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Order-disorder and the high-pressure $P\bar{1}$-$I\bar{1}$ transition in anorthite

R. J. ANGEL

Department of Geological Sciences, University College London, Gower St., London WC1E 6BT, England
and Department of Crystallography, Birkbeck College, Malet St., London WC1E 7HX, England

ABSTRACT

The displacive phase transition in anorthite from the low-pressure $P\bar{1}$ phase to the high-pressure $I\bar{1}$ phase has been followed in five samples with differing degrees of Al,Si order (quantified by Q_{OD}) by single-crystal X-ray diffraction. For natural anorthite ($Q_{OD} = 0.92$) the transition has been bracketed between 2.55 and 2.74 GPa. It displays first-order character with large discontinuities in the unit-cell angles and a ~0.15% decrease in the unit-cell volume at the transition. With increasing disorder ($Q_{OD} = 0.87, 0.85$) the transition is smeared out over a small pressure interval above 2.55 GPa. This is interpreted as arising from heterogeneities in Q_{OD}. With further disorder ($Q_{OD} = 0.82$) the transition becomes continuous with a transition pressure of 4.05(5) GPa, although there is also some evidence for the retention of some defects or residual heterogeneity in Q_{OD} in this sample as well. The most disordered sample studied ($Q_{OD} = 0.78$) transforms to the $I\bar{1}$ phase at 4.8(3) GPa and displays close to second-order behavior below the phase transition. Analysis of the orientation of the spontaneous strains associated with disordering of Al,Si and those associated with the $I\bar{1}$-$P\bar{1}$ transition shows them to be opposed. This accounts for the stabilization of the lower symmetry $P\bar{1}$ phase with decreasing Q_{OD}.

INTRODUCTION

The phase transitions in feldspars have been the subject of intense study not only because of their petrological importance but also because they provide an opportunity to study the interactions between slow order-disorder processes and fast displacive transitions in a material whose structure appears to encourage mean-field behavior.

At room pressure and temperature the structure of anorthite, $CaAl_2Si_2O_8$, displays $P\bar{1}$ symmetry and a unit cell with a *c* axis of ~14 Å. At pressures in excess of 2.5 GPa at room temperature (Angel et al., 1988; Angel, 1988) and at temperatures in excess of 240 °C at room pressure (Brown et al., 1963), anorthite undergoes a displacive phase transition to a structure that has $I\bar{1}$ symmetry. The transition from the high-temperature $I\bar{1}$ phase to the low-temperature $P\bar{1}$ phase is accompanied by changes in the lattice parameters of the crystal. These may be reformulated as a spontaneous strain that arises as a result of the transition.

At much higher temperatures partial disorder of the Al and Si within the tetrahedral framework may be induced and subsequently quenched into the structure (e.g., Bruno et al., 1976; Chiari et al., 1978). The unit-cell parameters of anorthite containing Al,Si disorder differ significantly from those of material with the same composition but with ordered Al,Si. This is true not only of intermediate plagioclase, in which partial disordering is responsible for the well-known high and low series (e.g., Kroll, 1983; Smith and Brown, 1988), but also for end-member anorthite. Detailed studies of the latter (Benna et al., 1985; Carpenter et al., 1990) show that the variations in the state of order are reflected in systematic variations of the unit-cell parameters. These changes in lattice parameters associated with disordering are also quantifiable as a strain. In this case the strain is measured relative to anorthite with a completely disordered Al,Si distribution with $C\bar{1}$ symmetry (Carpenter et al., 1990).

The structure of end-member anorthite at low pressures and temperatures can therefore be modified by two phase transitions that both give rise to lattice strains. Salje (1987) showed that the strains from these transitions are allowed to interact in certain ways, constrained by symmetry considerations, and that the behavior of anorthite at the displacive $P\bar{1}$-$I\bar{1}$ transition should be modified by changes in both the composition and the state of Al,Si order within the structure. The analysis by Salje (1987) was couched in terms of two order parameters which describe the extent of each of the two transitions: Q_{OD} quantifies the state of order, varying from unity for complete Al,Si order to zero for complete disorder, whereas Q_o describes the extent of the distortion arising from the $I\bar{1}$ to $P\bar{1}$ transition. The evolution of these two order parameters with temperature and pressure is modified by the strain-induced coupling (Salje and Devarajan, 1986) between them. Some of the predictions of Salje (1987) were confirmed by a series of experiments on well-ordered material (Redfern and Salje, 1987; Redfern et al., 1988) in which the unit-cell parameters of anorthite were followed through the $P\bar{1}$-$I\bar{1}$ phase transition at temperature. The results of a high-pressure study (Angel et al., 1989) of a

