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Displacive phase transition in anorthoclase: The "plateau effect" and the effect of T1-T2 ordering on the transition temperature

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ABSTRACT

The effects of compositional changes and nonsymmetry-breaking Al-Si ordering on the displacive phase transition in anorthoclase have been studied using X-ray powder diffraction. The results were analyzed using a model based on Landau theory.

The observed transition temperature, T_c^*, was found to be independent of orthoclase content in the range $0 < X_{Or} < 0.02$. For samples with $X_{Or} > 0.02$, T_c^* decreases linearly with increasing X_{Or}. This plateau behavior is explained by the finite volume of the strain field around each K^+ ion: Chemical mixing behavior is observed only for average K^+-K^+ distances of <20 Å.

Increasing Al-Si order between the T1 and T2 sites causes T_c^* to increase; this is unlike T1o-T1m ordering, which prevents the transition to monoclinic symmetry altogether. The range of T_c^* values reported in the literature is shown to be consistent with different degrees of T1-T2 order.

INTRODUCTION

The feldspar structure consists of an aluminosilicate framework, with large cations (principally Na, K, and Ca) in the large structural cavities. In a monoclinic feldspar (e.g., monalbite, $NaAlSi_3O_8$), the tetrahedral sites on which Al and Si sit form two sets of equivalent positions (that is, sites that are related by symmetry). These are conventionally labeled T1 and T2 (Megaw 1974a). In a triclinic feldspar, the monoclinic symmetry is broken, so there are four independent types of sites; e.g., the T1 set splits into independent sets T1o and T1m.

Alkali feldspars have several structural responses to changes in pressure, temperature, and composition, as reviewed in Megaw (1974a, 1974b), Ribbe (1983), Carpenter (1988), and Brown and Parsons (1994), among others. Each structural change can be described quantitatively by an order parameter, and the energetics of each change can be modeled by a Landau potential. There are three such changes, besides exsolution (which is not considered here): (1) A displacive phase transition results from the collapse of the feldspar crankshafts around the large Na and K cations. This reduces the symmetry of the structure from *C2/m* to $C\bar{1}$. The transition is second order (Salje 1985; Salje et al. 1985), and the order parameter *Q* can be defined in terms of the degree of collapse of the crankshafts, which can be measured using the lattice parameter α:

$$Q \propto \cos \alpha. \tag{1}$$

(2) Another structural change is that of an order-disorder phase transition involving the tetrahedral cations Al and Si. This is driven by the high energy of Al-O-Al linkages (the "aluminum avoidance" principle). Al goes to the T1o sites, while Si goes to the other three sites. This is quantified using two order parameters. The first describes the partition of Al and Si between the T1o and T1m sites. This process reduces the symmetry of the structure from *C2/m* to $C\bar{1}$, resulting in a phase transition that is nearly tricritical (Salje et al. 1985; Carpenter and Salje 1994). This process has the order parameter Q_{OD}, where

$$Q_{OD} = \frac{t_{1o} - t_{1m}}{t_{1o} + t_{1m}} \tag{2}$$

where t_X is the Al occupancy in the T*X* site. (3) There is also nonconvergent ordering of Al and Si between the T1 and T2 sites. This ordering process does not break the monoclinic symmetry (Carpenter and Salje 1994) and is described using the order parameter Q_t:

$$Q_t = \frac{t_1 - t_2}{t_1 + t_2}. \tag{3}$$

The structural state of a homogeneous alkali feldspar is described using the three order parameters *Q*, Q_{OD}, and Q_t. Therefore, its excess Gibbs free energy can be derived from the individual contribution associated with each *Q*, together with the coupling energies between them.

The way that a sample responds to changes in external variables, such as pressure and temperature, is constrained by the extreme sluggishness of Al and Si diffusion in feldspars. This means that neither Q_{OD} nor Q_t changes noticeably without prolonged heating at high temperatures.

The other structural variable is chemical composition. The natural feldspar system has three end-members: $NaAlSi_3O_8$ (Ab), $KAlSi_3O_8$ (Or), and $CaAl_2Si_2O_8$ (An). The choice of names commonly used for these minerals depends on their symmetry, that is, their values of *Q*, Q_{OD},

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and Q_t. Thus, sodium feldspar may be referred to as monalbite ($Q = 0$, $Q_{OD} = 0$), analbite ($Q \neq 0$, $Q_{OD} = 0$), or albite ($Q \neq 0$, $Q_{OD} \neq 0$). Anorthoclase is alkali feldspar (that is, an Ab:Or solid solution), with $Q_{OD} = 0$.

