

Thermodynamics of nonconvergent cation ordering in minerals: III. Order parameter coupling in potassium feldspar

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ABSTRACT

The thermodynamic consequences of Al-Si ordering in potassium feldspar under equilibrium conditions have been described quantitatively using a Landau free energy expansion in two order parameters. The first order parameter, Q_t , relates to nonconvergent ordering between T1 and T2 sites and the second, Q_{od} , relates to the symmetry-breaking ordering between T1o and T1m sites. Strong interactions occur between the two order parameters, as described by a term in $\lambda Q_t Q_{od}^2$, and the form of the resulting expansion is

$$G = -hQ_t + \frac{1}{2}a_t(T - T_{ct})Q_t^2 + \frac{1}{6}c_tQ_t^6 \\ + \frac{1}{2}a_{od}(T - T_{cod})Q_{od}^2 + \frac{1}{6}c_{od}Q_{od}^6 + \lambda Q_t Q_{od}^2.$$

The coupling coefficient, λ , was assumed to be temperature dependent, as $\lambda = -20.13T$, and a favored set of values for the coefficients is $h = 1650$ J/mol, $a_t = 22.28$ J/mol·K, $T_{ct} = 586$ K, $c_t = 14700$ J/mol, $a_{od} = 41.09$ J/mol·K, $T_{cod} = 239$ K, and $c_{od} = 9818$ J/mol. The monoclinic = triclinic transition temperature was assumed to be 753 K.

Equilibrium variations of Q_t and Q_{od} calculated from the expansion give small changes in energy associated with Q_t ordering in the stability field of monoclinic crystals. The monoclinic = triclinic transition is first order, with a jump in Q_{od} from 0 to 0.94, a jump in Q_t from 0.40 to 0.95, a latent heat of 7.2 kJ/mol, and a latent entropy of 9.5 J/mol·K. Below the transition, relatively large energy changes accompany Q_t and Q_{od} ordering. Coupling between Q_t and Q_{od} appears to outweigh coupling between Q_{od} and the triclinic strain in crystals with the modulated orthoclase structure, with the result that both Q_t and Q_{od} may be close to being homogeneous in orthoclase and adularia.

INTRODUCTION

In the first and second papers of this series (Carpenter et al., 1994; Carpenter and Salje, 1994), the use of a Landau free energy expansion to describe nonconvergent cation ordering in minerals was introduced. To show that the approach is perfectly general, the analysis of a system with two order parameters, one convergent and the other nonconvergent, is now presented. In principle the treatment of order parameter coupling that involves a component of nonconvergent ordering should be the same as for any normal phase transition with coupled order parameters; only details of which terms in the free energy expansion are allowed by symmetry may differ. Potassium feldspar is also of interest as an important geological material, and the nature of the sanidine = microcline transition has been the subject of considerable speculation and debate. The two ordering processes involved are the nonconvergent partitioning of Al and Si between T1 and T2 sites and the convergent partitioning between T1o and T1m associated with a symmetry change $C2/m = C\bar{1}$.

The literature on alkali feldspars is extensive, and readers are referred to the reviews of Ribbe (1983a, 1983b, 1984), Kroll and Ribbe (1983), Yund and Tullis (1983), Smith and Brown (1988), and Brown and Parsons (1989) for a comprehensive survey. However, almost the only attempt to model the complete ordering behavior of potassium feldspar appears to be that of Thompson and coworkers (Thompson, 1969, 1970; Thompson et al., 1974), in their pioneering use of series expansions to describe thermodynamic changes in minerals. Part of the problem has been that there are few reliable data relating to equilibrium in a critical temperature range below ~800 K. In this range, the thermodynamic behavior has to be reconstructed indirectly from measurements at higher temperatures and observations of natural samples. On the experimental side, high-quality calorimetric data are available for natural and heat-treated samples, though the enthalpy variations appear to correlate only with the nonconvergent order and show no deviations that might obviously be ascribed to the phase transition (Waldbaum and Robie, 1971; Hovis, 1974, 1988). Direct ordering

and disordering experiments have been successful in bracketing the equilibrium degree of nonconvergent order at high temperatures but not so successful at low temperatures (summarized in Fig. 3 of Brown and Parsons, 1989).

Evidence from natural specimens for the evolution of equilibrium ordering states at low temperatures comes in two forms. On the scale of a metamorphic terrain, it has been possible to estimate the equilibrium transition temperature by characterizing the structural states of individual feldspar crystals as a function of paleotemperature. A transition temperature of approximately 450–500 °C seems to be accepted (Bernotat and Bambauer, 1982; Bambauer and Bernotat, 1982; Bambauer et al., 1984; Kroll, 1991; Kroll et al., 1991). On an electron optical scale, interpretations of possible equilibrium states below this temperature have been clouded by the development of complex microstructures. The monoclinic modulated orthoclase structure is believed to be metastable with respect to triclinic microcline, while intermediate (triclinic) microclines seem to be composed of orthoclase + microcline intergrowths (Eggleton and Buseck, 1980; Fitz Gerald and McLaren, 1982; McLaren, 1984; Krause et al., 1986; Kroll et al., 1991; and see discussion by Brown and Parsons, 1989; Kroll et al., 1991). On the other hand, there seems to be no doubt that microcline with well-developed transformation twinning tends to show a degree of order that is in excess of ~95% (Bambauer and Bernotat, 1982; Bernotat and Morteani, 1982; Kroll and Ribbe, 1983, 1987; Ribbe, 1984). With regard to the nature of the monoclinic = triclinic phase transition, it remains possible to choose between two hypotheses. For example, Kroll and Voll (in Ribbe, 1983a), Kroll (1991), and Kroll et al. (1991) favored a first-order transition with a significant jump in the equilibrium degree of order, whereas Brown and Parsons (1989) concluded that the assembled evidence is more consistent with a continuous transition.

Rather than interpreting the available data for potassium feldspar in isolation, an alternative strategy for predicting the possible behavior might be to compare it with the more fully documented behavior of albite. This is only partially informative, however, because the driving mechanism for the $C2/m = C\bar{1}$ transition in albite is different, and triclinic states remain stable up to ~980 °C. The purely displacive part of the transition in albite has an equilibrium transition temperature that reduces steeply with increasing substitution of K for Na (Kroll et al., 1980). The pure order-disorder part has a lower transition temperature, but that appears to change only slightly with increasing K content. The transition lines must cross at some intermediate composition (e.g., see Fig. 6 of Brown and Parsons, 1989, or Fig. 9 of Carpenter, 1988). The result is, firstly, that the sequence of ordering and displacive driving forces is reversed between the endmembers, and, secondly, that the role of nonconvergent ordering in potassium feldspar assumes a significance over a much wider temperature interval than it does in sodium

feldspar. Furthermore, although at least two order parameters are needed to describe the thermodynamic behavior of albite and potassium feldspar, the significant ones turn out to be different in each case. Symmetry-breaking (convergent) Al-Si ordering is common to both. In albite the second is the symmetry-breaking displacive order parameter. As will be argued here, for potassium feldspar the important second effect appears to relate to nonconvergent ordering between the T1 and T2 sites, and not, as was suggested by Carpenter (1988), to the displacive effects.

The paper is divided into five sections. The background to an appropriate Landau free energy expansion is first outlined briefly. An analysis of the spontaneous strains accompanying ordering then follows. In a sense this merely formalizes the well-known dependence of lattice parameters on structural states (cf. Kroll and Ribbe, 1983, 1987; Ribbe, 1984; Hovis, 1986), but it is needed to demonstrate both that the Landau approach can be valid and that a common-strain mechanism for the coupling is unlikely. Values for the Landau coefficients are then extracted from the available experimental data, and a number of different solutions are explored to establish the uniqueness, or otherwise, of each possible set of coefficients. Finally, the implications of the model solutions for both the equilibrium phase relations and the structural state of modulated crystals are discussed. Throughout, the emphasis is on an initial need to justify the Landau approach, followed by the more specific need to produce a thermodynamic model that accounts explicitly and quantitatively for the equilibrium states of potassium feldspar. The mechanisms of structural evolution under nonequilibrium conditions are not considered.

LANDAU THEORY

Two independent order parameters are used here to describe the extent of Al-Si ordering in potassium feldspar. Q_i describes the nonconvergent ordering of Al and Si between T1 and T2 sites as

$$Q_i = \frac{X_{Al}^{T1} - X_{Al}^{T2}}{X_{Al}^{T1} + X_{Al}^{T2}} \quad (1)$$

where X_{Al}^{T1} is the fractional occupancy of the T1 site by Al, etc. Q_i corresponds exactly to the Z order parameter of Thompson (1969) and many subsequent workers. Given that $X_{Al}^{T1} + X_{Al}^{T2} = 0.5$, Q_i may be written in a simplified form (Harris et al., 1989; Kroll and Knitter, 1991; Salje and Kroll, 1991) as

$$Q_i = 4X_{Al}^{T1} - 1. \quad (2)$$

Q_{od} describes the symmetry-breaking ordering ($C2/m = C\bar{1}$) between T1o and T1m sites as

$$Q_{od} = \frac{X_{Al}^{T1o} - X_{Al}^{T1m}}{X_{Al}^{T1o} + X_{Al}^{T1m}}. \quad (3)$$

This form was introduced by Salje (1985) and is scaled

slightly differently from the Y parameter of Thompson (1969).