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TABLE 1. Sample data

Sample	T (°C)*	t (d)*	⟨⟨Al-O⟩⟩-⟨⟨Si-O⟩⟩**	Q_{OD}
VP	—	—	0.124	0.92
VP 3	1350 ± 5	21	0.118	0.87
VP 8	1413 ± 4	30.7	0.115	0.85
VP 7	1471 ± 3	7	0.111	0.82
VP 6	1533 ± 5	2.74	0.106	0.78

* These columns give nominal annealing times and temperatures. For complete details see Carpenter et al. (1985) and Angel et al. (1990).

** Difference in grand mean bond lengths (in angstroms) between the Al-rich and Si-rich tetrahedra in the structures as determined by Angel et al. (1990).

number of natural (well-ordered) anorthite samples ranging in composition from An_{100} to An_{89} showed some similarities to the high-temperature behavior, in that the transition becomes thermodynamically more continuous with increasing albite content in the anorthite. However, it is not clear whether this behavior is due directly to the replacement of Ca by Na or to the increase of Al,Si disorder induced by the coupled replacement of Al by Si as the albite content of anorthite is increased. This study of the $P\bar{1}$-$I\bar{1}$ transition in five anorthite samples of the same composition but differing states of Al,Si disorder (i.e., Q_{OD}) was carried out to resolve this question and to test further the applicability of Landau theory to the behavior of the feldspars. The results also provide an example of how small amounts of disorder within a crystal structure can affect dramatically its phase transition behavior at high pressures.

EXPERIMENTAL

The samples used in this study were all produced from the same batch of Val Pasmeda anorthite. The composition, as determined by electron microprobe analysis, corresponds to An_{100} (Carpenter et al., 1985). In addition to the untreated natural material, four batches of the anorthite were annealed at different temperatures between 1300 and 1550 °C so as to induce partial Al,Si disorder. Details of this treatment are provided by Carpenter et al. (1985) for two of the samples used in this study (Val Pasmeda, Val Pasmeda 3); the remainder were subjected to similar treatment but at higher temperatures (Val Pasmeda 8, Val Pasmeda 7, and Val Pasmeda 6; henceforth VP 8, VP 7, etc.). An estimate of the state of Al,Si order within all of these samples was made from the means of T-O bond lengths determined by single-crystal X-ray diffraction and structure refinement (Angel et al., 1990). Most of the experiments described here used the very same crystals as those used for structure determination. A summary of these data is provided in Table 1.

The variation of unit-cell parameters with pressure of each of these five anorthite samples was determined by single-crystal diffraction using Krisel-automated Picker four-circle diffractometers equipped with Mo X-ray sources typically operated at 40 kV/30 mA. Unit-cell parameters at each pressure were determined by vector-least-squares fitting of between ten and 15 (depending on accessibility) reflections between 10 and 18° 2θ, using $\lambda(K\bar{\alpha}) = 0.7107$ Å. In order to prevent crystal-offset errors, diffractometer aberrations, and asymmetric absorption by the diamond cells from systematically affecting the resultant cell parameters, the technique of diffracted-beam centering was employed (King and Finger, 1979). Experiments on samples VP and VP 3 were carried out at the Geophysical Laboratory using a modified Merrill-Bassett diamond-anvil cell (Hazen and Finger, 1982) and a 4:1 methanol : ethanol mixture as a pressure medium. Pressures were determined from the 2θ values of three 220 reflections from a fluorite crystal included within the cell (Hazen and Finger, 1981), using a new equation of state for fluorite (Angel et al., 1992). It is for this reason that, although some of the data for these two samples have been reported before (Angel et al., 1988; Angel and Ross, 1988; Angel et al., 1989), the pressures have been slightly revised. The same type of pressure cell and method of pressure measurement were employed for experiments at UCL for sample VP 8 and the initial experiments on VP 7 and VP 6. The data for these last two samples were supplemented by two sets of further experiments, using the fluorescence shift of ruby as the pressure calibrant. Modified Merrill-Bassett cells were used to obtain data below 5 GPa, and a DXR-4 cell (Diacell Products) was used for experiments to nearly 8 GPa. In the pressure range of 5–8 GPa a <1% increase in the R_1-R_2 split of the ruby fluorescence doublet was observed, indicating that the pressure medium may have become slightly nonhydrostatic (Adams et al., 1976), although no peak broadening was detectable. Unit-cell parameters for the five samples are reported in Table 2,[1] and the unit-cell angles are presented in graphical form in Figure 1. Note that there are no significant discrepancies between the unit-cell parameters of a given crystal determined using either the two different pressure cells or the two methods of pressure measurement. An analysis of the equations of state obtained from these data is presented elsewhere (Hackwell and Angel, 1992).

