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Structural States of Mg-Cordierite I: Order Parameters from Synchrotron X-Ray and NMR Data

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Abstract. The hexagonal to orthorhombic phase transition in synthetic Mg-cordierite has been studied by (i) measuring the spontaneous strain associated with the transition using Synchrotron X-ray powder diffraction and (ii) measuring the degree of Al, Si order in terms of the number of $Al-O-Al$ bonds per formula unit using solid state NMR spectroscopy. This defines the two order parameters Q and Q_{od} respectively, and their relationship as a function of annealing temperature and time is used to define the structural states of cordierite during the ordering sequence. The formation of modulated hexagonal cordierite within which a high degree of Al, Si order can be attained, results in a strongly non-linear relationship between Q and Q_{od}. The transition from modulated to orthorhombic cordierite is strongly first-order under all temperature conditions studied and involves a large step in Q, while Q_{od} changes continuously throughout the ordering sequence with no marked discontinuity at the phase transition. The lattice distortion, traditionally defined in cordierite by the Δ index provides no full information on the degree of Al, Si order in anhydrous Mg-cordierite, and both order parameters must be used to define its structural state. Transmission electron microscopy has been used to study the mechanism of the transformation from hexagonal to modulated to orthorhombic cordierite.

Introduction

Mg-cordierite, $Mg_2Al_4Si_5O_{18}$ is known to occur in two polymorphic forms. In the high temperature hexagonal structure ($P6/mcc$) stable above about 1450° C (Schreyer and Schairer 1961; Smart and Glasser 1977; Putnis 1980) the Al and Si atoms can have no long range order. Below this temperature the orthorhombic form ($Cccm$) is stable and within this structure Al and Si can attain complete order (Meagher and Gibbs 1977; Gibbs 1966; Cohen et al. 1977). Thus the hexagonal-orthorhombic transformation is associated with Al, Si ordering and recent studies have focussed on characterizing the "degree of order" attained as a function of temperature and annealing time in synthetic samples.

The issue treated in this paper is the relationship between the structural phase transition $P6/mcc-Cccm$ as characterized by methods which rely on changes in cell parameters, such as the distortion index Δ (Miyashiro 1957), and methods dependent on the degree of local order such as NMR spectroscopy (Fyfe et al. 1983a; Putnis et al. 1985) and heat of solution calorimetry (Carpenter et al. 1983). A hitherto unresolved difficulty in explaining the mechanism of this transformation has been to define the point at which the structure transforms to orthorhombic symmetry and relate this to the degree of Al, Si order.

One of the problems which has led to some misleading conclusions has been that in all previous papers the distortion index Δ has been assumed to vary continuously through the hexagonal to orthorhombic transformation even though it is known that under equilibrium conditions the symmetry change $P6/mcc$ to $Cccm$ must be first order. It was therefore assumed that under non-equilibrium conditions the transformation could be accomplished by some continuous mechanism, an interpretation supported by the continuous coarsening of microstructures observed by transmission electron microscopy (Putnis 1980) and the continuous change in enthalpy (Carpenter et al. 1983) and the number of $Al-O-Al$ bonds per formula unit (Putnis and Angel 1985). We show here that this interpretation has been based on X-ray diffractometry data of insufficient resolution and that new synchrotron X-ray experiments combined with electron microscopy and NMR spectroscopy lead to a different interpretation of the transformation mechanism as well as producing results amenable to theoretical treatment. Specifically we are now able to relate macroscopic changes in unit cell shape with the degree of Al, Si order using the order parameter theory recently described by Salje and Devarajan (1986).

The experimental results and conclusions are discussed in Part I of this paper and the theory in Part II (Salje 1987).