Following the approach set out in the first and second papers of this series (Carpenter et al., 1994, and Carpenter and Salje, 1994), the nonconvergent ordering is described by a Landau free energy expansion of the form

$$G = -hQ_t + \frac{1}{2}a_t(T - T_{ct})Q_t^2 + \frac{1}{4}b_tQ_t^4 + \frac{1}{6}c_tQ_t^6 \quad (4)$$

The linear term accounts for an energetic difference due to locating Al on T1 sites and Al on T2 sites that remains at all temperatures, and the h coefficient is thus an effective field, ensuring that the fully disordered state ($Q_t = 0$) does not have an equilibrium field of stability. Higher odd-order terms in Q_t are allowed by symmetry, since the ordering is nonconvergent, but these are assumed to be small. The remaining coefficients are typical of standard Landau free energy expansions, with the subscript t used to associate them with Q_t . As will be seen, there are insufficient experimental data to justify the inclusion of both fourth-order and sixth-order terms in the expansion. Trial values for the coefficients were therefore obtained with only Q_t^4 as the high-order term or with only Q_t^6 as the high-order term.

Q_{od} describes the monoclinic = triclinic transition, and, by symmetry, odd-order terms in the free energy expansion must be strictly zero. Again, there are insufficient experimental data to warrant an expansion with more than one high-order term. Given the apparent tendency for order-disorder processes in minerals to have small fourth-order terms (e.g., CO_3 orientational ordering in calcite: Redfern et al., 1989; cation ordering in omphacite: Carpenter et al., 1990), the expansion chosen to describe the contribution of Q_{od} alone has the form for tricritical phase transitions:

$$G = \frac{1}{2}a_{od}(T - T_{cod})Q_{od}^2 + \frac{1}{6}c_{od}Q_{od}^6 \quad (5)$$

The subscript od is used here to associate the coefficients with Q_{od} .

Although Q_t and Q_{od} are by definition independent order parameters in a geometric sense, they are expected to interact. In other words, a change in T1 and T2 ordering may induce a change in the degree of T1o and T1m ordering, and the energy changes due to such interactions may be accounted for by a coupling term in the free energy expansion. The lowest order term allowed by symmetry is linear in Q_t and quadratic in Q_{od} . For a complete description of the thermodynamics of ordering, the excess free energy (with respect to complete disorder, $Q_t = Q_{od} = 0$) is then given by

$$G = -hQ_t + \frac{1}{2}a_t(T - T_{ct})Q_t^2 + \frac{1}{4}b_tQ_t^4 \text{ (or } \frac{1}{6}c_tQ_t^6) \\ + \frac{1}{2}a_{od}(T - T_{cod})Q_{od}^2 + \frac{1}{6}c_{od}Q_{od}^6 + \lambda Q_t Q_{od}^2 \quad (6)$$

The coefficient λ defines the strength of the linear-quadratic coupling.

Conditions for equilibrium derived from Equation 6 are

$$\frac{\partial G}{\partial Q_t} = 0 = -h + a_t(T - T_{ct})Q_t \\ + b_tQ_t^3 \text{ (or } c_tQ_t^5) + \lambda Q_{od}^2 \quad (7)$$

and

$$\frac{\partial G}{\partial Q_{od}} = 0 = a_{od}(T - T_{cod}) + c_{od}Q_{od}^4 \\ + 2\lambda Q_t \text{ (for } |Q_{od}| > 0). \quad (8)$$

Excess enthalpies and entropies, again with respect to the fully disordered state, are given by

$$H = -hQ_t - \frac{1}{2}a_tT_{ct}Q_t^2 + \frac{1}{4}b_tQ_t^4 \text{ (or } \frac{1}{6}c_tQ_t^6) \\ - \frac{1}{2}a_{od}T_{cod}Q_{od}^2 + \frac{1}{6}c_{od}Q_{od}^6 + \lambda Q_t Q_{od}^2 \quad (9)$$

and

$$S = -\frac{1}{2}(a_tQ_t^2 + a_{od}Q_{od}^2). \quad (10)$$

Many of the background formalities to order parameter coupling have been summarized by Salje and Devarajan (1986), Carpenter (1988, 1992), and Salje (1990), and a more complete free energy expansion, including strain and gradient effects, has been given by Harris et al. (1989). In the present approach, the role of a displacive order parameter has been assumed to be small because the extrapolated transition temperature for a purely displacive transition in potassium feldspar would be well below 0 K (Thompson et al., 1974; Thompson and Hovis, 1979; Carpenter, 1988).

STRAIN ANALYSIS

As discussed in the first paper (Carpenter et al., 1994), the development of a spontaneous strain accompanying cation ordering processes has two immediate implications. Firstly, the strain provides an indirect measure of the macroscopic order parameter and may be used to characterize the structural states of experimental samples. Secondly, strain-order parameter coupling that leads to strains in excess of ~ 0.001 acts to promote classical Landau-type thermodynamic behavior (Cowley, 1976; Folk et al., 1976, 1979; Als-Nielsen and Birgeneau, 1977; Salje et al., 1987; Carpenter and Salje, 1989; Salje, 1990, 1992; Carpenter, 1992). In the case of Al-Si ordering in potassium feldspar, a third implication of the spontaneous strain relates to the possibility that coupling between the two order parameters Q_t and Q_{od} could occur by means of strains that are common to both.

For a monoclinic crystal, a suitable Cartesian coordinate system for describing the spontaneous strains has axes X , Y , and Z such that Y is parallel to the crystallographic b axis, X is parallel to the crystallographic a axis, and Z is perpendicular to both and is thus parallel to the c^* axis of the reciprocal lattice. The general equations of Schlenker et al. (1978) and Redfern and Salje (1987) may then be used to define the components e_1 – e_6 (in Voigt notation) of the strain tensor. The appropriate expres-

TABLE 1. Definitions of components of the spontaneous strain tensor for nonconvergent (monoclinic \rightarrow monoclinic) and convergent (monoclinic \rightarrow triclinic) processes in potassium feldspar

Monoclinic \rightarrow monoclinic	Monoclinic \rightarrow triclinic
$e_1 = e_{11} = \frac{a}{a_0} - 1$	$e_1 = \frac{a}{a_0} \sin \gamma - 1$
$e_2 = e_{22} = \frac{b}{b_0} - 1$	$e_2 = \frac{b}{b_0} - 1$
$e_3 = e_{33} = \frac{c \sin \beta}{c_0 \sin \beta_0} - 1$	$e_3 = \frac{c \sin \alpha \sin \beta^*}{c_0 \sin \beta_0^*} - 1$
$e_4 = 2e_{23} = 0$	$e_4 = \frac{c \cos \alpha}{c_0 \sin \beta_0^*} + \frac{a \cos \beta_0^* \cos \gamma}{a_0 \sin \beta_0^*}$
$e_5 = 2e_{13} = \frac{c \cos \beta}{c_0 \sin \beta_0} - \frac{a \cos \beta_0}{a_0 \sin \beta_0}$	$e_5 = \frac{a \sin \gamma \cos \beta_0^*}{a_0 \sin \beta_0^*} - \frac{c \sin \alpha \cos \beta^*}{c_0 \sin \beta_0^*}$
$e_6 = 2e_{12} = 0$	$e_6 = \frac{a}{a_0} \cos \gamma$

Note: these equations are derived from the general equations of Schlenker et al. (1978); a_0 , b_0 , c_0 , etc., are the lattice parameters of the reference state for the strain calculations.

* Reciprocal lattice dimensions.

sions for monoclinic \rightarrow monoclinic strains (i.e., relating to Q_1) and for monoclinic \rightarrow triclinic strains (i.e., relating to Q_{od}) are given in Table 1. Strictly speaking, the lattice parameters, a , b , c , α , β , and γ , should be measured at the temperature at which the crystals equilibrated, and the reference parameters, a_0 , b_0 , c_0 , α_0 , β_0 , and γ_0 , should be extrapolated to the same temperature from the stability field of the reference structure. In practice, variations in lattice parameters at room temperature in crystals with different states of order, as preserved during rapid cooling, appear to conform to the expected behavior of the more rigorously defined strains.

In both monoclinic and triclinic potassium feldspar crystals the values of the lattice parameter a and the lattice angle β change very little with changing Al-Si order. The a parameter is sensitive to compositional variations, however. Both b and c vary significantly with the degree of order, and it is well known that their variation is close to being linear with respect to Q_1 (Fig. 1, data from Kroll and Ribbe, 1983, and Kroll and Knitter, 1991; see also Fig. 1a of Kroll and Ribbe, 1987, and Fig. 11 of Hovis, 1986). Values of the reference state parameters, $b_0 = 13.043 \text{ \AA}$ and $c_0 = 7.172 \text{ \AA}$, have been obtained from a linear least-squares fit to the data for monoclinic crystals in Figure 1, and a value of $\beta_0 = 115.98^\circ$ has been determined by similar linear extrapolation of data from the same crystals (in Table 2 of Kroll and Ribbe, 1983, and Table 3 of Kroll and Knitter, 1991). Because of its sensitivity to composition and insensitivity to Al-Si order, the reference parameter a_0 is most conveniently taken as the value of a for each crystal of interest; this reduces any contributions to the strain from compositional effects alone. Values of $a_0 = 8.543 \text{ \AA}$ and $a_0 = 8.573 \text{ \AA}$, respectively, were used in relation to strains determined from the data of Kroll and Knitter (1991) and Blasi et al. (1984),

and $a_0 = a$ was used for calculations based on the data of Kroll and Ribbe (1983). Finally, since the reference state is monoclinic, α_0 and γ_0 are both 90° . Room-temperature strains have been calculated with respect to these reference parameters for monoclinic crystals (sanidine, orthoclase, and adularia, in Kroll and Ribbe, 1983; Kroll and Knitter, 1991), and for a range of triclinic crystals produced by progressively disordering natural microcline (in Blasi et al., 1984).