RESULTS

Unit-cell parameters

Natural Val Pasmeda anorthite undergoes a nonquenchable displacive phase transition between 2.55 and 2.74 GPa. As described by Angel et al. (1988, 1989), the transition from the $P\bar{1}$ to the $I\bar{1}$ phase is most clearly marked by a decrease of ~0.4° in the α and β unit-cell angles and an increase in γ of ~0.7°. There are also small decreases in the unit-cell edges, and together these produce a volume change at the transition of ~0.15% (Fig. 2). Together with the demonstrable hysteresis in the transition, these results show that the transition is thermodynamically first order.

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[1] Table 2 may be obtained by ordering Document AM-92-503 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

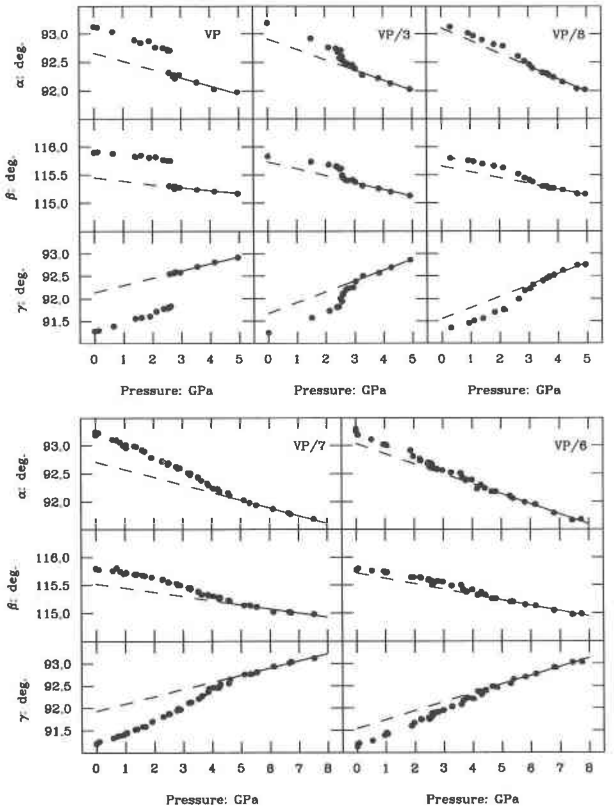


Fig. 1. The variation with pressure of the unit-cell angles of the five samples studied. Symbol size exceeds the experimental estimated standard deviations. The solid lines drawn through the data corresponding to the $I\bar{1}$ phases and continued to lower pressures as dashed lines are those used for extrapolation of the $I\bar{1}$ cell parameters to lower pressures.

