4}$$

for each Q_k. With the second sum identical to zero, the first sum for each Q_k is equivalent to an equilibrium relationship for a balanced reaction between the end-members. An independent set of reactions can always be chosen to have the form $\mu_k^* = \mu_s^*$ for $k = 1, 2, \ldots, s - 1$. In general, this equation is more convenient for formulating the equilibrium conditions than is the use of Equation A1-1 directly, particularly when the virtual chemical potentials are simple to formulate (as, for example, with symmetric formalism).

APPENDIX 2

Although the discussion in the text involved sillimanite, in which Al and Si mix on two sites in 1:1 proportion, in several other phases of interest, Al and Si mix in 1:n proportion across $n + 1$ sites. In this case the site distributions are as follows:

$$X_{\mathrm{Al}}^{\mathrm{t1}} = \frac{1 + nQ}{n + 1} \qquad X_{\mathrm{Si}}^{\mathrm{t1}} = \frac{n - nQ}{n + 1}$$
$$X_{\mathrm{Al}}^{\mathrm{t2}} = \frac{1 - Q}{n + 1} \qquad X_{\mathrm{Si}}^{\mathrm{t2}} = \frac{n + Q}{n + 1}. \tag{A2-1}$$

Ideal activities are then given by

$$a_{\mathrm{ordered}}^{\mathrm{ideal}} = \frac{1}{(n + 1)^{n+1}}(1 + nQ)(n + Q)^n$$
$$a_{\mathrm{disordered}}^{\mathrm{ideal}} = \frac{1}{n^n}(1 + nQ)^{1/(n+1)}(n - nQ)^{n/(n+1)} \cdot (1 - Q)^{n/(n+1)}(n + Q)^{n^2/(n+1)}. \tag{A2-2}$$

The activity coefficients are given by the regular-solution expressions for the macroscopic mixing of ordered and disordered end-members,

$$\mathrm{R}T \ln \gamma_{\mathrm{ordered}} = W(1 - Q)^2$$
$$\mathrm{R}T \ln \gamma_{\mathrm{disordered}} = WQ^2 \tag{A2-3}$$

and the equilibrium condition by

$$0 = \Delta H_{\mathrm{R}} + \frac{n}{n + 1}\mathrm{R}T \ln\frac{(n - nQ)(1 - Q)}{(1 + nQ)(n + Q)} + (2Q - 1)W. \tag{A2-4}$$

The critical temperature is found by solving this expression for T in the limit as $Q \rightarrow 0$:

$$T_c = \frac{2W}{\mathrm{R}(1 + n)}. \tag{A2-5}$$

The relationship between symmetric formalism W and the classical Bragg-Williams energy W_{bw}, for ease of comparison with values derived in the literature, is $W = \{(nW_{\mathrm{bw}})/[2(n + 1)]\}$, so that the critical temperature, using the classical Bragg-Williams energy, is $T_c = \{(nW_{\mathrm{bw}})/[\mathrm{R}(1 + n)^2]\}$.

If the total number of sites is a multiple of $n + 1$ [as in anorthite, where with $n = 1$ there are $2(n + 1)$ tetrahedra], then the energies require scaling by that multiple and the ideal activities require raising to the power of that multiple.