In monoclinic crystals, e_4 and e_6 are strictly zero. Both b and c vary linearly with Q_1 . For $\beta \approx \beta_0$, e_2 and e_3 must therefore also be linear functions of Q_1 , as expected for the general strain-order parameter dependence in nonconvergent systems (Carpenter et al., 1994). The component e_5 simplifies to approximately $-0.5e_3$ for $\beta \approx \beta_0 \approx 116^\circ$ and $a/a_0 \approx 1$. The value of e_1 is expected to be small but is zero if a_0 is set as the value of a for each crystal to exclude strains of compositional origin.

In triclinic crystals, the strain components e_4 and e_6 are symmetry breaking and are expected to vary linearly with the symmetry-breaking order parameter, Q_{od} (with the usual assumption that higher order strain coupling terms are small relative to the linear coupling term). The component e_6 can be used as a measure of Q_{od} , therefore, and e_4 is expected to be a linear function of e_6 with a common origin of zero (Fig. 2). Again with the normal assumption of high-order coupling terms being small, the nonsymmetry-breaking components would be expected to vary as $e_i \propto Q_{od}^2$ (Salje, 1990); however, e_2 , e_3 , and e_5 appear to vary linearly with e_6 (Fig. 2), i.e., as $e_i \propto Q_{od}$. The component e_1 remains small because of the limited variation of the a parameter, and values of b and c for triclinic crystals lie on or close to the extrapolated trends of the values for monoclinic crystals (Fig. 2). The only internally consistent conclusions that can be drawn from these strain

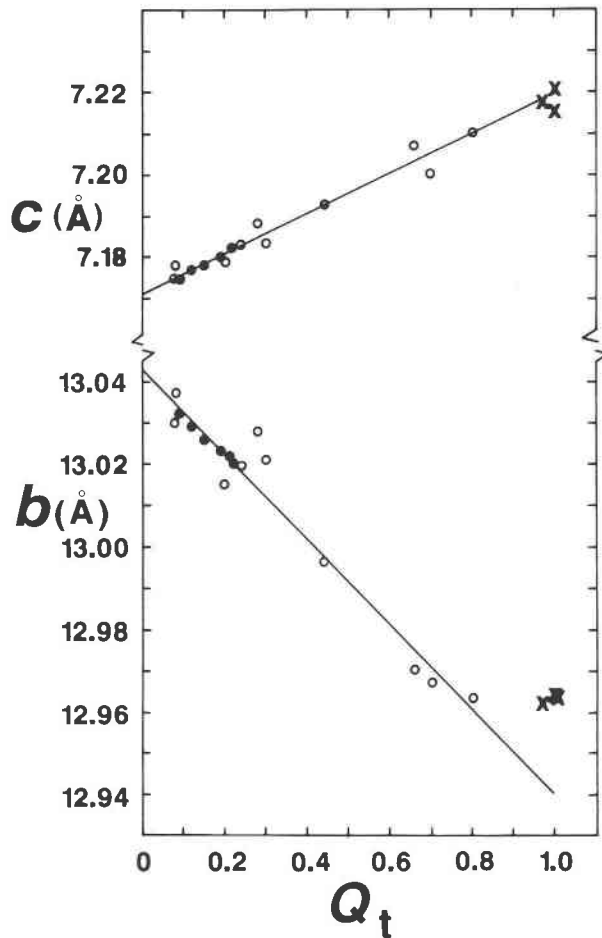


Fig. 1. Variation of b and c lattice parameters as a function of Q_t for monoclinic crystals (circles) and triclinic crystals (Xs). Data from Kroll and Ribbe (1983), open circles, and Kroll and Knitter (1991), solid circles. Extrapolation of the linear least-squares fit to the data for monoclinic crystals gives values of $b_0 = 13.043$ Å and $c_0 = 7.172$ Å for crystals with $Q_t = 0$ at room temperature. The slight divergence of b for triclinic crystals from the monoclinic trend suggests that Q_{od} ordering may have a small influence on the e_2 strain component.

relations are, firstly, that e_2 , e_3 , and e_5 arise almost exclusively from coupling with Q_t , secondly, that e_4 and e_6 are not affected significantly by coupling with Q_t in triclinic crystals, and, thirdly, that when Q_{od} has nonzero values it varies approximately linearly with Q_t in these samples. Note that e_2 , e_3 , and e_5 do not extrapolate to the origin in Figure 2 because Q_t does not go to zero at $Q_{od} = 0$.

Since e_2 , e_3 , and e_5 appear to couple predominantly with Q_t and e_4 and e_6 couple with Q_{od} , the principal strains associated with each order parameter can be analyzed separately. Strain matrices containing only e_1 , e_2 , e_3 , and e_5 , or only e_4 and e_6 , have been diagonalized to give the magnitudes and orientations of the principal strain components ϵ_1 , ϵ_2 , and ϵ_3 for microcline. From the Q_t strain matrix, the principal strain values are $\epsilon_{1,Q_t} = 0.007$, $\epsilon_{2,Q_t} = -0.006$, and $\epsilon_{3,Q_t} = -0.001$; from the Q_{od} strain matrix

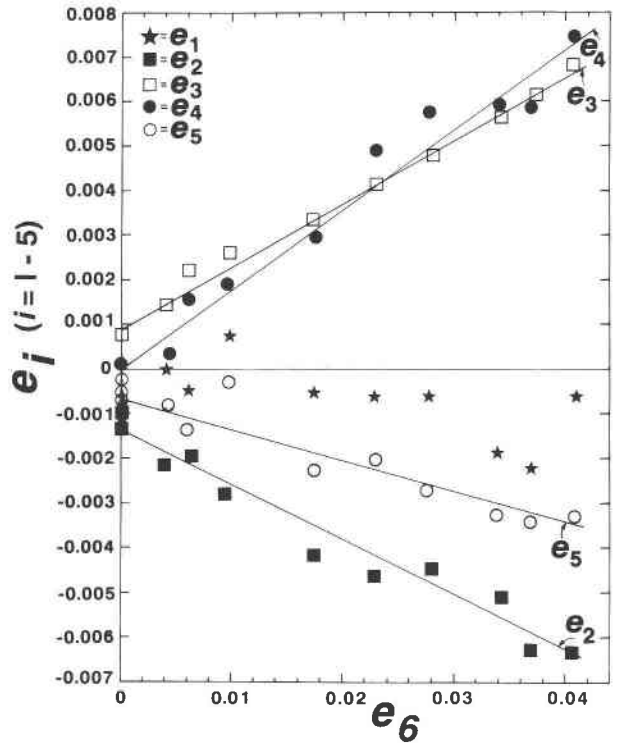


Fig. 2. Variations of the strain components e_1 , e_2 , e_3 , e_4 , and e_5 as a function of e_6 for triclinic crystals with a range of degrees of order produced by progressive disordering of microcline at 1050 °C (obtained using the lattice parameter data of Blasi et al., 1984). Straight lines are drawn in as guides for the eye for e_2 , e_3 , e_4 , and e_5 ; e_4 is expected to be proportional to e_6 , since both couple linearly with Q_{od} , but e_2 , e_3 , and e_5 only vary linearly with e_6 if they arise by linear coupling with Q_t and if Q_t , in turn, varies linearly with Q_{od} (for $Q_{od} > 0$). Note that e_4 goes through zero at $e_6 = 0$, which is consistent with this interpretation, and that e_2 , e_3 , and e_5 remain finite at $e_6 = 0$ because Q_t remains finite at $Q_{od} = 0$.

the values are $\epsilon_{1,Q_{od}} = 0.021$, $\epsilon_{2,Q_{od}} = 0$, and $\epsilon_{3,Q_{od}} = -0.021$ (with the microcline lattice parameters of Blasi et al., 1984). The relative orientations of the principal strains are shown in Figure 3. The largest Q_t strains coincide with zero values of the Q_{od} strains, and, although there is a small common strain in a plane that nearly includes $\epsilon_{1,Q_{od}}$, ϵ_{2,Q_t} , $\epsilon_{3,Q_{od}}$, and ϵ_{3,Q_t} , the orientation relationship is such that the total overlap is minimized. Calculations of the strain ellipsoids for the intermediate structural states of Blasi et al. (1984) show that this orientation relationship does not change significantly as a function either of Q_t or of Q_{od} .

Relative magnitudes of the total strains accompanying the two types of Al-Si ordering can be given in terms of a scalar strain, ϵ_s , which, following Redfern and Salje (1987), is given by

$$\epsilon_s = \sqrt{\sum_{i=1-3} \epsilon_i^2} \quad (11)$$

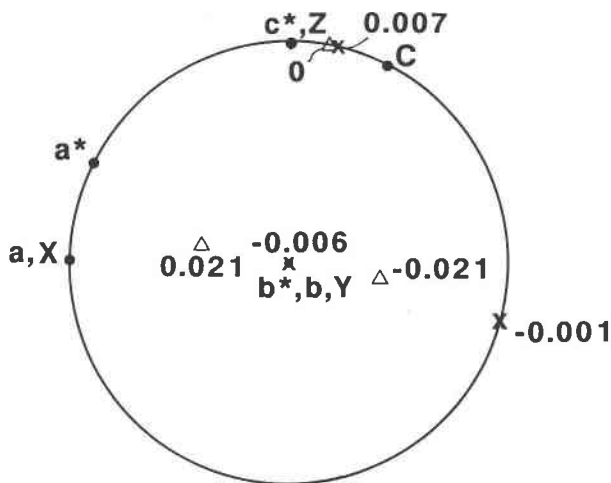


Fig. 3. Orientation of the principal spontaneous strains in microcline at room temperature, with respect to crystallographic axes *a*, *b*, and *c* and reciprocal lattice axes *a**, *b**, and *c** of sanidine, as calculated by diagonalizing matrices with only ϵ_4 and $\epsilon_6 \neq 0$ (Q_{od} ordering, open triangles), and with only ϵ_1 , ϵ_2 , ϵ_3 , and $\epsilon_5 \neq 0$ (Q_t ordering, Xs). Numbers by each point indicate the size of the principal strain in that direction. Note that the largest principal strain due to Q_t ordering coincides with a point of zero strain due to Q_{od} ordering. The next largest Q_t principal strain also coincides with a zero value for the Q_{od} strain, and there is almost no overlap between the Q_t and Q_{od} strains. X, Y, and Z denote Cartesian reference axes for the strain calculations.