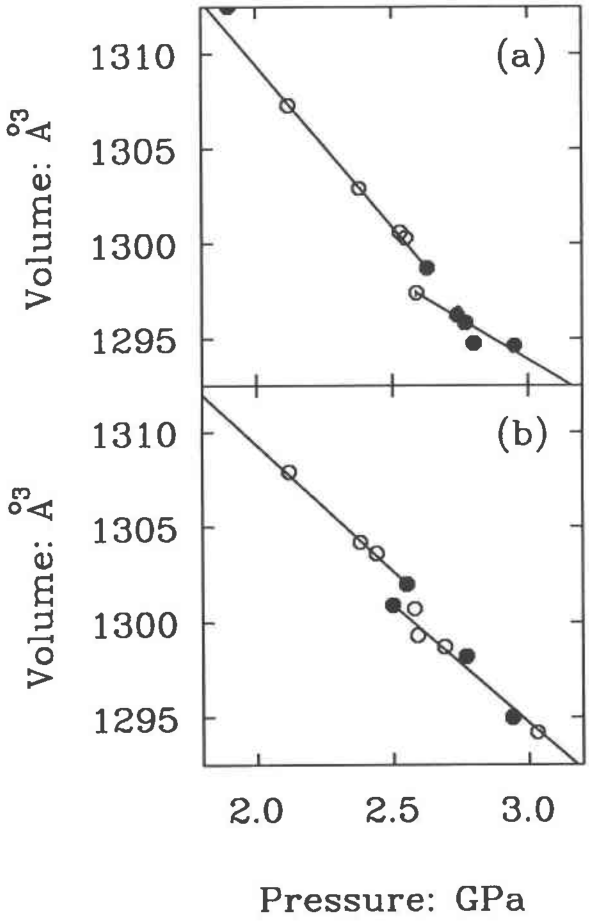


Fig. 2. The unit-cell volumes of **(a)** VP and **(b)** VP 3 in the region of their phase transitions. Symbol size exceeds the experimental estimated standard deviations; filled symbols represent data collected on increasing pressure, open symbols on decreasing pressure.

In the sample with the least amount of induced Al,Si disorder, VP 3, evidence for the same transition is provided by rapid changes with pressure in the unit-cell angles between 2.5 and 3.0 GPa. The magnitudes of the differences between the unit-cell angles of the low-pressure phase and those extrapolated from the high-pressure phase to just below the transition are much smaller than in the natural material: $\Delta\alpha \approx \Delta\beta \approx 0.2°$, $\Delta\gamma \approx 0.3°$. In addition it is clear that instead of a sharp discontinuity at a well-defined transition pressure, these changes are smeared out over the pressure range of 2.5–3.0 GPa (Fig. 1), although there is a suggestion that a sharp volume discontinuity (half the magnitude of that in the VP sample) is retained at the lower end of this pressure range (Fig. 2). These changes in transition character are continued in the next sample, VP 8, with similar differences between the unit-cell angles of the $P\bar{1}$ and $I\bar{1}$ phases below the transition (Fig. 1) but an increased width of transition smear, to 3.3 GPa. By contrast, the unit-cell angles of the two most disordered samples, VP 7 and VP 6, vary nonlinearly with pressure up to ~4.8 GPa where changes to linear trends are accompanied by distinct changes in slope but without any detectable discontinuity. Neither is there any detectable step in either the unit-cell edges or the volumes of these two samples, clearly indicating that the transition has become continuous in character.

Spontaneous strain

Since the phase transition from the high-pressure $I\bar{1}$ phase to the low-pressure $P\bar{1}$ phase does not involve a change in the point-group symmetry, the transition is properly termed nonferroic (e.g., Wadhawan, 1983), and there are no symmetry-breaking components of the spontaneous strain associated with the transition. All components of the spontaneous strain therefore transform as the identity representation, and given that the transition is also anti-ferro-distortive (i.e., a zone-boundary transition in which the primitive unit-cell volume is doubled), these components, ϵ_{ij}, should follow the order parameter of the transition as $\epsilon_{ij} \propto Q_o^2$. In practice, the propagation of the experimental uncertainties associated with the unit-cell determinations at high pressure results in considerable uncertainties in the values of the individual tensor coefficients. However, since there is considerable corre-