THEORY

Because changes in Q_{OD} and Q_t are very slow at low temperatures, the usual aim of a thermodynamic model is to predict changes in the displacive order parameter Q, which changes on a phonon timescale. Experimentally, the displacive transition is thermodynamically second order. Therefore, the Landau free energy is of the form

$$G = \frac{1}{2}\mathrm{A}(T - T_c)Q^2 + \frac{1}{4}\mathrm{B}Q^4 \qquad (4)$$

where the parameters A, B, and T_c can be found experimentally for any anorthoclase sample. For example, Salje et al. (1985) found A = 5.5 J/(mol·K), B = 2.3 kJ/mol, T_c = 416 K for a disordered anorthoclase, $Ab_{69}Or_{31}$. In Equation 4, A, B, and T_c are purely experimental parameters. To generalize the model, we need a theory relating these parameters with each of the other parameters of interest: Q_{OD}, Q_t, and X.

Relationship between Q_{OD} and Q

The principles involved in relating the behavior of Q to these other parameters can be seen by considering the coupling between Q_{OD} (the degree of Al-Si order) and Q, using the model described in Salje (1985). Because both transitions have the same symmetry, the lowest order coupling between them is bilinear; the total energy of the system is given by

$$G = \frac{1}{2}\mathrm{A}(T - T_c)Q^2 + \frac{1}{4}\mathrm{B}Q^4 + \lambda Q Q_{OD} + \frac{1}{2}\mathrm{A}_{OD}(T - T_{c_{OD}})Q_{OD}^2 + \frac{1}{6}\mathrm{C}_{OD}Q_{OD}^6. \qquad (5)$$

Equation 5 implicitly includes lattice-strain energies. This is described as renormalization in Salje (1985) and can be done because the strains are themselves functions of the order parameters. This process is the main mechanism responsible for the observed coupling term. The coupling between strains can be expressed as a function of the two order parameters. In comparison with Equation 24 of Salje (1985), Equation 5 does not have the terms in Q^6 and Q_{OD}^4 because these have been found experimentally to be negligible (Salje et al. 1985; Carpenter and Salje 1994).

To predict how Q varies with T, we set $\mathrm{d}G/\mathrm{d}Q = 0$, but not $\mathrm{d}G/\mathrm{d}Q_{OD} = 0$ (because Al-Si ordering is so slow that Q_{OD} is unlikely to be in thermodynamic equilibrium). We then have

$$\lambda Q_{OD} + \mathrm{A}(T - T_c)Q + \mathrm{B}Q^3 = 0. \qquad (6)$$

One important consequence of Equation 6 is that on heating, Q can only equal zero for $Q_{OD} = 0$. This result provides a test of the monoclinicity of the cation distribution.

If $Q_{OD} = 0$, which is the case for anorthoclase, all but the first two terms in Equation 5 vanish, and we obtain the simple second-order behavior of Equation 4:

$$Q^2 = \frac{T_c - T}{T_c}. \qquad (7)$$

The effects of Q_t and X can be similarly determined.

Relationship between Q_t and Q

The effect of Q_t has been studied in potassium feldspar (Carpenter and Salje 1994). Because the ordering given by Q_t is nonconvergent, odd-powered terms are allowed in the Landau polynomial. The lowest allowed coupling between Q_t and Q_{OD} is linear quadratic; bilinear coupling would be possible only if the two order parameters had the same symmetry. Carpenter and Salje (1994) postulated that this coupling is temperature dependent, with $\lambda = \lambda_0 T$. The temperature dependence of the coupling is due to the increase in phonon population with temperature.

Because Q_{OD} and Q have the same symmetry properties, it seems reasonable to assume that the coupling between Q_t and Q has the same form as that between Q_t and Q_{OD} (even if its magnitude is not the same). So when $Q_{OD} = 0$ (and any terms involving Q_{OD} vanish) the resulting expression is

$$G = \frac{1}{2}\mathrm{A}(T - T_c)Q^2 + \frac{1}{4}\mathrm{B}Q^4 + \lambda Q_t Q^2 - \mathrm{h}Q_t + \frac{1}{2}\mathrm{A}_t(T - T_{c_t})Q_t^2 + \frac{1}{6}\mathrm{C}_t Q_t^6. \qquad (8)$$

The fact that the coupling is linear quadratic, rather than bilinear, has an important effect on the behavior of $Q(T)$. For an experiment on a short timescale, Q_t is a constant. If Equation 8 is simplified to reflect this constraint, Q can be shown always to follow a second-order model:

$$G = \frac{1}{2}\mathrm{A}\left(T - T_c + \frac{2\lambda Q_t}{\mathrm{A}}\right)Q^2 + \frac{1}{4}\mathrm{B}Q^4 + G(Q_t \text{ only}). \qquad (9)$$

