

## Reversed brackets for the $P\bar{1} = I\bar{1}$ transition in anorthite at high pressures and temperatures

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### ABSTRACT

The  $P\bar{1}$  to  $I\bar{1}$  phase transition in end-member anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , has been reversed in-situ at high pressures and temperatures in an internally heated diamond-anvil pressure cell using single-crystal X-ray diffraction. The unit-cell parameters of anorthite were determined at 48 temperature-pressure points up to 255 °C and 2.6 GPa.

At high pressures and temperatures, from room temperature up to ~225 °C, the transition is marked by a first-order step in the unit-cell volume and the complete disappearance of  $c$  and  $d$  reflections from the diffraction pattern. From room temperature to ~195 °C and 2.1 GPa, the transition boundary is linear and nearly isobaric, with a slope,  $dP/dT$ , of  $-0.003$  GPa/°C. From 195 to 240 °C and 1.5 GPa the boundary is curved, with increasingly negative  $dP/dT$ , and the magnitudes of  $\Delta V$  and the scalar strain associated with the transition decrease to about 75% of their high-pressure values of ~0.2 and ~0.011%. From 1.5 GPa to room pressure, the boundary is isothermal at 240 °C and is marked by the disappearance of the  $c$  and  $d$  reflections, although there are no detectable discontinuities in the unit-cell parameters. The phase transition remains unquenchable over the entire boundary.

The distinct changes in character of the phase transition and the trajectory of the equilibrium boundary in  $P$ - $T$  space are associated with a crossover in the  $I\bar{1}$  phase field that is marked by a sudden change in cell parameters of this phase over the pressure interval of ~1.5–2.0 GPa.

### INTRODUCTION

Well-ordered end-member anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , has symmetry  $P\bar{1}$  at room temperature and pressure. On heating to above 240 °C, anorthite undergoes a phase transition to a structure with  $I\bar{1}$  symmetry, as evidenced by the disappearance from the diffraction pattern of the superstructure reflections with indices  $h + k = \text{even}$ ,  $l = \text{odd}$  and  $h + k = \text{odd}$ ,  $l = \text{even}$  (denoted  $c$  and  $d$  reflections: Bown and Gay, 1958). This transition at room pressure was first reported by Brown et al. (1963) and has subsequently been studied quite extensively. The transition is essentially displacive in structural terms, there being no change in the primary coordination of any of the atoms and no change in the distribution of the Al and Si atoms among the tetrahedral sites. Extensive studies of this transition have been undertaken to characterize its thermodynamic nature. The evolution of the unit-cell parameters with temperature has been used to demonstrate that the transition is close to being tricritical in the Landau sense (Redfern and Salje, 1987) in the well-ordered end-member, and that the elastic component of the intensities of the superstructure  $c$  and  $d$  reflections also follows tricritical behavior (Adlhart et al., 1980; Redfern

and Salje, 1987). The diffraction experiments of Adlhart et al. (1980) also demonstrated that the persistence of the intensities of the  $c$  and  $d$  reflections in a weakened state reported by Laves et al. (1970), Czank et al. (1970), Czank (1973), and Ghose et al. (1993) is due to inelastic processes or weak fluctuations within the crystal structure just above the transition. Infrared modes of the  $I\bar{1}$  phase show excess broadening, but it is restricted to an interval of 100 K above the transition temperature at room pressure (Redfern and Salje, 1992), indicating that whatever dynamic component is involved in the structure just above the transition dies out at higher temperatures. The question as to whether these dynamic fluctuations involve the tetrahedral framework and are a driving force for the transition, as suggested by Ghose et al. (1988), or whether they are just a secondary process, such as correlated Ca motion within the cavities of an essentially static framework, as suggested by the NMR observations of Staehli and Brinkmann (1974) and Phillips (1990), has yet to be resolved. Certainly the high-temperature structure determinations by Czank (1973), Foit and Peacor (1973), and Ghose et al. (1993) did show split sites for the Ca atoms that resemble an average of the  $P\bar{1}$  sites, but it must be remembered that the diffraction intensities used to refine the structures include the non-Bragg component identified by Adlhart et al. (1980).

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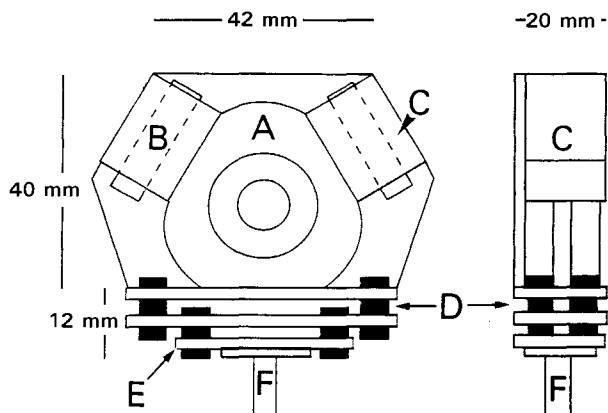


Fig. 1. The heated DAC used for these experiments. A = modified Merrill-Bassett type diamond-anvil cell, with  $B_4C$  seats. B = 150-W cartridge heater. C = brass block containing cartridge heater and control thermocouple (not shown). D = ceramic spacers for insulation. E = metal mounting plates. F = mounting pin to fit standard goniometer head.