This gives $\epsilon_{s,Q_t} = 0.010$ and $\epsilon_{s,Q_{od}} = 0.029$ for the Blasi et al. microcline. In each case the volume strains, defined as

$$V_s = \frac{V - V_0}{V_0} \approx \sum_{i=1-3} \epsilon_i \quad (12)$$

are close to zero. In other words, the spontaneous strains are close to being purely shear deformations.

In summary, both Q_t and Q_{od} couple with macroscopic strains to a significant extent. This would be expected to promote Landau-like thermodynamic behavior, as discussed earlier. There is very limited overlap between these two strains, however, to the extent that they appear to be mutually exclusive in orientation. The strain components of both sets of strains conform closely to the relation $Q \propto \epsilon_i$ expected both for nonconvergent ordering and for convergent ordering when ϵ_i has the same symmetry as Q . The observation that the strain components associated with each order parameter vary linearly with each other also implies that Q_{od} varies approximately linearly with Q_t in triclinic crystals. Finally, the scalar strain, ϵ_{s,Q_t} , may provide a useful parameter for calibrating the degree of order of crystals for which only lattice parameters are known. It includes changes in the parameters *b*, *c*, and β , and so depends to a lesser extent than in some calibrations on individual lattice parameter variations. Figure 4 shows a possible calibration using strains calculated from the data of Kroll and Ribbe (1983) and Kroll and Knitter (1991). A linear least-squares fit to the data for mono-

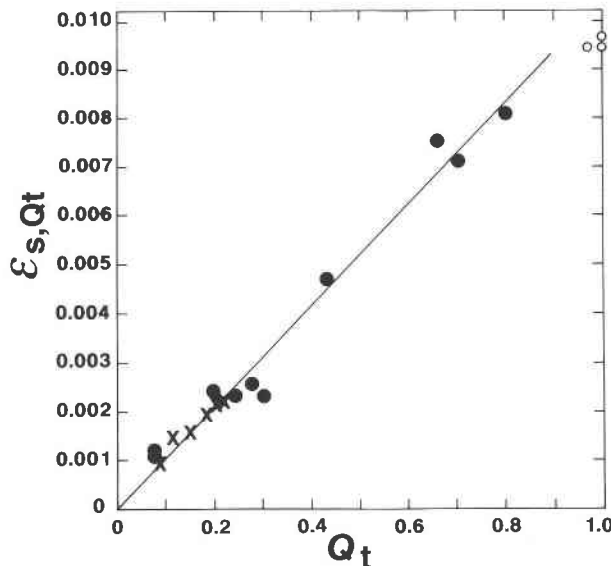


Fig. 4. Variation of the scalar strain, ϵ_{s,Q_t} , associated with Q_t ordering. Solid circles (monoclinic crystals) and open circles (triclinic crystals) determined from lattice parameters and Q_t data of Kroll and Ribbe (1983). For each sample the reference value of a_0 was taken as the value of *a* for the crystal. For triclinic crystals ϵ_{s,Q_t} was calculated from the strain components ϵ_1 , ϵ_2 , ϵ_3 , and ϵ_5 alone. Xs are from data of Kroll and Knitter (1991) with $a_0 = 8.543 \text{ \AA}$. The straight line is a least-squares fit to the data, giving the calibration $Q_t = 96.00\epsilon_{s,Q_t}$. Values of ϵ_{s,Q_t} for triclinic crystals fall just below the extrapolation of this line because there is a small ϵ_2 strain associated with Q_{od} .

clinic crystals is

$$Q_t = 96.00\epsilon_{s,Q_t}. \quad (13)$$

CALIBRATION OF THE LANDAU EXPANSION

Nonconvergent ordering: Q_t

For crystals with $Q_{od} = 0$, the equilibrium condition represented by Equation 7 simplifies to

$$0 = -1 + \frac{a_i}{h}(T - T_{ci})Q_t + \frac{b_i}{h}Q_t^3 \left(\text{or } \frac{c_i}{h}Q_t^5 \right). \quad (14)$$

Values of the ratios a_i/h , b_i/h (or c_i/h) and the critical temperature, T_{ci} , can be determined if the equilibrium variation of Q_t with temperature is known. The most recent data for homogeneous sanidine crystals equilibrated at high temperatures are those of Kroll and Knitter (1991) and Salje and Kroll (1991). Their four values, $Q_t = 0.240$ at 923 K, 0.180 at 1023 K, 0.135 at 1123 K, and 0.092 at 1323 K, together with the assumption that Q_t would equal unity at 0 K in the absence of any T1o/T1m ordering, have been used to constrain values for these coefficient ratios. A further constraint is provided by available data suggesting that Q_t has a value between ~ 0.30 and 0.44 at the equilibrium monoclinic = triclinic transition temperature. These limits correspond to the values of Q_t for the most ordered natural crystals without ortho-

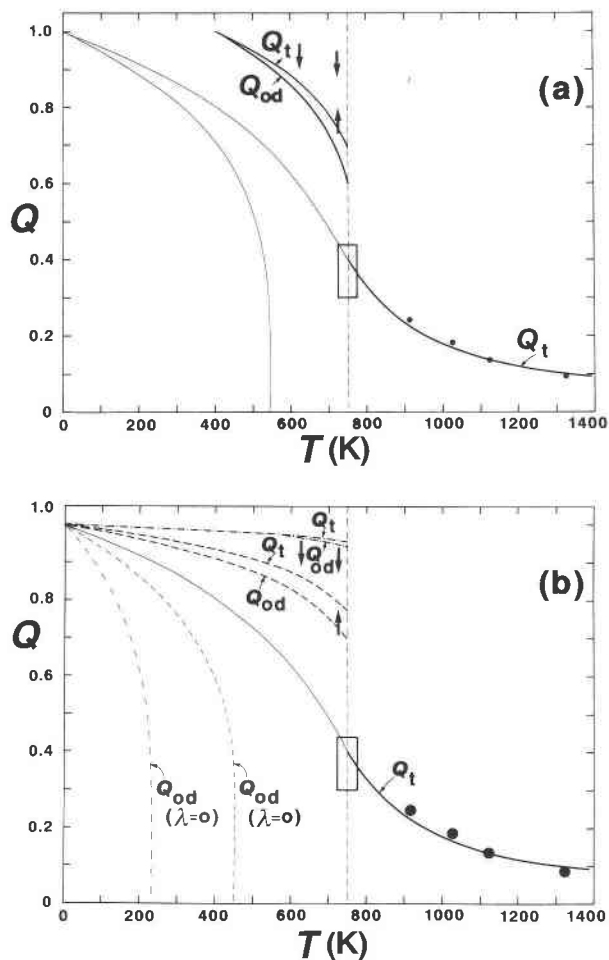


Fig. 5. Calculated variations of Q_{od} and Q_t . Solid circles represent data points of Kroll and Knitter (1991); the box signifies uncertainties for the equilibrium transition temperature, T_{cod}^* , and for the value of Q_t at $T = T_{cod}^*$. (a) Equilibrium variations (heavy lines) for a model with $\lambda = \text{constant}$ and $Q_t = Q_{od} = 1$ at 400 K. Light lines indicate the hypothetical variation of Q_t and Q_{od} in the absence of coupling. Arrows indicate possible limiting values of Q_t from results of Senderov and Yas'kin (1975, 1976). (b) Equilibrium variations (heavy lines) for models with $\lambda = a_i T$ and either $Q_t = Q_{od} = 0.98$ at 450 K (dot-dash line), or $Q_t \approx 0.80$, $Q_{od} \approx 0.75$ at 700 K (broken line). Light lines indicate hypothetical variations of Q_t and Q_{od} in the absence of coupling.

class modulations and the most disordered natural crystals with modulations, as generally observed (Kroll and Ribbe, 1983; and see the discussion in Brown and Parsons, 1989). The most ordered but unmodulated monoclinic crystals produced experimentally have $Q_t \approx 0.42$ (Brown and Parsons, 1989). For the calculations presented in this paper, the maximum equilibrium value of Q_t in monoclinic sanidine is assumed to develop at an equilibrium temperature of 753 ± 20 K, the most recent estimate of the $C2/m = C\bar{1}$ transition temperature (Kroll et al., 1991).