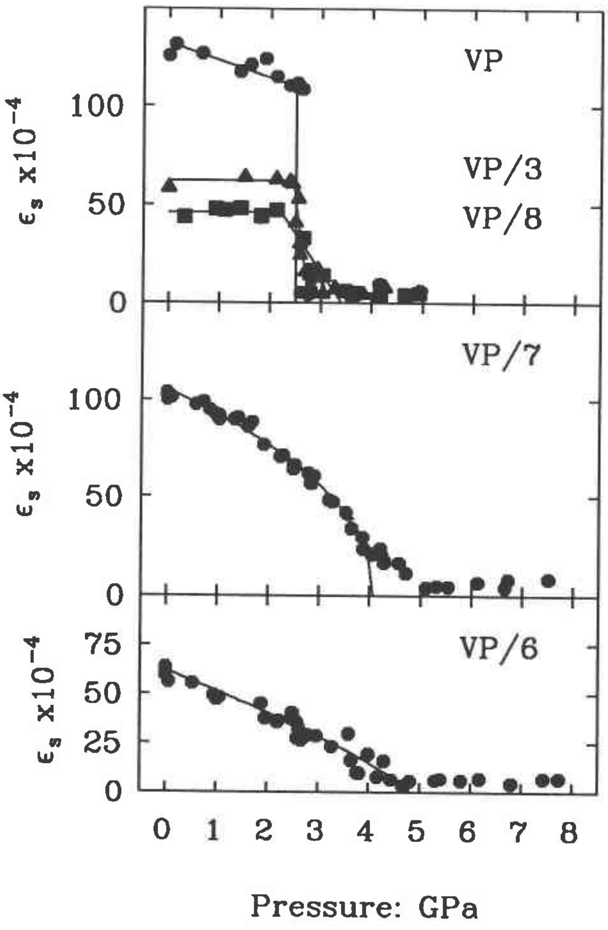


Fig. 3. The variation of the scalar strain, ϵ_s, with pressure for the five samples studied. In each case the magnitude of "ϵ_s" calculated for data points above the transition gives an indication of the uncertainties involved. The lines in the top plot have no significance; those on the VP 7 and VP 6 plots are the fits to the scalar strain reported in the text.

lation between at least some of the estimated standard deviations of the individual unit-cell parameters, the uncertainty in the scalar strain obtained from the diagonalized strain tensor coefficients ϵ_i, $\epsilon_s = \sqrt{\Sigma_i \epsilon_i^2}$ (Aizu, 1970; Redfern and Salje, 1987) is proportionately less than that of individual ϵ_{ij}. For this reason, the relationship $\epsilon_s \propto Q_o^2$ was used to analyze the results of the current high-pressure experiments. This approach was shown by Redfern and Salje (1987) to be suitable for the characterization of the $I\bar{1}$-$P\bar{1}$ transition in ordered Val Pasmeda anorthite at elevated temperature and was applied subsequently to studies of the same transition in anorthite-rich plagioclases at both high temperature (Redfern et al., 1988) and high pressure (Angel et al., 1989) and to partially disordered end-member anorthite at high temperature (Redfern, unpublished data).

The tensor components that represent the spontaneous strain arising from the transition of the high-pressure $I\bar{1}$ phase to the low-pressure $P\bar{1}$ phase were evaluated using the axial conventions described by Schlenker et al. (1978) and the equations of Redfern and Salje (1987). Estimates of the unit-cell parameters of the $I\bar{1}$ phase within the stability field of the $P\bar{1}$ phase were obtained by linear extrapolations of the unit-cell parameters against pressure. A procedure of stepwise analysis was used to ensure that only data clearly obtained within the stability field of the $I\bar{1}$ phase were used as a basis for these extrapolations; intermediate data or those of uncertain affinity were excluded. A practical indication of the uncertainty in ϵ_s values calculated for the various $P\bar{1}$ unit-cell determinations is provided by the values calculated for $I\bar{1}$ unit cells, which in the absence of experimental uncertainties would be identically zero. These are plotted along with the values of ϵ_s for the $P\bar{1}$ unit cells in Figure 3.