High-pressure studies (Angel et al., 1988, 1989; Angel, 1988, 1992) have revealed that the application of pressure to the anorthite structure at room temperature also results in a phase transition to a structure with  $\bar{I}\bar{I}$  symmetry, the same as that observed at high temperatures. The pressure at which this transition occurs has been shown to increase with the albite content of the anorthite (Angel et al., 1989) and with the degree of disorder of the Al and Si within the tetrahedral framework of the structure (Angel, 1992). For well-ordered end-member anorthite, the transition occurs between 2.55 and 2.74 GPa at room temperature, but, in contrast to the continuous nature of the  $P\bar{I}$  to  $\bar{I}\bar{I}$  transition at high temperatures, it is first order in character with a  $\sim 0.2\%$  volume change and demonstrable hysteresis. Nevertheless, the transition is nonquenchable on the time scale of the X-ray experiments, and the high-pressure phase cannot be recovered to room pressure. The structure of the high-pressure phase, in contrast to that at high temperatures, shows single sites for the Ca atoms within a framework with true  $\bar{I}\bar{I}$  symmetry (Angel, 1988).

We have now undertaken a series of in-situ measurements of the cell parameters of end-member anorthite at simultaneous high pressures and temperatures to determine by in-situ reversals whether the phase transitions at high pressure and at high temperature are related.

#### EXPERIMENTAL METHODS

All experiments were performed in a modified Merrill-Bassett type diamond-anvil cell with heating provided by two commercial 150-W miniature cartridge heaters contained within external brass blocks clamped to the pressure cell (Fig. 1), driven by a PID-type controller. Feedback for control of the heater power was provided by a thermocouple buried within one of the heater blocks, and sample temperatures were taken from a thermocouple

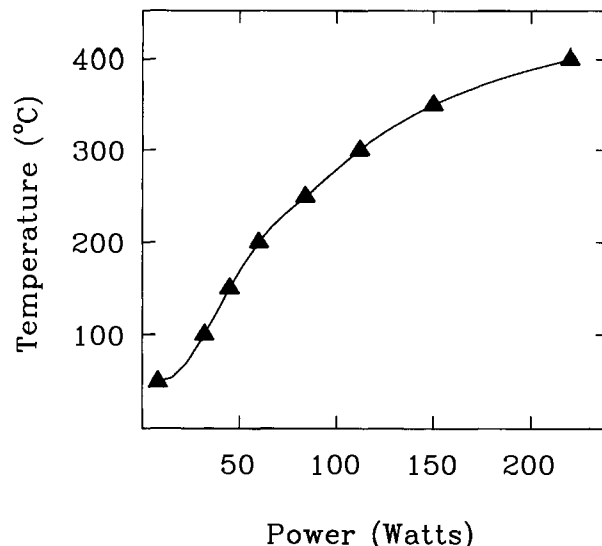


Fig. 2. Sample temperature within the heated DAC as a function of heater power.

welded to the gasket close to the sample position. Measurements with thermocouples distributed across the gasket and fixed to the diamond anvils showed that no temperature gradients of more than  $\pm 2^\circ C$  exist across the central part of the cell. This lack of thermal gradients is the advantage of this experimental arrangement, compared with the use of smaller wire-wound heaters around the anvils themselves (Hazen and Finger, 1981; Ogata et al., 1987). However, the larger separation of the heaters from the sample position, coupled with the need to keep thermal insulation to a minimum to maintain X-ray access, does result in larger fluctuations in sample temperature compared with the Hazen and Finger (1981) design: we measured temperature fluctuations of  $\pm 7^\circ C$  at the sample position in our cell during rotation of the cell on the diffractometer. A power vs. sample temperature curve for the assembly is shown in Figure 2.

The Be platens normally used as backing plates for the diamond anvils cannot be used for high-temperature experiments, and these were replaced by sintered boron carbide platens. Finite-element strain calculations (Adams et al., 1993) indicated that these would be catastrophically weakened by the drilling of an axial hole for optical access to the cell, and so undrilled platens were employed. This gave rise to the major experimental difficulty with this cell, that of having to load and pressurize the cell blind. On the basis of our experience, we would recommend in the future the use of other materials, such as steel (Ogata et al., 1987) or tungsten carbide, for the platens of heated pressure cells, even for single-crystal studies, drilled with conical holes to provide both optical and X-ray access to the sample. These would have the additional advantage of extending the pressure range of the cell beyond the  $\sim 3$ -GPa limit at which the undrilled  $B_4C$  platens break.