Experimental

The starting material for the experimental runs was stoichiometric Mg-cordierite glass. The method of preparation of the glass and its chemical analysis have been described elsewhere (Putnis 1980). The glass was devitrified by annealing in air at temperatures of 1180° C, 1290° C and 1400° C. In all cases the first crystallization product was hexagonal cordierite which on annealing ultimately transformed to orthorhombic cordierite. The run products were studied using Synchrotron X-ray powder diffractometry to determine the nature of the line splitting associated with the hexagonal-orthorhombic transformation. Transmission electron microscopy was used to describe the microstructural changes associated with the transformation, and the degree of local Al, Si order was defined using "*magic angle spinning*" NMR spectroscopy as described by Putnis et al. (1985).

Strain Measurements Using Synchrotron Radiation

The scattering experiments were performed using the powder diffractometer at the synchrotron source in Daresbury (beam line 9.1). Synchrotron radiation of peak energy 3.5 GeV was monochromatized using a Si(*111*) monochromator and monochromatic radiation of wavelength 1.4725 Å has been used for all measurements. The wavelength calibration was obtained using Si as an internal standard. The second monochromator crystal was slightly tilted in order to avoid higher order scattering. The monitored total primary intensity was 11400 cps and was stable within 0.2 percent during the period of our experiments (28 h). As no intensity measurements were necessary during the course of the present investigations, no absolute calibration of the diffracted intensity was needed. The detection system consisted of an energy dispersive EG&G detector which was used with a small energy window in order to reduce background scattering. No further use of the energy dispersive mode was made, the maximum level of background scattering was found to be 50 cps with a vertical beam width of ca. 2 mm.

The powder samples consisted of stuffed glass capillaries with a diameter of 0.3 mm which were mounted on a spinning goniometer head. The spinning frequency was 5 Hz. The rotation axis of the spinner was aligned with respect to the rotation axis of a Stoe one-circle diffractometer. The distance between the powder sample and the entrance slit of the detector was ca. 1 m. All samples were measured with exactly the same experimental arrangement, only the capillaries were changed on the goniometer head and aligned optically (±0.2 mm).

The angular resolution of the diffractometer was tested by scanning the (*111*) line of the internal Si standard. The *full width at half maximum height* (FWHM) was found to be 0.06° 2θ, which was deemed small enough for the present investigations. The observed diffraction patterns of several cordierite samples are shown in Figure 1. They clearly demonstrate the good angular resolution of the diffractometer and the excellent signal to noise ratio. We furthermore emphasise that the very narrow line profiles were encountered for all cordierite samples independent of their annealing temperatures and times. These findings are in complete contrast to earlier reports on line broadening effects observed with classical X-ray powder diffractometers.

Results

Synchrotron X-ray Diffractometry

In the hexagonal-orthorhombic transformation the (*211*) peak in the hexagonal structure splits into the (*131*), (*421*) and (*511*) peaks of the orthorhombic structure and the distortion index was defined by Miyashiro as

$$\Delta = 2\theta_{131} - \frac{2\theta_{511} + 2\theta_{421}}{2}.$$

Accordingly, the X-ray spectra were recorded to monitor the behaviour of the (*211*) peak through the transition.

The observed scattering profile of the (*211*) line of hexagonal cordierite (Figure 1a) is almost identical with the instrumental resolution function of the powder diffractometer at the Daresbury synchrotron source. This implies that the correlation length in cordierite is large even for samples that have crystallized from glass after very short annealing times. The deconvoluted effective correlation lengths are always longer than 300 Å.

In cordierite which has been annealed for a sufficiently long time such that the structural transformation to the orthorhombic form is almost achieved, a new feature was found in the spectra. The spectrum shown in Figure 1b shows the sharp (*211*) peak of the hexagonal phase superposed to a broad scattering profile which appears rather symmetrically on both sides of the powder line. The scattering angles are different from those of the orthorhombic form and cannot be confused with a partial transformation of hexagonal cordierite into the orthorhombic form. The line profile is identical with those of satellite reflections arising from a modulated structure. The modulation vector however, does not have a unique length but rather varies continuously between very low values, beyond the resolution of this experiment, and a maximum value of ca. 0.9 Å^{-1}. The corresponding minimum wavelength of the modulation is approximately 10 Å. The structural transformation between hexagonal cordierite and its orthorhombic form is, according to these results, precursored by an intermediate structural state which is different from both the hexagonal and the orthorhombic structures. The line profile strongly suggests a well defined structural state characterized by a hexagonal matrix with lower symmetry modulations.