The effect of Q_t is to renormalize the observed T_c:

$$\frac{\mathrm{d}G}{\mathrm{d}Q} = \mathrm{A}Q\left(T - T_c + \frac{2\lambda_0 T Q_t}{\mathrm{A}}\right) + \mathrm{B}Q^3$$

$$Q^2(T) = \frac{\mathrm{A}}{\mathrm{B}}\left[T_c - T\left(1 + \frac{2\lambda_0 Q_t}{\mathrm{A}}\right)\right]$$

$$T_c^*(Q_t) = T_c\left(1 - \frac{\lambda_0 Q_t}{\mathrm{A}}\right)^{-1}. \qquad (10)$$

Relationship between X and Q: The plateau effect

The effect of composition can be analyzed using a method described in Salje (1995). The essence of this technique is consideration of the behavior of an end-member (in this case, analbite) coupled with the effect of a solute (sanidine). Equation 4 therefore becomes

$$G(Q, T, X) = \frac{1}{2}A_0(T - T_{c0})Q^2 + \frac{1}{4}B_0Q^4 + \frac{1}{2}A_1(X)Q^2 + G(X) \quad (11)$$

where A_0, B_0, and T_{c0} are the Landau coefficients for the end-member, $A_1(X)$ is the coupling between the solute and the displacive transition, and $G(X)$ is the self energy of the solute. The equilibrium path of $Q(T)$ is given by

$$Q^2 = \frac{A_0(T_c^* - T)}{B} \qquad T_c^* = T_{c0} - \frac{A_1}{A_0}. \quad (12)$$

Thus, the effect of composition, X, on the transition temperature, T_c^*, depends on the way that the coupling term A_1 depends on composition. There are two main mechanisms to consider: (1) For high concentrations of solute, the distortion fields around the solute atoms overlap to produce a homogenous field. In this case, $A_1(X)$ is proportional to X. (2) At lower solute concentrations, the solute atoms are further apart, so their distortion fields do not overlap (Iiyama and Volfinger 1976; Newton and Wood 1980). In this case, their effect on most of the crystal is an indirect one, with coupling taking place through the framework of the host. Again, $A_1(X)$ is proportional to X, though with a different proportionality constant. It is likely that the effect at lower solute concentrations is weaker than that at higher concentrations.

These predictions can be summarized as follows. If $Q_{OD} \neq 0$, no phase transition to monoclinic symmetry would be observed on heating, though in principle T_c could still be determined as one of the parameters in Equation 7. If $Q_{OD} = 0$, (1) the observed T_c^* would generally be linear with X, and at low values of X, a plateau, where T_c^* is independent of X, would be expected; (2) increasing values of Q_t would raise the observed value of T_c^*.

EXPERIMENTAL METHODS

Anorthoclase powder samples were produced by the method described in Kroll et al. (1986). The starting material was an albite from Alp Rischuna, Valais (sample no. 5028 from the Harker collection, Cambridge University). This was disordered by hydrothermal annealing (P_{H_2O} = 200 bars) at 1250 K for 8 d. The Al-Si disorder was verified by X-ray diffraction, and the composition ($Ab_{99.6}Or_{0.4}$) was determined by electron microprobe analysis. The K end-member was produced by ion exchange of this material in molten KCl at 1120 K for 6 h. The resulting composition was $Ab_{1.2}Or_{98.8}$.

Samples in the range $X_{Or} \leq 0.08$ were then produced by weighing and mixing the end-members. The mixed samples were then pressed into pellets, wrapped in platinum foil, and homogenized at 1270 K for 3 d. The homogeneity and Al-Si state of these samples was checked as part of the subsequent X-ray analysis.

The experiments were performed on the high-temperature diffractometer described in Salje et al. (1993). The sample was mounted on a platinum resistance-heating strip, and the sample temperature was measured using a Pt-Rh thermocouple attached to this strip. Temperature calibration of the heater was performed with respect to several known phase transitions. Uncertainties in the corrected temperatures are on the order of 2–3 K. X-rays were generated using an Inel XRG3000 generator, and a focused Cu$K\alpha_1$ beam was produced using a crystal monochromator. The diffracted beams were detected using an Inel 4K-PSD position-sensitive detector. Pure Si was used as an internal standard for calibration of the 2θ angles. This calibration considered the changes in 2θ(Si) resulting from thermal expansion. Recording of the diffraction patterns started when the sample reached the target temperature, and each diffraction pattern was collected in <2 h. To check that no irreversible changes took place in the sample on heating, the data for 470, 670 K, etc., were collected during heating of the sample, and the data for 370, 570 K, etc., were collected during cooling.