The crystals used for this study were taken from a batch of Val Pasmada anorthite supplied to us by M. A. Carpenter. This anorthite has been extensively characterized by calorimetry (Carpenter et al., 1985), NMR (Kirkpatrick et al., 1987), and single-crystal diffraction (Angel et al., 1990). It has essentially end-member composition (An content =  $99.5 \pm 0.5$  mol%; Carpenter et al., 1985) and contains about 4% Al-Si disorder on the tetrahedral sites (Angel et al., 1990). The room-pressure temperature evolution of the heat capacity, unit-cell parameters, and infrared modes of this anorthite through the  $P\bar{I}$  to  $\bar{I}\bar{I}$  phase transition at 240 °C were reported by Wruck (1986), Redfern and Salje (1987), and Redfern and Salje (1992), respectively. Single crystals were loaded into the high-pressure cell by gluing them to one of the diamond-anvil faces with a diluted high-temperature cement. Unit-cell parameters measured from a crystal loaded in this way without pressure fluid showed that the evolution of anorthite cell parameters with temperature followed that reported by Redfern and Salje (1987) at room pressure. The cell parameters measured in this cell at high pressure and ambient temperature agree with those reported in Angel (1992), who used a conventional Merrill-Bassett diamond-anvil cell. These observations indicate (1) that our temperature measurements are correct, and (2) that the method of mounting the sample has no significant effect on the behavior of the anorthite. The hydrostatic pressure medium used was the conventional 4:1 methanol to ethanol mixture, and pressure was determined from the temperature and the lattice parameters of a fluorite crystal included in the cell, through the equation of state for  $\text{CaF}_2$  (Angel, 1993). Note that the choice of whether  $K'$  in the equation of state of  $\text{CaF}_2$  is constant or a function of temperature (Angel, 1993) makes no significant difference to the calculated pressures. Reported pressures are estimated to have a precision of  $\pm 0.08$  GPa, derived from the uncertainty in measured fluorite unit-cell volumes and the normal temperature fluctuation during an experiment. An indication of the accuracy of these pressures, at least at moderate temperatures, is provided by the consistency of the reversals in this  $P$ - $T$  cell with those obtained at room temperature in a conventional Merrill-Bassett cell (Angel et al., 1988; Angel, 1992) in which pressures were determined by the ruby fluorescence method.

The diffraction measurements were performed on a Picker four-circle diffractometer, equipped with a Mo X-ray tube from which  $K\alpha$  radiation ( $\lambda = 0.7093$  Å) was obtained by use of a  $\beta$  filter. Apart from additional baffles and insulation to prevent heating of the  $\chi$  circle, the experimental configuration resembled that described by Hazen and Finger (1982). The diffractometer was operated in fixed- $\phi$  mode (Hazen and Finger, 1982), and the crystal was mechanically centered on the diffractometer by iteratively using the calculated crystal offset errors from the results of the eight-position centering technique of King and Finger (1979) applied to selected strong reflections from the anorthite crystal. Once the offset errors

were reduced to negligible levels, the cell was heated to the desired temperature and allowed to equilibrate, and then the unit cells of the fluorite and the anorthite crystals were determined by the eight-position centering technique, which allows small residual offset errors and diffractometer aberrations to be eliminated from the determination of cell parameters. Fluorite cell volumes, and hence pressures, were determined both before and after each anorthite unit-cell determination.

The unit-cell parameters of anorthite were determined at 48 temperature-pressure points (Table 1), in addition to the room-pressure data described above. The mechanical characteristics of the pressurized diamond cell dictate that increasing temperature also results in a small increase in pressure, at a rate of approximately 0.0025 GPa/°C, such that data are collected on lines of slightly positive slope  $dP/dT$ . In addition, it was found difficult to maintain pressure within the cell in experiments that started at pressures below  $\sim 1.0$  GPa and at the highest temperatures achieved, and so data are sparse at pressures below 1.5 GPa.

## RESULTS

At high pressures and low temperatures the phase boundary is marked by significant discontinuities in the unit-cell angles of anorthite and the complete disappearance of the  $c$  and  $d$  reflections within the  $\bar{I}\bar{I}$  phase field, as was reported for room-temperature experiments (Angel, 1988, 1992). The changes in unit-cell angles at the transition give rise to a small volume change, of the order of 0.2% at room temperature (Angel et al., 1988) and significant spontaneous strain. The magnitude of the scalar strain (Redfern and Salje, 1987) accompanying the transition is shown as a function of transition temperature in Figure 3. The magnitude of the scalar strain calculated from pairs of adjacent data points across the transition remains essentially constant from room temperature up to  $\sim 225$  °C, 1.8 GPa, showing that the transition remains first-order in character. Despite the first-order step in the strain there is no evidence for significant hysteresis at the phase transition, at least within the precision of the temperature and pressure measurements, and all data points, whether true reversals or not, are therefore plotted in Figure 4. Up to temperatures of  $\sim 200$  °C the transition boundary is linear and near-isobaric, with a  $P$ - $T$  slope of  $-0.003$  GPa/°C.

The tight reversals on the boundary between  $\sim 225$  and  $\sim 240$  °C show that the boundary has increasing slope,  $dP/dT$ , over the  $P$ - $T$  range 195 °C and 2.1 GPa to 240 °C and 1.5 GPa with increasing temperature (Fig. 4). This is due to rapid changes in the unit-cell parameters of the  $\bar{I}\bar{I}$  phase in this temperature interval, the most obvious of which is the  $\gamma$  angle whose variation is displayed in Figure 5. These changes in unit-cell parameters lead to an increase in volume of the  $\bar{I}\bar{I}$  phase relative to that of the  $P\bar{I}$  phase, whose cell parameters are relatively invariant over its entire stability field (e.g., Fig. 5). The magnitude of  $\Delta V (= V_{\bar{I}\bar{I}} - V_{P\bar{I}})$  for the transition  $P\bar{I}$  to  $\bar{I}\bar{I}$