If these observations were made for a crystal in thermodynamic equilibrium, the modulated structure would clearly define a new phase of cordierite. As such equilibrium experiments have not yet been performed we are not able to define this phase as a stable phase in a thermodynamic sense. However, the appearance of this structural state as a metastable phase of cordierite during the annealing process is documented by the present findings. In the present experiments the modulated phase was found as a precursor to the orthorhombic structure at all annealing temperatures. The question as to whether the modulated structure is a stable phase at equilibrium is discussed below in the section on equilibrium disordering experiments.

With longer annealing times the orthorhombic phase appears abruptly as three peaks (*131*, *511* and *421*) in place of the *211* hexagonal peak (Fig. 1c). The annealing time interval over which the modulated structure and orthorhombic structure coexist is very short compared with the time scale of Al, Si ordering at these temperatures. An important observation is that the orthorhombic phase appears with an almost fully distorted structure with a distortion index approaching that of the final equilibrium state. The distortion index determined from synchrotron radiation measurements has a maximum value of 0.25. Orthorhombic cordierites with shortest annealing times gave minimum Δ values of 0.22. This shows that the distortion index does not change continuously with time and that previous data e.g. Putnis (1980) was presumably of insufficient resolution. Furthermore, this large discontinuity in the distortion index with annealing time exists at all three annealing temperatures in each case suggesting a nucleation and growth mechanism for the formation of orthorhombic cordierite from the modulated structure. This point will be taken up again in the discussion of the microstructural development associated with the transformation.

Transmission Electron Microscopy

In earlier work it has been established that the first-formed hexagonal cordierite crystallized from glass is well crystalline, defect free and homogeneous (Putnis 1980). With continued annealing at 1200° C the hexagonal cordierite first develops a "tweed" microstructure indicating orthogonal modulations in the degree of order and/or lattice strain. With continued annealing this microstructure progressively coarsens, eventually developing cross-hatched twins within the orthorhombic phase. Thus the transformation appears to be continuous microstructurally. In the present work the same microstructural development was observed in the 1180° C runs. The modulated structure observed as the superposed diffuse scattering in the X-ray spectra (Fig. 1b) correlates with the development of the "tweed" microstructure. The subsequent abrupt nucleation of the orthorhombic phase observed in the X-ray spectra is not however obvious in the microstructure. We can conclude therefore that at this temperature the orthorhombic phase appears as a large number of twin-related nuclei within the modulated structure and that the continued growth of these nuclei produces the apparently continuously coarsening microstructure.

Annealing cordierite glass at 1400° C similarly produces homogeneous hexagonal cordierite which transforms to the modulated structure with time. Continued annealing results in the nucleation of orthorhombic cordierite at relatively widely-spaced intervals compared with the lower temperature experiments. These nuclei grow rapidly, totally replacing the tweed microstructure. The apparently continuous changes observed at lower temperatures when nucleation was more dense are not seen here, although no significant differences can be seen in the development of the X-ray powder spectra at the two annealing temperatures. Figure 2 compares the evolution of the microstructures at 1185° C and 1400° C as observed by diffraction contrast images in the transmission electron microscope. The time-scale of the transformations from hexagonal to modulated to orthorhombic in the experiments described here is summarized in Figure 3.