Lattice parameter refinements were performed using an iterative least-squares procedure for reflections with 2θ ≤ 65°. Typically, 45 reflections were used. The initial basis for indexing the patterns was that given by Kroll et al. (1986). The room-temperature pattern for Or_0 was then used to index the room-temperature pattern for Or_1 and subsequently the other samples in order of increasing Or content. Each of these room-temperature patterns was then used to index the patterns for 370 K, etc., until all the patterns were indexed. This procedure ensured that all the patterns were indexed consistently.

For each sample at each temperature, the Al site occupancies t_{1o}, t_{1m}, and t_2 were calculated from the lattice parameters with use of the equations in Kroll and Ribbe (1987). The values of Q, Q_{OD}, and Q_t were then determined using Equations 1–3. No systematic variation in Q_{OD} or Q_t was found, so an average was taken from all these data. This confirms the idea that short-term heating under dry conditions has no detectable effect on the distribution of Al and Si.

RESULTS

The parameter $\cos^2\alpha$ was found to vary linearly for $T < T_c^*$, and so T_c^* was taken to be the temperature at which this linear extrapolation reached zero. For $T > T_c^*$, the diffraction data implied a monoclinic structure. The graphs for Or_0, Or_1, and Or_8 are shown in Figure 1. Table 1 gives the values of T_c^* for all the samples studied, and Figure 2 shows a phase diagram of these data.

Because a transition to a monoclinic structure was observed, there must be complete macroscopic disorder between the T1o and T1m sites. This result is confirmed by the direct calculation of site occupancies using lattice parameters, which yields $Q_{OD} = 0$ ($t_{1o} = t_{1m}$) to within the experimental error of this method.

However, this result does not rule out the possibility of Al-Si partition between the T1 and T2 sites. As Equations 9 and 10 show, different values of Q_t alter the observed

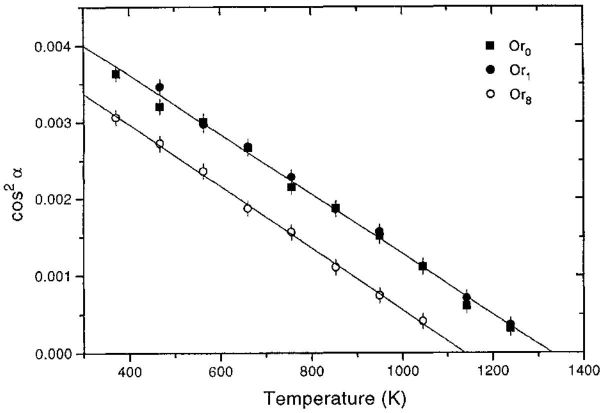

Figure 1. Linear dependence of $\cos^2\alpha$ on temperature for samples Or_0, Or_1, and Or_8. Intermediate samples are omitted for clarity.

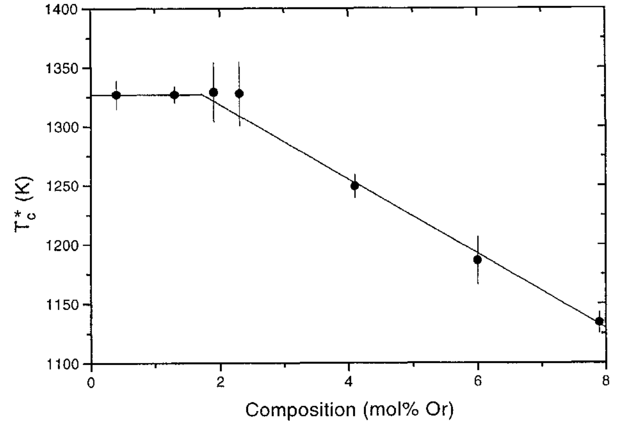

Figure 2. Variation of T_c^* with composition for synthetic anorthoclase. For $X_{Or} < 0.02$, T_c^* is constant. For $X_{Or} > 0.02$, T_c^* is linear with composition.

transition temperature, but the transition remains second order.

To test this prediction, the values of Q_t and T_c^* obtained above for sample Or_0 were compared with those from other studies of analbite. The small amounts of K in some of these samples do not affect T_c^* because they are all well within the plateau regime. The results are shown in Table 2 and Figure 3.