TABLE 1. Cell parameters of the  $P\bar{1}$  and  $\bar{1}\bar{1}$  phases

$P$ (GPa)	$T$ (°C)	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	$V$ (Å <sup>3</sup> )
<b><math>P\bar{1}</math> phase</b>								
1.23	21	8.125(3)	12.822(8)	14.097(10)	92.89(9)	115.82(3)	91.55(5)	1318.3(1.3)
2.31	21	8.084(3)	12.778(4)	14.042(4)	92.74(3)	115.77(2)	91.74(3)	1302.6(7)
2.47	21	8.084(3)	12.785(4)	14.039(3)	92.72(2)	115.74(2)	91.77(3)	1303.3(7)
2.32	60	8.089(3)	12.784(5)	14.040(5)	92.74(3)	115.73(3)	91.70(4)	1304.3(8)
2.49	60	8.087(2)	12.780(5)	14.039(4)	92.71(3)	115.73(2)	91.77(3)	1303.4(7)
2.35	71	8.086(3)	12.792(4)	14.034(4)	92.79(3)	115.75(2)	91.72(3)	1303.8(7)
2.37	72	8.088(3)	12.78(4)	14.037(4)	92.75(3)	115.75(2)	91.73(3)	1303.4(7)
2.33	92	8.090(5)	12.788(6)	14.045(7)	92.75(5)	115.70(4)	91.72(6)	1305.6(1.3)
2.37	93	8.092(3)	12.783(4)	14.041(5)	92.71(3)	115.70(2)	91.72(3)	1305.1(7)
2.11	142	8.097(3)	12.781(3)	14.055(4)	92.74(3)	115.76(2)	91.74(4)	1306.4(7)
2.14	163	8.103(4)	12.791(3)	14.053(5)	92.75(5)	115.74(3)	91.72(6)	1308.4(8)
1.97	176	8.101(5)	12.804(8)	14.056(7)	92.65(6)	115.68(4)	91.85(7)	1310.3(1.2)
1.31	188	8.131(2)	12.817(7)	14.098(6)	92.92(5)	115.72(2)	91.58(3)	1319.9(9)
1.75	197	8.117(4)	12.804(7)	14.071(9)	92.87(6)	115.71(4)	91.61(5)	1314.0(1.1)
1.87	198	8.108(4)	12.812(7)	14.069(7)	92.72(6)	115.72(3)	91.55(6)	1313.3(1.1)
1.35	206	8.136(2)	12.823(9)	14.093(7)	92.83(5)	115.75(3)	91.67(3)	1320.6(1.1)
1.62	211	8.117(4)	12.796(6)	14.075(5)	92.80(4)	115.70(3)	91.64(5)	1313.7(9)
1.95	211	8.113(8)	12.803(6)	14.069(14)	92.82(13)	115.68(7)	91.70(11)	1313.3(1.8)
1.75	212	8.130(5)	12.837(6)	14.078(9)	92.80(6)	115.70(4)	91.61(6)	1320.3(1.2)
1.63	220	8.119(5)	12.818(12)	14.071(7)	92.94(8)	115.73(4)	91.60(7)	1315.4(1.5)
1.05	230	8.141(7)	12.838(11)	14.109(12)	92.89(10)	115.64(6)	91.75(10)	1325.5(1.9)
1.39	230	8.141(3)	12.827(9)	14.106(4)	92.84(4)	115.69(2)	91.70(5)	1323.6(1.1)
1.40	230	8.130(5)	12.822(6)	14.085(7)	92.74(6)	115.73(4)	91.61(7)	1319.2(1.1)
1.70	232	8.115(8)	12.815(5)	14.087(12)	92.97(10)	115.70(6)	91.44(11)	1316.3(1.6)
1.08	233	8.140(3)	12.845(2)	14.111(6)	92.96(5)	115.68(3)	91.51(4)	1325.9(7)
1.08	245	8.142(4)	12.828(6)	14.103(6)	92.95(6)	115.69(3)	91.55(6)	1323.7(1.0)
1.38	245	8.130(7)	12.811(2)	14.090(11)	92.81(10)	115.69(6)	91.63(10)	1319.0(1.5)
<b><math>\bar{1}\bar{1}</math> phase</b>								
2.49	71	8.064(2)	12.762(4)	13.995(4)	92.29(3)	115.28(2)	92.52(3)	1298.4(6)
2.57	93	8.068(3)	12.761(4)	13.998(4)	92.30(3)	115.26(2)	92.44(3)	1299.5(7)
2.36	93	8.069(3)	12.768(5)	14.003(5)	92.35(3)	115.31(3)	92.44(4)	1300.2(8)
2.35	98	8.078(4)	12.778(5)	14.015(6)	92.37(4)	115.27(3)	92.38(4)	1304.2(9)
2.50	101	8.065(4)	12.773(6)	14.006(5)	92.34(4)	115.35(3)	92.47(4)	1299.9(9)
2.38	111	8.075(4)	12.778(5)	14.016(6)	92.36(4)	115.26(3)	92.38(5)	1304.0(1.0)
2.43	123	8.070(3)	12.764(4)	14.004(5)	92.35(3)	115.25(3)	92.39(3)	1300.9(7)
2.27	168	8.075(5)	12.771(4)	14.025(7)	92.58(7)	115.27(4)	92.32(7)	1303.6(1.1)
2.18	174	8.082(3)	12.778(6)	14.027(3)	92.47(3)	115.30(2)	92.49(4)	1305.4(8)
2.30	178	8.085(4)	12.782(3)	14.031(4)	92.43(3)	115.33(3)	92.27(4)	1306.7(7)
2.15	184	8.092(2)	12.783(5)	14.037(5)	92.51(4)	115.35(2)	92.22(3)	1308.2(0.8)
2.16	189	8.095(4)	12.784(3)	14.039(9)	92.47(6)	115.34(4)	92.34(5)	1308.9(1.0)
2.08	195	8.090(3)	12.784(9)	14.032(5)	92.39(5)	115.38(3)	92.28(5)	1307.5(1.1)
2.30	198	8.082(7)	12.776(16)	14.018(10)	92.54(14)	115.31(5)	92.23(15)	1304.5(2.1)
2.17	209	8.090(6)	12.781(7)	14.027(8)	92.50(6)	115.30(5)	92.30(8)	1307.3(1.3)
1.84	226	8.097(5)	12.785(2)	14.047(8)	92.43(7)	115.38(4)	92.19(8)	1310.0(1.6)
2.29	228	8.093(7)	12.796(10)	14.034(10)	92.43(8)	115.25(5)	92.30(9)	1310.4(1.7)
1.71	234	8.113(11)	12.795(4)	14.073(15)	92.54(10)	115.46(9)	91.95(14)	1315.4(2.2)
1.74	240	8.116(4)	12.852(46)	14.071(5)	92.63(10)	115.49(3)	91.80(12)	1321.1(4.8)
1.08	255	8.142(7)	12.821(5)	14.100(9)	92.77(7)	115.60(5)	91.82(9)	1323.5(1.4)
1.15	255	8.140(5)	12.835(20)	14.098(7)	92.65(7)	115.68(3)	91.76(8)	1324.1(2.3)