The scalar strain of the natural sample, VP, displays a sharp discontinuity just above 2.5 GPa, confirming the first-order nature of the transition. With increasing disorder the decrease in the size of the steps in the unit-cell angles at the transition is reflected in the decreased magnitudes of the steps in the scalar strain (Fig. 3) which, although they too begin at 2.5 GPa, are smeared out to higher pressures. The two most disordered samples, VP 7 and VP 6, exhibit a continuous decrease in ϵ_s with increasing pressure within the $P\bar{1}$ stability field, which allows an estimate of the transition pressure, P_{tr}, to be obtained through fitting the ϵ_s data with a power-law equation of the form

$$\epsilon_s \propto (P_{tr} - P)^{2\beta}. \qquad (1)$$

Whereas the transition pressure obtained for the most disordered sample, VP 6, is 4.8(3) GPa, in good agreement with the pressure at which the variation in unit-cell angles with pressure becomes linear (Fig. 1), the transition pressure of VP 7 obtained by fitting the ϵ_s data, 4.06(5) GPa, is some 0.7 GPa below that point. The scalar strain between 4.0 and 4.7 GPa is also quite clearly nonzero in VP 7 (Fig. 3). This smearing of the transition is similar to that displayed by samples VP 3 and VP 8 and can be interpreted as arising from heterogeneity in the state of Al,Si order within all three samples. The critical exponents, β, obtained from fitting the ϵ_s data are 0.23(1) for VP 7 and 0.40(6) for VP 6. These values indicate that the former exhibits close to tricritical behavior (for which β would be ¼), whereas the latter is intermediate between tricritical and second order (β = ½).

DISCUSSION

The thermodynamic analysis of anorthite-rich feldspars developed by Salje (1987) has been remarkably successful in explaining their behavior at high temperatures. Here it is applied to the changes in transition behavior at high pressure that have been described in this paper. The excess free energy of the $P\bar{1}$ phase relative to a (disordered) $C\bar{1}$ reference state can be expressed in terms of the two order parameters Q_o and Q_{OD}:

$$\begin{aligned} G_{\mathrm{ex}} = {} & \tfrac{1}{2}a_{\mathrm{o}}(T - T_{\mathrm{co}})Q_{\mathrm{o}}^2 + \tfrac{1}{4}b_{\mathrm{o}}Q_{\mathrm{o}}^4 + \tfrac{1}{6}c_{\mathrm{o}}Q_{\mathrm{o}}^6 \\ & + \tfrac{1}{2}a_{\mathrm{d}}(T - T_{\mathrm{cd}})Q_{\mathrm{OD}}^2 + \tfrac{1}{4}b_{\mathrm{d}}Q_{\mathrm{OD}}^4 + \tfrac{1}{6}c_{\mathrm{d}}Q_{\mathrm{OD}}^6 \\ & + e_{\mathrm{o}}\epsilon Q_{\mathrm{o}}^2 + e_{\mathrm{d}}\epsilon Q_{\mathrm{OD}}^2 + f\epsilon^2 \qquad (2) \end{aligned}$$

where T_{co} and T_{cd} are the transition temperatures for the $I\bar{1} \rightarrow P\bar{1}$ and $C\bar{1} \rightarrow I\bar{1}$ transitions in isolation; a, b, and c are constants; e_{o} and e_{d} are the coupling coefficients of the two order parameters Q_{o} and Q_{OD} to the strain; and the coefficient f is a function of the elastic constants of the material. By applying the conditions that the crystal is stress free when in equilibrium and that in a low-temperature experiment the state of Al,Si order stays fixed (i.e., Q_{OD} is constant), the excess free energy, G'_{ex}, of the $P\bar{1}$ phase with respect to the $I\bar{1}$ phase may be derived:

$$\begin{aligned} G'_{\mathrm{ex}} = {} & \tfrac{1}{2}a_{\mathrm{o}}\left(T - T_{\mathrm{co}} - \frac{e_{\mathrm{o}}e_{\mathrm{d}}Q_{\mathrm{OD}}^2}{a_{\mathrm{o}}f}\right)Q_{\mathrm{o}}^2 \\ & + \tfrac{1}{4}\left(b_{\mathrm{o}} - \frac{e_{\mathrm{o}}^2}{f}\right)Q_{\mathrm{o}}^4 + \tfrac{1}{6}c_{\mathrm{o}}Q_{\mathrm{o}}^6. \qquad (3) \end{aligned}$$