Discussion

The plateau effect and some consequences

The plateau at the Na end of the anorthoclase solid solution extends to a composition of about 2 mol% Or. This is somewhat larger than the estimate in Salje (1995), which predicted that a typical plateau would extend to ~1% of solute.

Other feldspars have even larger plateaus. According to Wood and Redfern (1995), the transition temperature of plagioclase is independent of composition from albite to $Ab_{90}An_{10}$. In the system $Cu_{1-x}Zn_xWO_4$, T_c is constant between $x = 0$ and 0.12 (Redfern et al., in preparation; Redfern and Schofield, in preparation).

Another feature of these results is that the plateau appears to be flat in all these cases; i.e., the transition temperature is independent of composition. This observation implies that the strain fields around each solute atom do not overlap. As a result, most of the crystal is not affected by the defects. This is consistent with the idea that the feldspar framework is made up of almost rigid tetrahedra, with relatively floppy links between the tetrahedra (Dove et al. 1991). In the limiting case of perfectly rigid tetrahedra, the strain fields would be of infinite extent. However, local deformations (such as those around K^+ ions) can be absorbed by the structure over relatively short distances because of distortions within the tetrahedra.

The length scale of this relaxation can be determined from the extent of the plateau ($X = 2\%$). The edge of the plateau corresponds to a ratio of about 1:12 unit cells containing a K^+ ion because there are 4 formula units in the 7 Å cell. For a uniform distribution of K^+ on Na^+ sites, this implies a typical K^+-K^+ separation of just over 2 unit cells.

The strain fields around each K^+ ion just begin to overlap at this composition, which implies that the distorted region around each K^+ ion is 2–2.5 unit cells across (i.e., ~20 Å).

Another example of a crystal structure relaxing around a defect is the thick wall that surrounds a twin boundary. In a separate paper (Hayward et al., in preparation) we show that these appear to be on a similar scale, typically 2–3 unit cells wide at room temperature. Similarly, the surface relaxations observed by Harrison and Salje (1994) in fine-grained anorthoclase powder were approximately 20 Å thick.

The larger plateaus seen in plagioclase and Cu-rich scheelite imply smaller distortion clouds. For example, the 10% plateau in plagioclase corresponds to a solute atom in every other unit cell.

Table 1. Compositions and T_c^* values of synthetic anorthoclase samples used in this study

Sample	mol% Or	T_c^* (K)
Or_0	0.4	1327(12)
Or_1	1.3	1327(7)
Or_{1H}	1.9	1329(25)
Or_2	2.3	1328(27)
Or_4	4.1	1249(10)
Or_6	6.0	1186(20)
Or_8	7.9	1134(9)

Table 2. T_c^* values for the displacive transition in analbite samples with varying Q_t

Source	Q_t	T_c^* (K)
Kroll et al. (1980)	0.12	1257
Okamura and Ghose (1975)	0.02	1203
Wood and Redfern (1995)	0.12	1239
This study	0.22	1327

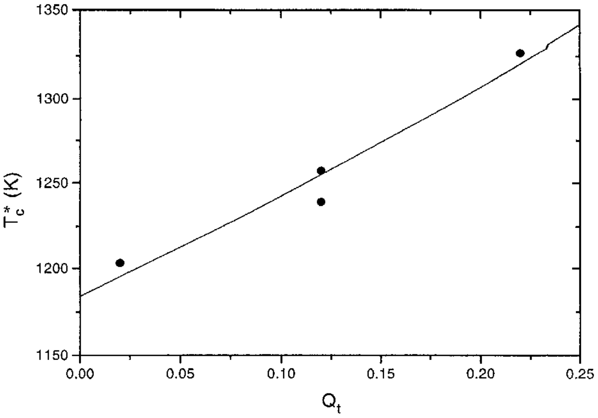

FIGURE 3. Variation of T_c^* with Q_t, showing a best fit to the model in Equation 10.

Strength of Q-Q_t interaction

Equation 11 showed how the observed transition temperature, T_c^*, should vary with Q_t. From this, the strength of the Q-Q_t coupling constant $\lambda_0 T$ can be determined. The best-fit parameters in Figure 3 are $T_c = 1184$ K, $\lambda_0/A = -0.562$. For analbite, A = 8.230 J/(mol·K) (Wood, personal communication), and therefore $\lambda_0 = -4.6$ J/(mol·K). This value of λ_0/A is comparable to that for Q_{OD}-Q_t coupling, −0.490 (Carpenter and Salje 1994). However, the energy of the Q_{OD}-Q_t interaction is much greater because of the large value of A associated with Q_{OD}.

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