therefore decreases, and hence  $dP/dT (= \Delta S/\Delta V)$  increases in magnitude, with increasing temperature. These changes in unit-cell angles are also responsible for the decrease of the size of the first-order step in scalar strain at 1.5 GPa to ~75% of its value at lower temperatures (Fig. 3).

At a temperature of ~230–240 °C, where the changes in unit-cell angles of the  $\bar{1}\bar{1}$  phase are most rapid (Fig. 5), the phase boundary appears to become essentially isothermal. In this regime the phase boundary is not marked by any significant discontinuity in cell parameters, but we were able to distinguish experimental points within the  $P\bar{1}$  stability field by carrying out  $\omega$  scans with the four-circle diffractometer at the calculated positions of  $c$  and  $d$  reflections. The  $P\bar{1}$  field is identified by the presence of

sharp but weak reflections at these positions, and the  $\bar{1}\bar{1}$  field by their complete absence; at 255 °C and 1.1 GPa there was no evidence for even diffuse intensity at the  $c$  and  $d$  positions, such as that observed at room pressure (e.g., Laves et al., 1970; Czank et al., 1970; Czank, 1973). The position of this portion of the boundary is constrained by the tight reversal at 230 °C and 1.7 GPa and the previously reported room-pressure inversion temperature of 240 °C for this material (e.g., Redfern and Salje, 1987; Wruck, 1986). In addition, our data at 1.1 GPa provide a reversed bracket between 230 °C (two data points) and 255 °C (two data points). The two data points at 245 °C, 1.1 and 1.4 GPa, appear on the basis of the presence of sharp  $\bar{1}\bar{1}\bar{1}$  (i.e.,  $c$ -type) reflections to be within the  $P\bar{1}$  stability field. However, it is quite possible that

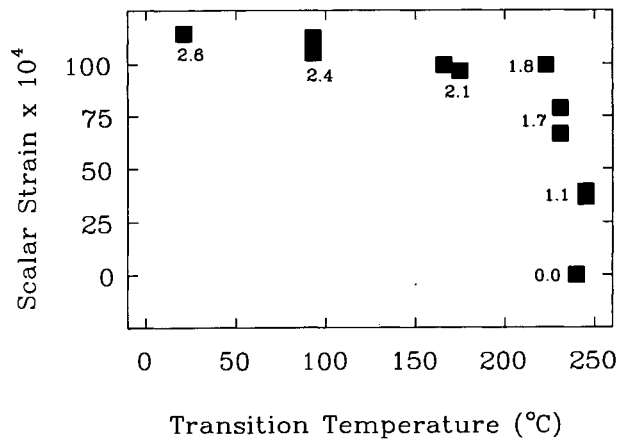


Fig. 3. The variation of the scalar spontaneous strain (as defined by Redfern and Salje, 1987) at the  $P\bar{1} = \bar{1}I$  transition calculated from closely spaced pairs of data points on either side of the transition line. Points are plotted against the temperature of the transition line between the two data points, and the numbers on the diagram give pressures of the transition line at that point.

the uncertainty and fluctuations in the temperature of the experiment may mean that the true sample temperatures were slightly less than that of the boundary at the time at which the superstructure positions were scanned.

#### DISCUSSION

Our experimental data show that the  $P\bar{1} = \bar{1}I$  phase transition previously observed in anorthite at high pressure does lie upon the same equilibrium phase boundary as the room-pressure transition with the same symmetry change previously investigated by many workers. However, the phase boundary that we have determined for the transition in anorthite has some unusual features for what initially appears to be a single phase transition that does not involve a fluid phase. Of especial note is the fact that the boundary appears to be almost linear and isobaric over a substantial temperature range at high pressures, whereas it is essentially isothermal over a pressure range of 1.7 GPa at high temperatures. This is in contrast to other displacive transitions, which usually have linear transition lines over wide ranges of pressure and temperature (e.g.,  $\text{BiVO}_4$ : Wood et al., 1980; Hazen and Marthas, 1982). The behavior that we have observed therefore provides a stringent test of thermodynamic models for the behavior of anorthite, as well as constraining ideas about the microscopic nature of the transitions.