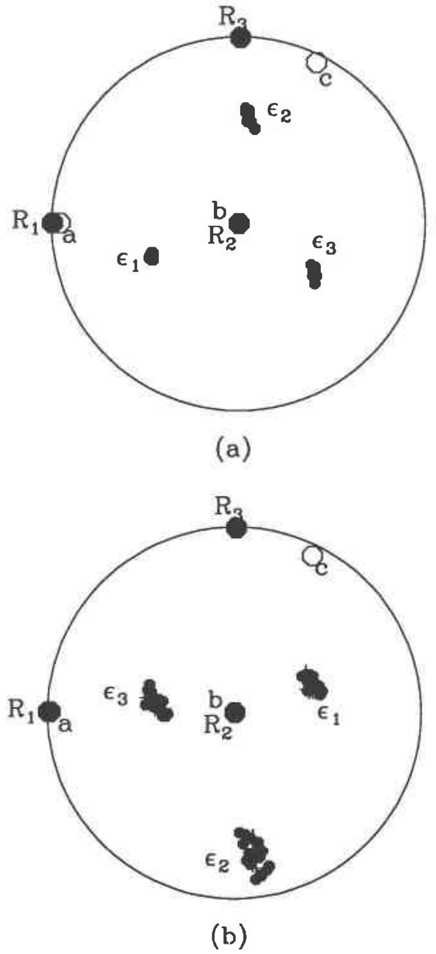
By making the assumption that the excess volume associated with the $I\bar{1} \rightarrow P\bar{1}$ transition, V_{ex}, is proportional to Q_{o}^2 in the same way that the excess entropy, S_{ex}, is assumed to vary with Q_{o}^2, the equation can be rearranged in terms of pressure (Carpenter, 1992) as

$$G'_{\mathrm{ex}} = \tfrac{1}{2}a_{\mathrm{vo}}\left(P - P_{\mathrm{tr}}\right)Q_{\mathrm{o}}^2 + \tfrac{1}{4}\left(b_{\mathrm{o}} - \frac{e_{\mathrm{o}}^2}{f}\right)Q_{\mathrm{o}}^4 + \tfrac{1}{6}c_{\mathrm{o}}Q_{\mathrm{o}}^6 \qquad (4)$$

where the transition pressure, P_{tr}, is a function of both the experimental temperature, T_{exp}, and Q_{OD}:

$$P_{\mathrm{tr}} = \frac{a_{\mathrm{o}}}{a_{\mathrm{vo}}}\left(T_{\mathrm{co}} - T_{\mathrm{exp}} + \frac{e_{\mathrm{o}}e_{\mathrm{d}}Q_{\mathrm{OD}}^2}{a_{\mathrm{o}}f}\right). \qquad (5)$$

The observation that the $P\bar{1}$ phase is stabilized, that is, the pressure of the $P\bar{1} \rightarrow I\bar{1}$ transition is increased by decreasing Q_{OD}, indicates that the coupling between these two order parameters, represented by $e_{\mathrm{o}}e_{\mathrm{d}}/a_{\mathrm{vo}}f$ in Equation 5, is negative. The physical reason for this sign of coupling coefficient is evident from the relative orientations of the principal axes of the spontaneous strain tensors associated with the two phase transitions. As for the $I\bar{1} \rightarrow P\bar{1}$ transition at temperature (Redfern and Salje, 1987; Redfern et al., 1988), the strain associated with the transition at high pressure is approximately planar, with the two nonzero principal axes oriented close to the (001) plane (Fig. 4a). The axis representing a positive value of strain lies between the [100] and [010] directions. The spontaneous strain arising from ordering associated with the $C\bar{1} \rightarrow I\bar{1}$ transition was determined by Carpenter et al. (1990). Although this strain is not planar, the two axes of the strain ellipsoid with largest magnitudes are also oriented quite close to the (001) plane (Fig. 4b). However, the sense of this strain is reversed in comparison with that of the $P\bar{1} \rightarrow I\bar{1}$ transition; the direction of the negative principal strain lies approximately between [100] and [010]. The strain arising from ordering therefore opposes that arising from the $P\bar{1} \rightarrow I\bar{1}$ transition, decreasing the stability of the $P\bar{1}$ phase. As the state of order is decreased, however, the magnitude of the strain arising from the $C\bar{1} \rightarrow I\bar{1}$ transition is decreased, so it becomes easier for the structure to deform as a result of the $I\bar{1} \rightarrow P\bar{1}$ transition and the stability field of the $P\bar{1}$ phase is thereby expanded. This behavior is in direct contrast with that of albite and albite-rich alkali feldspars (Salje, 1985; Salje et al., 1985) in which the displacive and ordering transitions couple in such a way that the low-symmetry phase is stabilized by increasing Al,Si order.