Values for the coefficient ratios were found by applying

a linear least-squares fitting program (kindly provided by T.J.B. Holland) to a set of six linear equations, represented by Equation 14 with each of the four experimental values of Q_t and T inserted, plus $Q_t = 1$ at 0 K and $Q_t \approx 0.40$ at 753 K. This was repeated with either Q_t^3 or Q_t^5 as the high-order term, and, although somewhat different numerical results were obtained, the variations of Q_t with temperature that they generate are not significantly different. Subsequent calculations using Q_t^3 and Q_t^5 as the high-order term in Equation 14 were continued in parallel. Again, however, although they lead to different values for the coefficient ratios, the overall thermodynamic picture does not differ in any major way. With more data it might be possible to distinguish between the two solutions, but for the present they would be equally valid. For the sake of consistency and with the assumption that the sixth-order term tends to be important in Landau free energy expansions for describing cation ordering reactions, only results for the tricritical type of equation (Q_t^5 in Equation 14) are given here. Attempts to fit values for the coefficients of both the Q_t^3 and Q_t^5 terms resulted in high correlations and are not justified by the available data.

The final fit coefficients were $a_i/h = 0.0135$, $T_{ct} = 586$ K, and $c_i/h = 8.91$. These give the variation of Q_t shown in Figure 5, with $Q_t = 0.402$ at 753 K. This fit differs from that used by Salje and Kroll (1991), who were interested in kinetic aspects of the Q_t ordering at high temperatures, primarily because of the constraint $Q_t = 1$ at 0 K introduced here.

Coupling between Q_t and Q_{od}

There are insufficient experimental data to fit values for the coefficients of Q_{od} in the same way as was achieved for Q_t . The nature of any general solution based on Equation 6 is quite clear, however. From the two criteria for equilibrium (Eqs. 7 and 8), two solutions are $Q_t \neq 0$, $Q_{od} = 0$ and $Q_t \neq 0$, $Q_{od} \neq 0$. There will therefore be two free energy curves to consider, the first with the former condition substituted into Equation 6 to define the monoclinic phase, and the second with the latter condition to define the triclinic phase. Since $Q_t = 0$ is not a solution, the value of Q_{od} in the triclinic phase cannot go continuously to zero at any temperature, and the monoclinic \rightleftharpoons triclinic transition is necessarily first order in character, so long as there is any coupling between Q_t and Q_{od} . The transition point is defined by the temperature at which the two free energy curves cross ($\Delta G = 0$ for $C2/m = C\bar{1}$).

To be more specific it is necessary to introduce some constraints based on what little information there is concerning the temperature dependence of ordering in microcline. Firstly, Equation 8 may be rewritten as

$$0 = \frac{a_{od}}{h}(T - T_{cod}) + \frac{c_{od}}{h}Q_{od}^4 + \frac{2\lambda}{h}Q_t. \quad (15)$$

In the absence of coupling, the transition at T_{cod} would yield $Q_{od} = 1$ for 0 K, giving the standard relationship between a_{od} , T_{cod} , and c_{od} for a tricritical transition: T_{cod}

= c_{od}/a_{od} , thereby reducing the number of independent variables by one.

A second constraint is provided by the observation that natural microcline has values of Q_i and Q_{od} close to 1. Attempts to find values of the coefficients in Equation 15 that reproduce such high degrees of order at geologically reasonable temperatures with λ as a constant failed because they also produced the unphysical result $Q_i > 1$ and $Q_{od} > 1$ at lower temperatures. It is well known that the order parameter for many phase transitions levels off more sharply at high degrees of order (characteristically well below room temperature) than would be predicted using a normal Landau series expansion, and so-called order parameter saturation (Salje, 1990; Salje et al., 1991) may be implicated here. The required leveling off can be reproduced adequately by adding terms that become significant as $Q \rightarrow 1$, but these terms are quantifiable only when rather good experimental data for the equilibrium temperature dependence of Q over a large temperature interval are available. Such data are unlikely to be generated for potassium feldspar because of the extreme sluggishness of Al-Si diffusion at low temperatures, and, in order to explore the implications of a constant coupling coefficient, it is necessary to resort to a gross simplification. Thus, arbitrarily, $Q_i = Q_{od} = 1$ has been selected as an equilibrium state at 400 K. Although it is clearly unphysical, it has the merit of allowing some potentially reasonable approximations for the variations in excess free energy, enthalpy, and entropy at geologically relevant temperatures to be examined.

A value of the coupling parameter, λ/h , can be obtained by inserting the chosen equilibrium values of Q_i and Q_{od} at 400 K into Equation 7, rewritten as

$$\frac{\partial G}{\partial Q_i} = 0 = -1 + \frac{a_i}{h}(T - T_{ct})Q_i + \frac{c_i}{h}Q_i^5 + \frac{\lambda}{h}Q_{od}^2. \quad (16)$$

Using the values of a_i/h , c_i/h , and T_{ct} derived above gives $\lambda/h = -5.40$. The same condition inserted into Equation 15, along with this value of λ/h , then provides the second equation constraining the possible values of a_{od}/h , T_{cod} , and c_{od}/h .

The third constraint needed to determine values for the three unknowns is provided by the fact that the excess free energies of the monoclinic and triclinic structure must be identical at the transition temperature, 753 K. Individual pairs of trial values of Q_i and Q_{od} at 753 K, as permitted by Equation 16, were substituted into Equation 15 to yield an equation in the Q_{od} coefficient ratios for this temperature. The three equations in these coefficient ratios were then solved in each case, and the values obtained used to calculate G/h at 753 K from Equation 6 (with Q_i^6 terms in place of Q_i^5 terms and divided by h) for the monoclinic ($Q_i = 0.402$) and triclinic ($Q_i \neq 0$, $Q_{od} \neq 0$) structures. The procedure was repeated until a set of coefficients that gave an identical value of G/h for the two structures was found, namely, $a_{od}/h = 0.027$, $T_{cod} = 547$ K, and $c_{od}/h = 14.8$ (for $\lambda/h = -5.40$). By substitution of these coefficient ratios back into Equations 15 and

16, the equilibrium values of Q_i and Q_{od} shown in Figure 5a were determined. The picture that emerges is reasonably consistent with limiting experimental data for the variation of Q_i below 450 °C, as extracted by Brown and Parsons (1989) from the data of Senderov and Yas'kin (1975, 1976). The calculated values of Q_{od} and Q_i are also closely similar to each other, as is found in natural microcline crystals. On the basis of the tricritical description for Q_{od} , the monoclinic \rightleftharpoons triclinic transition temperature would be expected to be 547 K if there were no coupling to Q_i .

If saturation effects are not important for Al-Si ordering in potassium feldspar at geological temperatures and Equation 6 provides an adequate representation of the real thermodynamic behavior, it follows that the coupling coefficient must be temperature dependent. For physically valid solutions of the equilibrium order parameters ($Q_i \leq 1$, $Q_{od} \leq 1$ at 0 K), the value of λ must be zero at 0 K. As a first approximation, a linear temperature dependence may be anticipated, i.e.,

$$\lambda = a_\lambda T. \quad (17)$$

A value of a_i/h has been derived, as before, from Equation 16 for each of two assumed low temperature states, which may be regarded as being representative of a range of possible behaviors: $Q_i = Q_{od} = 0.98$ at 450 K, or $Q_i = 0.80$ and $Q_{od} = 0.75$ at 700 K. Iterating through permitted equilibrium values of Q_i and Q_{od} at 753 K and the consequent free energy differences between monoclinic and triclinic crystals, to ensure $\Delta G = 0$ at the first-order transition as before, gave $a_{od}/h = 0.0249$, $T_{cod} = 239$ K, $c_{od}/h = 5.95$, $a_i/h = -0.0122$ K⁻¹ and $a_{od}/h = 0.0254$, $T_{cod} = 456$ K, $c_{od}/h = 11.59$, $a_i/h = -0.00878$ K⁻¹, respectively. The predicted variations in Q_{od} and Q_i derived from substituting these values and the earlier values for a_i/h , T_{ct} , and c_i/h into Equations 15 and 16 are shown in Figure 5b. The phase transition remains first order in character, but only the first result is consistent with the high degrees of order found in natural microcline. The second result, however, is more consistent with the limited experimental data below 450 °C. If higher values of Q_i and Q_{od} had been assumed for 450 K, the first order step at 753 K would have been larger.

Absolute values for the coefficients from calorimetric data

Trial values for the excess enthalpy due to ordering in crystals with $Q_i = Q_{od} = 1$, i.e., $H_{Q=1}$, were used to calculate absolute values of the coefficients in conjunction with the ratios derived from the conditions for equilibrium. For the case of $\lambda = \text{constant}$, the expression for H has already been given (Eq. 9). If $\lambda = a_\lambda T$, the excess enthalpy becomes

$$H = -hQ_i - \frac{1}{2}a_i T_{ct} Q_i^2 + \frac{1}{6}c_i Q_i^6 - \frac{1}{2}a_{od} T_{cod} Q_{od}^2 + \frac{1}{6}c_{od} Q_{od}^6 \quad (18)$$

(from $H = G + TS$, $S = -dG/dT$). Sets of coefficients

TABLE 2. Sets of coefficients for four solutions to the Landau free energy expansion

Solution no. Model	1	2	3	4
$\lambda =$	constant,	$\lambda = a_i T,$	$\lambda = a_i T,$	$\lambda = a_i T,$
$Q_i = Q_{od}$	$Q_i = Q_{od}$	$Q_i \approx 0.80,$	$Q_i = Q_{od}$	$Q_i = Q_{od}$
$= 1$ at	$Q_{od} \approx 0.75$ at	$= 0.98$	$= 0.98$	$= 0.98$
400 K	700 K	at 450 K	at 450 K	at 450 K
$H_{Q=1}$	-8000	-8000	-8000	-9000
h	580	1091	1467	1650
a_t	7.83	14.73	19.80	22.28
T_{ct}	586	586	586	586
c_i	5168	9721	13070	14700
a_{od}	15.66	27.71	36.53	41.09
T_{cod}	547	456	239	239
c_{od}	8582	12650	8735	9818
λ	-3132	—	—	—
a_λ	—	-9.58	-17.90	-20.13
$-(\frac{1}{2}a_i + \frac{1}{2}a_{od} + a_\lambda)$	-11.75	-11.64	-10.27	-11.56

Note: units for H , h , c_i , c_{od} , and λ are in J/mol; a_i , a_{od} , and a_λ in J/mol·K; T_{ct} and T_{cod} in K.

calculated for $H_{Q=1} = -8000$ or -9000 J/mol are given in Table 2. Excess enthalpies for model equilibrium values of Q_i and Q_{od} are compared with the solution calorimetric data of Hovis (1988) in Figure 6.