#### Microscopic mechanisms

The single-crystal structure determinations at pressures just below and just above the  $P\bar{1}$  to  $\bar{1}I$  transition at room temperature show that it mostly involves the tilting of the essentially rigid tetrahedra that make up the framework of the structure (Angel, 1988). Accompanying this change in framework conformation is the apparent re-

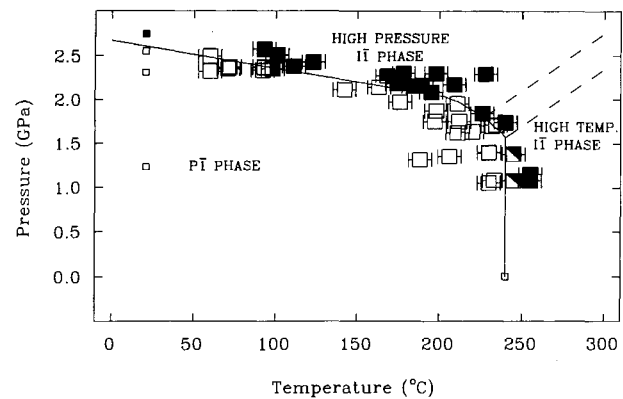


Fig. 4. Phase diagram for the  $P\bar{1} = \bar{1}I$  transition in anorthite. The experimental data points are shown by the squares with error bars; solid symbols are in the  $\bar{1}I$  stability field, open symbols in the  $P\bar{1}$  stability field at 245 °C, and their significance is discussed in the text. The length of the error bars indicates a maximum fluctuation in temperature of  $\pm 7$  °C, and the vertical size of the symbol the  $\pm 0.08$  GPa uncertainty in pressure determination. The pair of dashed lines delineates the region of rapid change in the cell angles of the  $\bar{1}I$  structure shown in Fig. 5.

striction of the Ca atom to a single site within each of the cavities in the framework (Angel, 1988). By contrast, single-crystal structural studies (Ghose et al., 1993) in the neighborhood of the  $P\bar{1}$  to  $\bar{1}I$  transition at high temperature (and room pressure) show dispersed or split sites for the Ca atoms, although the framework is virtually body-centered. Ghose et al. (1993) were also able to show

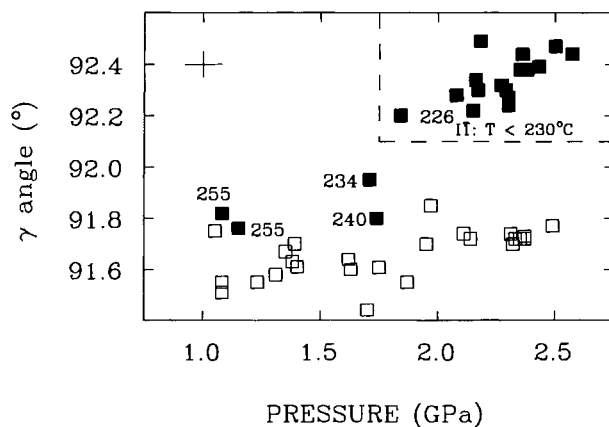


Fig. 5. Variation in the  $\gamma$  unit-cell angle of anorthite with temperature and pressure. Solid symbols are data from the  $\bar{1}I$  stability field, open symbols from the  $P\bar{1}$  stability field. Numbers on the diagram indicate the temperature at which the data were collected. Experimental uncertainties are indicated by the cross in the top left corner. Note that the  $\gamma$  angle of the  $P\bar{1}$  phase remains essentially constant and independent of temperature across its entire stability field, whereas that of the  $\bar{1}I$  phase changes rapidly between 240 and 225 °C, indicating that the  $\bar{1}I$  phase undergoes a crossover or phase transition in this  $P$ - $T$  interval.

that, close to the phase transition, certain O atoms appear to possess significant anharmonic motion, which presumably contributes to the excess line broadening observed in the infrared spectra of anorthite by Redfern and Salje (1992). Detailed comparisons of the structure of the high-pressure  $\bar{I}\bar{I}$  phase (Angel, 1988) with those determined both close to the transition at high temperature (e.g., Czank, 1973; Ghose et al., 1993) and at higher temperatures (Czank, 1973; Foit and Peacor, 1973) show them to be quite distinct (Christy and Angel, 1995). In particular, the high-pressure structure differs from those determined at high temperature in the Al-O-Si bond angles (up to 23° difference) within the four-membered rings of tetrahedra lying approximately parallel to (010) and in the apparent distribution of the Ca atoms within each of the cages of the framework. Although, in principle, it would be possible for the high-temperature structure to evolve continuously into that at high pressure (and room temperature), we would propose that the rapid change in unit-cell parameters in the  $\bar{I}\bar{I}$  phase in the temperature range 230–240 °C at ~1.7–2.0 GPa indicates that the structural changes within the  $\bar{I}\bar{I}$  phase are mainly restricted to this narrow interval in  $P$ - $T$  space. It is clear from the structural data that we have already discussed that the structural changes within this  $P$ - $T$  interval must involve (1) tetrahedral tilting to change the conformation of the framework from that of the high-temperature form to that of the high-pressure form, and (2) the suppression of the split nature of the Ca sites. One might further expect that the dynamic elements of the high-temperature structure are also suppressed at high pressure. However, further conclusions about the microscopic structural changes must await the precise determination of the anorthite structure in-situ at high pressures and temperatures adjacent to the crossover regime.