Magic-angle Spinning NMR Spectroscopy

It is now well established that ^{29}Si NMR of solids using magic-angle spinning, can be used to determine Si environments in silicates (Lippmaa et al. 1980, 1981). In framework structures ^{29}Si chemical shifts depend on whether a given SiO_4 tetrahedron is linked to four, three, two, one or no AlO_4 tetrahedra (Engelhardt et al. 1981; Fyfe et al. 1983b). These local environments or structural units are usually denoted Si(4Al), Si(3Al) etc.. Each type of environment gives rise to a separate peak in the NMR spectrum, and the areas under those peaks are directly proportional to the populations of the respective structural units in the sample (Fyfe et al. 1983b).

In cordierite these peaks are well resolved in the NMR spectrum (Fig. 4) and peak assignments are relatively straightforward. The discussion of assignments and experimental methods as well as the relevant structural details of cordierite have been recently published (Putnis et al. 1985). Here we present data for the ^{29}Si peak areas for

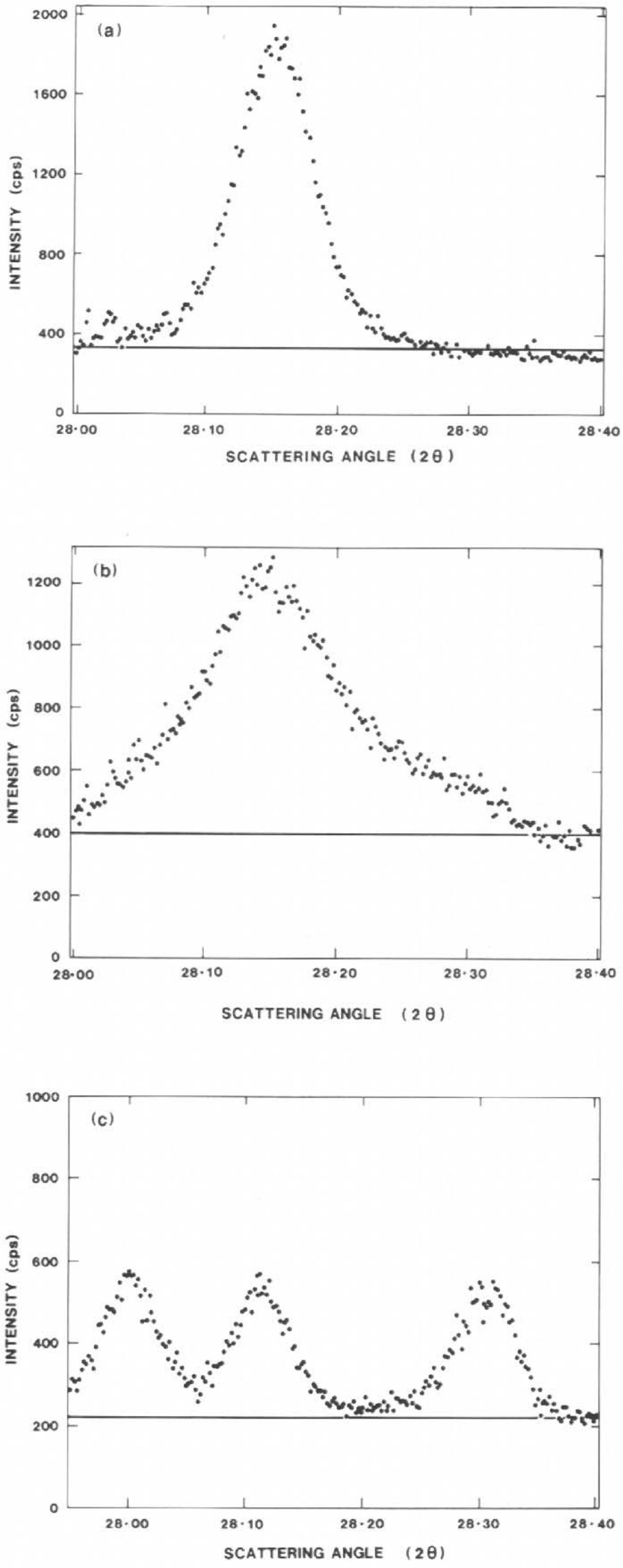

Fig. 1a–c. Synchrotron X-ray powder diffraction spectra over a narrow range of 2θ angles. (**a**) The (*211*) peak of hexagonal cordierite. (**b**) The (*211*) peak of modulated cordierite. (**c**) In orthorhombic cordierite the (*211*) peak is replaced by the (*511*), (*421*) and (*131*) peaks