When comparing calculated excess enthalpies, H , with experimental heats of solution, ΔH_{soln} , it is necessary to select a value for ΔH_{soln} that will correspond to $H = 0$. This can be done by choosing a common scale for which the greatest overlap between calculated and experimental values occurs. In Figure 6, the data are plotted as a function of Q_i , and $H = 0$ has been selected at $\Delta H_{soln} = 613.2$ kJ/mol. There is a good general correlation between the calorimetric results and all the model solutions, but in detail the agreement is less convincing. At small degrees of order, within the sanidine stability field ($Q_i < 0.402$), the constant λ solution (solution 1 in Fig. 6) gives enthalpy changes that are too small. Increasing the value of $H_{Q=1}$ gives steeper variations in H but only slightly so. The steepest variation in H over this range of Q_i values is given by the $\lambda = a_i T$ solution with $Q_i = Q_{od} = 0.98$ at 450 K and $H_{Q=1} = -9000$ J/mol (solution 4 in Table 2 and Fig. 6). The ΔH_{soln} values for crystals that have Q_i in a range characteristic of modulated orthoclase and adularia (the four central points in Fig. 6) plot on or above an extrapolated line between the equilibrium triclinic and equilibrium monoclinic values in the case of solution 4. Thus, only for this solution would a homogeneous crystal with intermediate values of Q_i and Q_{od} have a lower enthalpy than a modulated crystal with the same average Q values. The other solutions (1, 2, and 3 in Table 2, Fig. 6) would predict homogeneous structures with higher (less negative) enthalpies of ordering than those of the observed modulated structures, which is counter to the expectation that the modulation represents a defect structure carrying some positive excess energy. The lowest dotted line in Figure 6 gives the excess enthalpy for homogeneous (unmodulated) crystals with metastable degrees of order, with the assumption of $Q_i = Q_{od}$ in Equa-

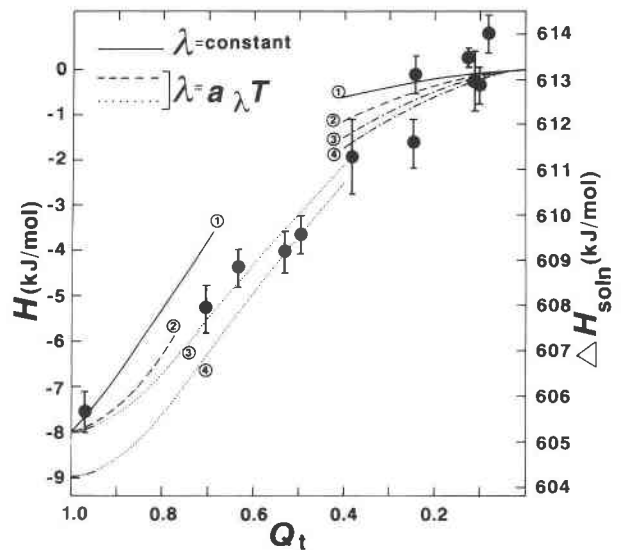


Fig. 6. Calculated enthalpy variations (left scale) compared with measured ΔH_{soln} values (right scale) from Hovis (1988), as a function of Q_i . The calculated variations are for solutions 1–4. In each case there is a discontinuity corresponding to the first-order break in both Q_i and Q_{od} . In the cases of solutions 3 and 4, both equilibrium (dot-dash lines) and metastable (dotted lines) variations are shown. Data represented by the dotted lines were calculated for metastable triclinic crystals with $Q_i = Q_{od}$ and the coefficients from solutions 3 and 4; they pass approximately through the four central data points from modulated crystals with values of Q_i typical of modulated orthoclase and adularia. Modulations were not immediately apparent on a TEM scale in the crystals with $Q_i = 0.53$, however (Hovis, 1988).

tion 18 with the coefficients of solution 4. It is interesting to note that ΔH_{soln} for the sample with $Q_i = 0.53$ (the Madagascar orthoclase of Hovis, 1988) plots on this line and that the crystals did not appear to contain obvious modulations when examined by transmission electron microscopy (Hovis, 1988).

The most reliable solution calorimetric data are those obtained from crystals with different degrees of order but identical impurity contents, defect chemistries, etc. Hovis (1988) reported results for ion-exchanged Amelia albite and for the same ion-exchanged Amelia albite after disordering at ~ 1050 °C (Hovis, 1974, 1988). The measured differences in ΔH_{soln} between these two samples, 8380 ± 620 J/mol, can be compared with 8780 J/mol calculated from solution 4 using $Q_i = 0.97 \rightarrow Q_i = 0.081$ (the values of Q_i used by Hovis, 1988). The quoted uncertainty is $\pm 1\sigma$. Waldbaum and Robie (1971) measured an enthalpy difference of 8170 ± 1340 J/mol between ion-exchanged Amelia albite and disordered crystals that were ion-exchanged after the disordering. Assuming $Q_i = 0.97$ for Amelia albite and taking $Q_i = 0.14$ for albite equilibrated at ~ 1060 °C, from the structure refinement of Winter et al. (1979), the equivalent enthalpy calculated from solution 4 is 8600 J/mol. The only natural sample of Hovis (1974, 1988) that appears to have equilibrated in the

monoclinic stability field is Eifel sanidine. The measured enthalpy difference between this sample ($Q_t = 0.248$) and its heat-treated equivalent ($Q_t = 0.106$) is 1300 ± 680 J/mol (Hovis, 1988). For comparison, the calculated value is 562 J/mol, which, if uncertainties of approximately ± 0.02 in Q_t were taken into account, would just be within 1σ of the measured value. Similar data for orthoclase and adularia have not been compared in the same way because of the possible influence of strain modulations. Perhaps an overall assessment of the success (or otherwise) of the Landau expansion in reproducing measured enthalpy variations, however, should be left as the comparison of predictions from solution 4 with all the calorimetric data of Hovis (1988) in Figure 6, since the individual data were not used explicitly to determine the absolute values of the Landau coefficients.

Excess entropies due to ordering, with $\lambda = \text{constant}$, are given by Equation 10. If λ is a linear function of T , the excess entropy becomes

$$S = -\frac{1}{2}a_t Q_t^2 - \frac{1}{2}a_{od} Q_{od}^2 - a_\lambda Q_t Q_{od}^2. \quad (19)$$

The excess free energies, G , are given by Equation 6. Equilibrium variations in H , S , and G have been calculated for solutions 1 and 4 and are shown in Figure 7. Calculated latent heats and latent entropies for the $C2/m = C\bar{1}$ transition are 3.02 kJ/mol, 4.01 J/mol·K (solution 1), and 7.17 kJ/mol, 9.53 J/mol·K (solution 4), respectively.

DISCUSSION

The most positive aspect of the approach set out here is that it reproduces the gross features of Al-Si ordering in potassium feldspar that are believed to represent equilibrium behavior. In particular, both the discrete monoclinic = triclinic phase transition and the nonconvergent ordering in monoclinic crystals are accounted for quantitatively. Many solutions for, and slight variations of, the basic free energy expansion have been explored, and these serve to show that, in spite of the nonuniqueness of each of the resulting sets of coefficients, the same general pattern emerges. With falling temperature, small free energy changes associated with Q_t ordering are followed first by a first-order transition and then by relatively large energy changes accompanying Q_t and Q_{od} ordering. The coupling term in Q_t and Q_{od} causes the transition to become first order if it were continuous without coupling or would enhance the first-order character if the uncoupled transition were already discontinuous. The assumed tricritical behavior of pure Q_{od} ordering is probably not unreasonable in the light of closely similar behavior for pure ordering in albite (Salje et al., 1985). The solutions ascribe a substantial proportion of the excess energy associated with Q_t ordering to the linear field term and a substantial proportion of the excess free energy at geological temperatures to the interactions between Q_t and Q_{od} .