### Crossover transition

The comparisons of the  $\bar{I}\bar{I}$  structures observed at high pressures and at high temperatures, together with the rapid change in unit-cell parameters of the phase in the temperature range 230–240 °C, suggest that  $\bar{I}\bar{I}$  anorthite undergoes a previously unreported crossover or a phase transition at high pressures and temperatures. This transition (or crossover) involves no symmetry change, and so the change from the high-temperature regime to the high-pressure regime can be considered to be an “isosymmetric transition” (Christy, 1995). In such a case the free energy of the  $\bar{I}\bar{I}$  phases can be described by an expansion in a structural order parameter,  $Q_i$ , that includes all powers of  $Q_i$ :

$$G_{\text{ex}} = aQ_i + bQ_i^2 + cQ_i^3 + dQ_i^4 + \dots \quad (1)$$

where  $a, b, c, \dots$  are coefficients. Christy (1995) showed that this equation can have two distinct stable minima for  $G_{\text{ex}}$ . The two corresponding stable values of  $Q_i$  represent two structural states of the material that have the same symmetry but different structures. If the coefficients in Equation 1 vary with temperature or pressure then the

two distinct structural states can be stable in different regions of  $P$ - $T$  space, separated by an isosymmetric transition line. Christy (1995) showed that, depending upon the relative magnitudes of the coefficients in Equation 1, the transition between the two structural states of the material could either be first-order in character, or it could be a continuous crossover without discontinuities in the derivatives of  $G_{\text{ex}}$ . In either case, the transition from one structural state to the other occurs over a small interval in the parameter space, such that a continuous variation of the parameters in Equation 1 with pressure and temperature produces a sudden transition from one structural state to the other. It should be noted that, in contrast to symmetry-breaking transitions, the value of  $Q_i$  is not required to go to zero at the phase transition.

Equation 1 therefore accounts for the crossover or phase transition observed in the  $\bar{I}\bar{I}$  field. The complete description of the behavior of anorthite in the pressure and temperature regime under consideration then requires the addition of terms to the free energy expansion in Equation 1 that describe the  $\bar{I}\bar{I}$  to  $P\bar{I}$  transition. Since it has been so successful in describing the behavior of anorthite at the  $\bar{I}\bar{I}$  to  $P\bar{I}$  transition at room pressure (e.g., Salje, 1987; Redfern and Salje, 1987), the obvious addition is the normal 2-4-6 Landau free energy expansion in the order parameter  $Q_o$ , where  $Q_o$  is the order parameter of the  $\bar{I}\bar{I} \rightarrow P\bar{I}$  transition. We also add the lowest order coupling terms that are allowed (even powers of  $Q_o$  and all powers of  $Q_i$ ), resulting in the free energy expansion:

$$\begin{aligned} G_{\text{ex}} = & (aQ_i + bQ_i^2 + cQ_i^3 + dQ_i^4) \\ & + [(b_o + 2\lambda)Q_o^2 + d_oQ_o^4 + f_oQ_o^6] \\ & + (3c_cQ_iQ_o^2 + 6d_cQ_i^2Q_o^2 + \dots) \end{aligned} \quad (2)$$

where  $a, b, c, \dots$  and  $b_o, d_o, \dots$  are again coefficients. For phase transitions to occur, at least some of the coefficients in the free energy expansion must be functions of pressure or temperature. Although the data are insufficient to determine either the values of the coefficients or their possible variations, we would note that the simplest requirement is that the coefficient of  $Q_i$  is temperature- and pressure-dependent in order to generate the crossover transition in the  $\bar{I}\bar{I}$  phase, and that the coefficient of  $Q_o^2$  varies in the normal way with temperature to generate the zone-boundary transition. Three distinct structures can then develop in the system described by Equation 2. When  $Q_o = 0$ , Expansion 2 reduces to that in Equation 1, and, as we have discussed above, the expansion yields two stable values of  $Q_i$ , which correspond in anorthite to the high-pressure  $\bar{I}\bar{I}$  and the high-temperature  $\bar{I}\bar{I}$  phases, respectively. The third phase has  $Q_o \neq 0$  and corresponds to the cell-doubled  $P\bar{I}$  phase. The nearly isothermal and nearly isobaric portions of the phase boundary then correspond to two  $P\bar{I} \rightleftharpoons \bar{I}\bar{I}$  transitions that involve the same  $P\bar{I}$  phase but different  $\bar{I}\bar{I}$  phases (with very different thermodynamic properties related to their different values of  $Q_i$ ), and the region of sharpest curvature occurs at the

intersection of the  $P\bar{1} = I\bar{1}$  boundary with the crossover (or phase transition) line between the two  $I\bar{1}$  structures.