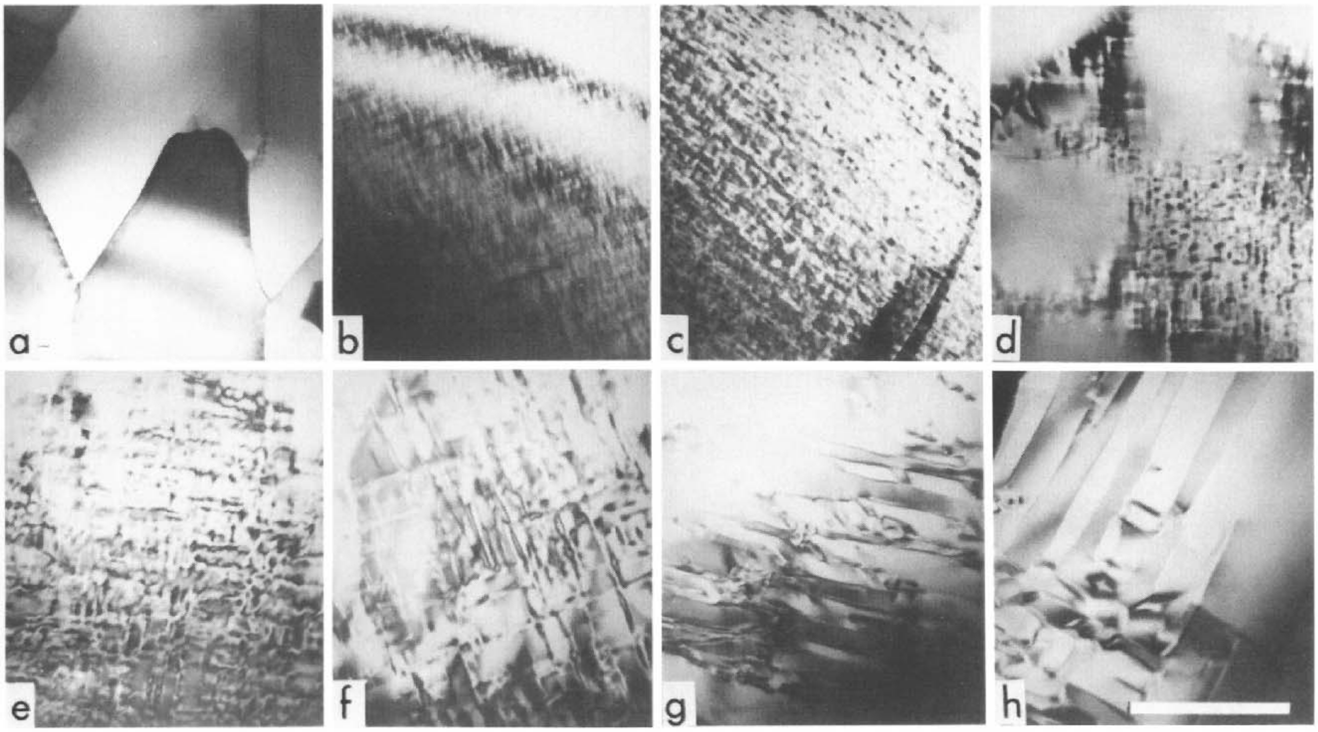

Fig. 2a–h. Transmission electron micrographs illustrating the evolution of microstructures observed during the transformation from hexagonal to orthorhombic cordierite. At 1400° C the transformation sequence is a → b → c → d, where orthorhombic cordierite nucleates within the modulated structure. At lower temperatures the sequence is a → b → c → e → f → g → h, the finer scale of nucleation of orthorhombic cordierite appearing to produce a continuously coarsening microstructure. The length of the scale bar is 0.2 μm