One consequence of the strong coupling between Q_t and Q_{od} is that crystals having $Q_{od} \neq 0$ would tend to

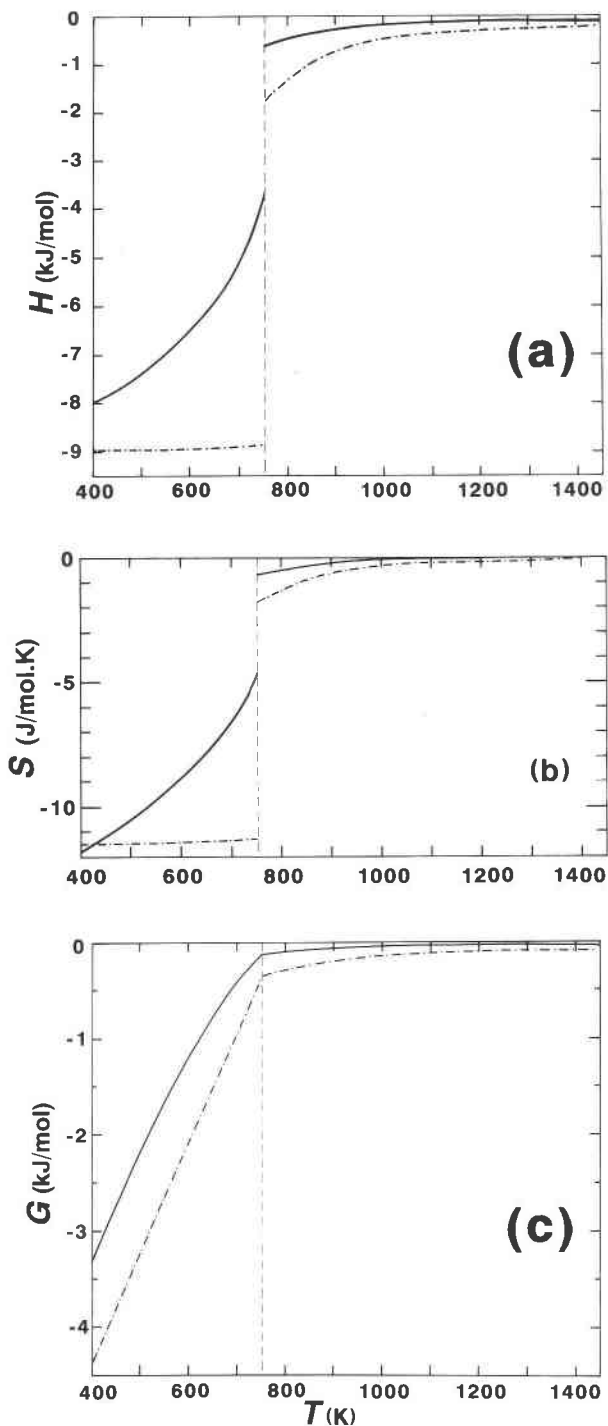


Fig. 7. Calculated variations of excess enthalpy (a), entropy (b), and free energy (c) from solutions 1 (solid lines) and 4 (dot-dash lines). The broken line marks the monoclinic = triclinic phase transition.

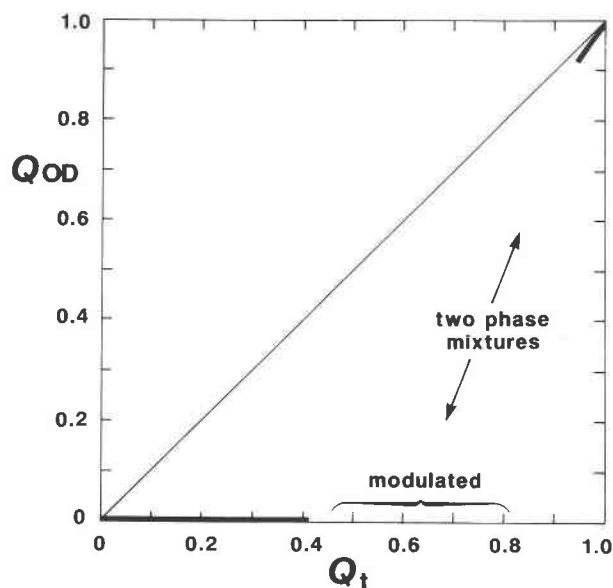


Fig. 8. Equilibrium variations of Q_t and Q_{od} calculated from solution 4. $Q_t = 0$ only at infinite T and $Q_t = Q_{od} = 1$ at 0 K. A large first-order discontinuity is predicted at 753 K between monoclinic crystals with $Q_t = 0.40$, $Q_{od} = 0$ and triclinic crystals with $Q_t = 0.95$, $Q_{od} = 0.94$. Modulated structures and so-called intermediate microcline (which may be two-phase intergrowths) would be metastable with respect to microcline.

evolve with $Q_t \approx Q_{od}$ (values of Q_{od} are restricted to $\leq Q_t$ by stoichiometry). This means that changes in physical properties arising from changes in Q_{od} might show a close correlation with changes in Q_t , explaining, for example, why no discernible break occurs in the slope of the data of Hovis (1988) for ΔH_{soln} against Q_t for monoclinic and triclinic crystals. According to this argument, even in the modulated structures the local values of Q_{od} may be close to the values of Q_t obtained from macroscopic measurements. Such a possibility is considered in more detail in the following section. On the other hand, particular strain variations appear to arise as a consequence of coupling only with Q_t or only with Q_{od} . Making the connection between a macroscopic change of interest and the particular order parameters on which it depends, as set out formally here, should in the future allow clearer distinctions to be made as to the relative dependence of properties on the convergent and nonconvergent ordering processes.

Even with the limited data available, there are sound reasons for favoring solution 4 as the most valid quantitative description. Firstly, it is physically reasonable and does not require approximations that give unreal results, such as $Q_t, Q_{od} > 1$. It requires a temperature-dependent coupling coefficient that is also plausible from a physical point of view. The coupling mechanism does not appear to arise from overlapping macroscopic strains, since the separate strains due to Q_t and Q_{od} develop in an orthogonal, i.e., mutually exclusive, manner. A microscopic

mechanism involving, for example, lattice vibrations is more likely. If local strains due to changes in Q_t or Q_{od} were influenced by, and themselves influenced the pattern of, phonons, the coupling would diminish with the phonon amplitudes. This would lead to a steady decrease in λ , with its possible disappearance at 0 K. The linear relation used in the solution may only be an approximation for some nonlinear variation, of course.

Solution 4 produces the best fit with the solution calorimetric measurements of Hovis (1988). It also gives the closest approximation to an equality of Q_{od} with Q_t in triclinic crystals. This is consistent with the progressive disordering results for microcline of Blasi et al. (1984), who found $Q_{od} \approx Q_t$ between values of ~ 0.1 and 1. The lowest equilibrium degree of order in a triclinic crystal is predicted to be $Q_t \approx 0.95$ and $Q_{od} \approx 0.94$ (at 753 K). This limit can be adjusted to some extent by choosing values of Q_t and Q_{od} greater than 0.98 at 450 K, but it cannot be reduced by much if the high degrees of order found in natural microcline are to be reproduced. The equilibrium phase diagram in order parameter space is thus as shown in Figure 8. Modulated structures are regarded as being metastable with respect to microcline, and, in accordance with the TEM observations of Eggleton and Buseck (1980), Fitz Gerald and McLaren (1982), McLaren (1984), Krause et al. (1986), and Kroll et al. (1991), samples described as "intermediate" microcline are presumed to contain intergrowths of modulated regions and homogeneous triclinic regions. Favoring solution 4 in this way calls into question the experimental results of Senderov and Yas'kin (1975, 1976). Clearly, further order-disorder experiments below ~ 750 K and alternative solubility or phase equilibrium experiments would be of great value in providing an independent test of the model.

Up to this point no assumptions have been made concerning the origin of excess entropy accompanying the ordering. It must be predominantly configurational but can contain nonconfigurational contributions. The total expected excess configurational entropy is given in the usual way as $4R(0.25 \ln 0.25 + 0.75 \ln 0.75) = -18.7$ J/mol·K. This may be compared with calculated values for the excess entropy at $Q_t = Q_{od} = 1$ from Equation 19, which are in the range -10 to -12 J/mol·K (Table 2). The implicit assumption of $S \propto Q^2$ in standard Landau free energy expansions means that the calculated Landau excess entropy and the purely configurational entropy can be similar but are not necessarily identical (see Fig. 4 of Carpenter et al., 1994). In the present case, the comparison is also complicated by the proposed participation of phonons in the coupling mechanism, but the total calculated excess entropy is clearly small relative to the ideal configurational entropy. As a further refinement, the latter can be split artificially into two parts. For crystals with $Q_t = Q_{od} = 0$ evolving to $Q_t = 1$ and $Q_{od} = 0$, the ideal configurational entropy change would be -7.17 J/mol·K, and for crystals with $Q_t = 1$, $Q_{od} = 0$ evolving to $Q_t = 1$, $Q_{od} = 1$, it would be -11.53 J/mol·K. These values

may be compared with -11.1 and -20.5 J/mol·K derived from the values of a_t and a_{od} , respectively, when the coupling is ignored. At least the model solutions all have $a_{od} > a_t$.

Finally, it is perhaps helpful to readers more familiar with the series expansions used by Thompson et al. (1974) to highlight those aspects of the present approach based on Landau theory that are most distinct. They relate to the treatment of all three of the primary excess properties, S , H , and G . Here the excess entropy has been described entirely by quadratic terms in Q_t and Q_{od} , with the additional contribution of the temperature-dependent coupling term. This greatly simplifies the problem of accounting for nonconfigurational or short-range ordering contributions, which are included automatically in the calibration of the coefficients a_t , a_{od} , and a_λ . Thompson et al. (1974) truncated their expansion for H after second-order terms, whereas an additional high-order term for each order parameter is included in the Landau expansion. Experience gained from the study of many phase transitions and many materials is sufficient to indicate that such higher order terms are likely to be real. The most significant difference, however, is the inclusion in the expansion for free energy of a coupling term to describe the influence of Q_t on Q_{od} , and vice versa. Such a coupling effect was not considered by Thompson et al. (1974) and is the principal cause of the discontinuity at the monoclinic = triclinic transition suggested here, in contrast with the thermodynamically continuous behavior shown in their Figure 13.