### Coupling between the transitions

The field of strong influence of the  $I\bar{1} = I\bar{1}$  transition on the  $P\bar{1} = I\bar{1}$  phase transition can be estimated by comparing the predictions of the Landau expansion for the evolution of the  $P\bar{1}$  phase that excludes consideration of the crossover with our experimental results. Angel (1992) extended the Landau analysis of Salje (1987) to high pressure and showed that the transition pressure,  $P_{tr}$ , is a function of the experimental temperature,  $T_{exp}$ , and the fixed state of Al-Si disorder quantified by the order parameter  $Q_{OD}$ :

$$P_{tr} = \frac{a_o}{a_{vo}} \left( T_{co} - T_{exp} + \frac{e_o e_d Q_{OD}^2}{a_o f} \right) \quad (3)$$

where  $a_o$  and  $a_{vo}$  are constants,  $e_o$  and  $e_d$  are the coefficients coupling 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. This equation predicts the correct sign of the effect of Al-Si disorder on the transition pressure (Angel, 1992). This equation also defines the  $P\bar{1} = I\bar{1}$  phase boundary in  $P$ ,  $T$ , and  $Q_{OD}$  space. If the coefficients in this equation remain constant, as they appear to do with respect to temperature at room pressure (e.g., Redfern and Salje, 1987; Redfern et al., 1988; Redfern, 1992), then Equation 3 defines a linear equilibrium phase boundary throughout  $P$ - $T$  space. Our experimental results (Fig. 4) show that this is valid from room temperature up to  $\sim 200$  °C and also over the isothermal portion of the phase boundary from room pressure to  $\sim 1.5$  GPa. The influence of the crossover or phase transition in the  $I\bar{1}$  phase is therefore negligible in these regions and is restricted to a narrow region of  $P$ - $T$  space around the crossover or phase transition itself. This in turn suggests that (1) the strain coupling of the crossover with the  $P\bar{1} = I\bar{1}$  transition is weak, and (2) all the thermodynamic and structural changes in the  $I\bar{1}$  field are indeed restricted to this narrow interval.

The success of previous analyses (e.g., Salje, 1987; Redfern and Salje, 1987; Redfern et al., 1988; Redfern, 1992) of the transition behavior of anorthite that omitted consideration of the newly discovered crossover can now be explained. Previous experiments on the  $P\bar{1} = I\bar{1}$  transition in anorthite have been restricted to either varying temperature at room pressure or varying pressure at room temperature. In both cases the zero, or very weak, coupling between  $Q_i$  and  $Q_o$  means that  $Q_i$  will remain exactly or nearly constant during such experiments, and no influence of the crossover is detectable.

### CONCLUSIONS

In-situ reversals of the  $P\bar{1} = I\bar{1}$  transition in anorthite have revealed that although phase transitions at high pressures and at high temperatures are related, they involve an  $I\bar{1}$  phase with different structural states. The curvature of the  $P\bar{1} = I\bar{1}$  transition line is due to its

intersection with an isosymmetric,  $I\bar{1}$  to  $I\bar{1}$ , crossover or phase transition in the  $I\bar{1}$  phase at high temperatures and  $\sim 1.8$  GPa. This transition or crossover (the current experimental data do not distinguish the two) separates the stability fields of two structurally distinct  $I\bar{1}$  structures (Christy and Angel, 1995), whose thermodynamic properties are also significantly different. The presence of the crossover or phase transition also explains why the cell parameters extrapolated to room pressure and temperature from the  $I\bar{1}$  phase at high pressures (Angel, 1992) do not match those extrapolated from the high-temperature phase to the same conditions (Redfern and Salje, 1987). More data are therefore required on the evolution of the structure of the  $I\bar{1}$  phases of anorthite at high temperatures and pressures in order to evaluate both the nature of this isosymmetric transition and its trajectory in  $P$ - $T$  space. The significant changes in thermodynamic properties that accompany the isosymmetric transition may have an effect on other reactions and transformations in which anorthite is involved, but we have demonstrated qualitatively that the coupling of the isosymmetric transition to the  $P\bar{1} = I\bar{1}$  transition is weak, except in the immediate vicinity of the crossover.

From the point of view of the physics of the  $P\bar{1} = I\bar{1}$  phase transition, it is also important to know the trajectory of the isosymmetric transition to be able to extrapolate it into the stability field of the  $P\bar{1}$  structure and so be able to define a unique  $I\bar{1}$  reference state from which to calculate the excess properties of the  $P\bar{1}$  phase. Given the absence of anomalous behavior in the evolution of the precisely determined cell parameters of anorthite at room pressure down to temperatures of 22 K (Redfern and Salje, 1987; Redfern et al., 1988), one would suggest that the extrapolated line of the isosymmetric transition is sufficiently shallow to have a positive intercept on the pressure axis at zero absolute temperature.

### ACKNOWLEDGMENTS

We would like to thank S.A.T. Redfern, E. Salje, M.A. Carpenter, and A.G. Christy for extensive discussions on the nature of the phase transitions in anorthite. This work was supported by the Mineralogical Society of America in the form of its 1990 Crystallography Award to R.J.A., by the Royal Society in the form of a 1983 University Research Fellowship to R.J.A., and by the NERC with a research studentship to T.P.H.

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MANUSCRIPT RECEIVED JULY 5, 1994

MANUSCRIPT ACCEPTED NOVEMBER 11, 1994