(a)

(b)

Fig. 4. Stereograms showing the orientation of the principal strains for the (**a**) $I\bar{1} \rightarrow P\bar{1}$ in sample VP at pressure and (**b**) $C\bar{1} \rightarrow I\bar{1}$. Data for the latter are taken from Carpenter et al. (1990), in which paper the stereogram was incorrectly plotted because a left-handed axial set was used. R_1, R_2, and R_3 represent the poles of the orthogonal axial set used in calculating the strain tensor.

In addition to the large changes in the $P\bar{1}$-$I\bar{1}$ transition pressure that accompany disordering of Al and Si within anorthite, there is also a change in transition character from first order in the natural sample to a smeared first-order step in VP 3 and VP 8. Consideration of Equations

4 and 5 shows that changes in a homogeneous Q_{OD} cannot be responsible for changing transition character, as this is determined by the signs and magnitudes of the coefficients of Q_o^4 and Q_o^6. However, in his analysis of the high-temperature behavior of anorthite (corresponding to Eq. 3 above), Salje (1987) was able to show that smearing of the transition should occur when the state of Al,Si order becomes heterogeneous on the length scale of a few hundred angstroms. The same analysis is directly applicable to the transformations at high pressure because of the similarity of form of Equations 3 and 4. If each structural block of homogeneous order were completely isolated from the rest of the crystal, it would undergo the $P\bar{1}$-$I\bar{1}$ transition at a specific pressure determined by its local Q_{OD}. In reality, the structural blocks are all part of the same tetrahedral framework, so the behavior of each is modified by the strain field of its neighbors. The macroscopic behavior of the crystal, as reflected in the unit-cell parameters and the derived ϵ_s, results from the coupling, through the strain, of all of these blocks. These inferences about the homogeneity of the several samples studied here are reasonable in the light of their different thermal histories. Whereas the natural VP sample has experienced a long, low-temperature thermal history and therefore has developed a constant state of Al,Si order throughout the crystal, the VP 3 and VP 8 samples were quenched from high temperature. It is therefore quite conceivable, as noted by Carpenter et al. (1990), that either a fully homogeneous state of Al,Si order was not attained in these samples during the high-temperature treatment or that partial reordering occurred during the quenching procedure.

The analysis of Salje (1987) also suggests that such a change in the thermodynamic character of the $I\bar{1} \rightarrow P\bar{1}$ transition could be induced by a further reduction in the correlation length of the state of Al,Si order within the crystals below that which gives rise to the smearing of the transition. Such a process appears to be responsible for the change to continuous transition behavior observed in the two samples annealed at the highest temperatures. Alternative explanations for these changes in transition character include the possible coupling of Q_o with another displacive phase transition or that V_{ex} may not be proportional to Q_o^2. The final resolution of this question requires further experimental data.

Finally, the comparison of the high-pressure behavior of the end-member anorthite described here with that of anorthite-rich plagioclase (Angel et al., 1989) provides some insight into the relative importance of Al,Si order and the substitution of Na for Ca in determining the structural behavior of plagioclase feldspars. Both sets of samples display an increase in the $P\bar{1} \rightarrow I\bar{1}$ transition pressure as the state of Al,Si order is decreased, together with a trend from first-order character to a more continuous transition. This similarity in behavior suggests that it is the state of Al,Si order that is the dominant factor in determining the behavior of anorthite-rich plagioclase feldspars and that the substitution of Na for Ca merely provides a mechanism, through the coupled substitution of Si for Al, for inducing further Al,Si disorder.

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