STRUCTURAL STATES OF MODULATED CRYSTALS

The modulations found in orthoclase and adularia crystals have attracted interest from both structural and energetic points of view since they were first described by McConnell (1965). McConnell's interpretation of local triclinic distortions in a macroscopically monoclinic crystal appears to be generally accepted, as does his suggestion that they develop as metastable alternatives in place of the transition to microcline (Nissen, 1967; McConnell, 1971; McLaren, 1974, 1984; Eggleton and Buseck, 1980; Fitz Gerald and McLaren, 1982; McLaren and Fitz Gerald, 1987; Smith and Brown, 1988; Brown and Parsons, 1989). The energy changes associated with the relevant lattice distortions and with Al-Si ordering alone are known to be comparable in magnitude (Eggleton and Buseck, 1980), but there remains a question as to whether the Al-Si configuration varies on a local scale so as to follow the distortions exactly. Evidence from infrared spectroscopy excludes the possibility of large local variations in Al-Si order (Harris et al., 1989). As a consequence of the present analysis, there may now be sufficient quantitative information to suggest why relatively homogeneous states of Al-Si order should be favored.

The lattice distortions in orthoclase and adularia involve, primarily, variations in the γ angle and can therefore be characterized in terms of modulations in the strain component e_6 . In macroscopically triclinic crystals large

e_6 strains arise by coupling with Q_{od} , and, if there are modulations in e_6 , there may also be some energetic advantage due to the coupling that favors modulations in Q_{od} . On the other hand, Q_t does not couple with a triclinic strain and would be expected to remain homogeneous in both monoclinic and triclinic crystals. It has been argued that Q_t and Q_{od} are strongly coupled, with the implication that if Q_t is homogeneous the coupling would tend to favor Q_{od} also being homogeneous. Thus, there is a competition between Q_{od} - e_6 coupling, favoring an inhomogeneous Al-Si distribution, and Q_t - Q_{od} coupling, favoring a homogeneous distribution. Both these coupling energies can be estimated to find which is dominant.

The total excess free energy of the modulated structure may be written as

$$G = L(Q_{od}) + L(Q_t) + a_\lambda T Q_t Q_{od}^2 + \lambda_6 e_6 Q_{od} + \frac{1}{2} C_{66} e_6^2 + \text{gradient terms} \quad (20)$$

where $L(Q_{od})$ and $L(Q_t)$ are the Landau free energy expansions in Q_{od} and Q_t , much as before. Bilinear coupling between e_6 and Q_{od} , with λ_6 as the coupling coefficient, and the elastic energy, $\frac{1}{2} C_{66} e_6^2$, with C_{66} as the relevant elastic constant, are now included explicitly. The competing coupling term is $a_\lambda T Q_t Q_{od}^2$, as before, whereas energy contributions from gradients in e_6 or Q_{od} are not specified. From this equation, the condition for equilibrium with respect to an e_6 strain is

$$\frac{\partial G}{\partial e_6} = 0 = \lambda_6 Q_{od} + C_{66} e_6 \quad (21)$$

and, hence

$$\lambda_6 = -\frac{C_{66} e_6}{Q_{od}} \quad (22)$$

By extrapolation from the γ lattice angle of natural microcline, the value of e_6 in crystals with $Q_{od} = 1$ would be ~ 0.042 . C_{66} for microcline has been measured as 37.4 GPa (Ryzhova and Aleksandrov, 1965), and substituting these values into Equation 22 gives $\lambda_6 = -1.71 \times 10^5$ J/mol. If a crystal with $Q_{od} = Q_t = 0.6$ is considered, the coupling energy $\lambda_6 e_6 Q_{od}$ would be approximately -2.6 kJ/mol (again with the assumption of a linear relationship between Q_{od} and e_6 , as expected for bilinear coupling). For the situation illustrated in Figure 9a, with modulations in both e_6 and Q_{od} , the total energy from this coupling term would be substantially smaller because most of the crystal would have $|Q_{od}| < 0.6$. For a crystal with $Q_{od} = Q_t = 0.6$ at ~ 650 K, the coupling energy $a_\lambda T Q_t Q_{od}^2$ would be approximately -2.8 kJ/mol. For the situation envisaged in Figure 9b, with the modulation only in e_6 , the whole of this coupling energy is available to stabilize the crystal. There would, in addition, still be some favorable Q_{od} - e_6 coupling, since regions of the crystal would be deformed in the correct sense with respect to Q_{od} .

From these simple calculations it appears that the competing coupling effects would substantially favor the form

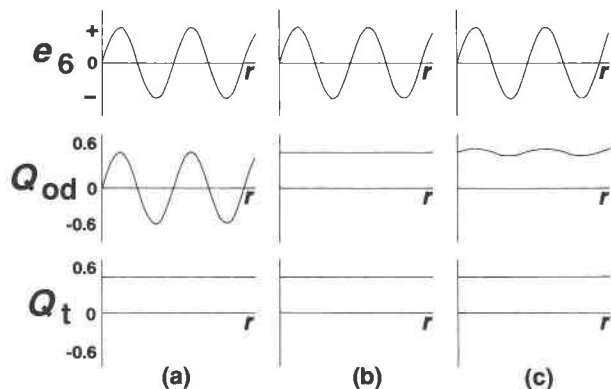


Fig. 9. Schematic variations of Q_t (nonconvergent Al-Si ordering), Q_{od} (convergent ordering), and e_6 (triclinic strain) as a function of distance, r , in modulated orthoclase crystals. (a) Coupling between Q_{od} and e_6 greatly outweighs coupling between Q_{od} and Q_t such that Q_{od} is modulated. (b) Coupling between Q_{od} and Q_t greatly outweighs coupling between Q_{od} and e_6 such that Q_{od} is homogeneous. (c) Possible variations of Q_t , Q_{od} , and e_6 in modulated crystals. The true variations in Al-Si order may be determined by some intermediate weighting of the coupling energies to give small variations in Q_{od} .

of variation shown in Figure 9b. In reality, local variations in Q_{od} must occur to some extent as a consequence of the coupling to the e_6 modulations (Fig. 9c). The modulations in real crystals occur in two dimensions, giving a tweed texture, possible gradient energies have been ignored, and the values of Q_t , Q_{od} , and T selected are slightly arbitrary, but the result is consistent with the infrared evidence of Harris et al. (1989). The amplitude of any modulation in Q_{od} is probably small, but conventional structural refinements using diffraction data would not reveal either the modulation or the nonzero Q_{od} values, if the refinements included the initial assumption of monoclinic symmetry.

It has already been pointed out that the calorimetric data for orthoclase and adularia imply enthalpies of ordering that are indistinguishable from, or only slightly less than, the excess enthalpies of homogeneous crystals with $Q_t \approx Q_{od}$ (Fig. 6). If the conclusion is correct that, because of the strong Q_t - Q_{od} coupling, the values of Q_{od} and Q_t are about the same in modulated crystals, the enthalpy change due to the formation of the strain modulations alone must be small. It follows that the driving force for a transition from the modulated monoclinic state to a homogeneous triclinic state is also small, therefore. Such a lack of driving energy is often invoked as a contributing factor to the metastable persistence of orthoclase and adularia in nature (e.g., Smith and Brown, 1988; Brown and Parsons, 1989; and references therein).

The overall importance of the triclinic strain in promoting the monoclinic = triclinic transition can also be determined. T_{cod} , the equilibrium temperature for a hypothetical $C2/m = C\bar{1}$ transition with no coupling to Q_t , is renormalized by the linear coupling between Q_{od} and

e_6 . The unrenormalized value, $T_{cod,unren}$, for a transition in which e_6 was also suppressed can easily be derived from Equation 20 (e.g., see Salje and Devarajan, 1986, or Carpenter, 1992) as

$$T_{cod,unren} = T_{cod} - \frac{\lambda_6^2}{a_{od}C_{66}}. \quad (23)$$

For solution 4 (Table 2) and the value of λ_6 determined above, this gives $T_{cod,unren} = 65$ K. Such a small value indicates that the driving force for pure Q_{od} ordering is not very significant. Coupling with e_6 raises the transition temperature, T_{cod} , to 239 K (solution 4). This latter effect and the coupling to Q_t evidently provide most of the energy that drives the phase transition.

CONCLUSIONS

A thermodynamic model has been developed in which the parameters can have a clear physical meaning. The reliability of values derived for these parameters is, of course, dependent on the quality of the experimental data used in the fitting procedures. Even so, the need simultaneously to generate a feasible equilibrium phase diagram from the condition $\partial G/\partial Q = 0$ and to match an extensive set of enthalpy data provides a stringent test of self-consistency. The overall approach also provides some insights into the factors controlling the stabilities of different structural states of potassium feldspar.

A quantitative hypothesis against which further experiments may be designed is encapsulated in the final preferred Landau expansion for the total excess free energy (in J/mol):

$$G = -1650Q_t + 11.14(T - 586)Q_t^2 + 2450Q_6^2 + 20.55(T - 239)Q_{od}^2 + 1636Q_{od}^6 - 20.13TQ_tQ_{od}^2.$$

This describes a first-order $C2/m = C\bar{1}$ transition at 753 K, with breaks in Q_t and Q_{od} of $0.40 \rightarrow 0.95$ and $0 \rightarrow 0.94$, respectively. Coupling between Q_t and Q_{od} and between Q_{od} and the triclinic strain account for a substantial proportion of the energy stabilizing triclinic states.

It is hoped that this example, together with the innovations suggested for single-order parameter systems and solid solutions in Carpenter et al. (1994) and Carpenter and Salje (1994), leads to practical formulations for the thermodynamic properties of minerals that undergo nonconvergent ordering in nature.

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