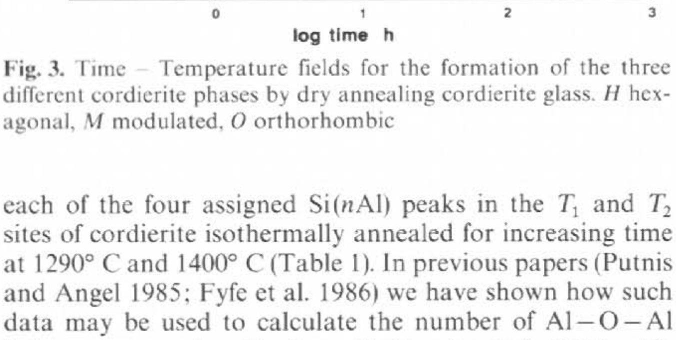

Fig. 3. Time – Temperature fields for the formation of the three different cordierite phases by dry annealing cordierite glass. *H* hexagonal, *M* modulated, *O* orthorhombic

each of the four assigned Si(nAl) peaks in the T_1 and T_2 sites of cordierite isothermally annealed for increasing time at 1290° C and 1400° C (Table 1). In previous papers (Putnis and Angel 1985; Fyfe et al. 1986) we have shown how such data may be used to calculate the number of Al–O–Al linkages per unit cell of cordierite, denoted N(Al–Al). Al, Si ordering reduces N(Al–Al) to zero in the perfectly ordered orthorhombic form, and hence the progressive reduction in N(Al–Al) may be used as a measure of the degree of local Al, Si order.

In Figure 5(a–c) the N(Al–Al) bonds per unit cell is plotted against the logarithm of the annealing time at three different temperatures. The data for the 1185° C runs (Fig. 5a) are from Putnis et al. (1985) where this was interpreted as a linear decrease in N(Al–Al) with log time. The slope is -0.31. At 1290° C the interpretation of the data in terms of a single straight line is somewhat equivocal – nevertheless the best fit gives a slope of -0.36. At 1400° C the data points are somewhat more scattered, the best linear fit having a slope of -0.24. However the data are fitted there is no doubt that at 1400° C the cordierite is less well ordered compared to similar time runs at lower temperatures.

This reduction in the rate of ordering at 1400° C does not coincide with a reduction in the rate of transformation to the orthorhombic structure. Indeed at 1400° C the structure is orthorhombic after 2.75 h annealing, compared with more than 5 h at 1290° C and 160 h at 1180° C (Fig. 3). Clearly, the transformation to orthorhombic symmetry takes place at a lower degree of local Al, Si order at higher temperatures. This can also be seen when comparing the TEM and X-ray data with the NMR data. After 2.75 h at 1400° C the average number of Al–O–Al bonds per unit cell in the sample is around 0.8; after 5 h at 1290° C it is about 0.5 and after 160 h at 1180° C the N(Al–Al) is about 0.4. The same point can be made about the N(Al–Al) bonds at the onset of the modulation. At 1400° C the modulated structure appears after 15 min annealing when N(Al–O–Al) is about 1.1 whereas at 1180° C the modulation appears after 6 h (Putnis and Bish 1983) when the N(Al–O–Al) is less than 0.9. If it is assumed that the visibility of the modulation by a strain-contrast mechanism in TEM implies the same local strain, it may be suggested that a smaller degree of order at 1400° C results in the same local strain as a higher degree of order at 1180° C i.e. that at 1400° C the cordierite is elastically softer.

Equilibrium Disordering Experiments

To investigate further the possibility that the modulated structure may have an equilibrium stability field, experi-

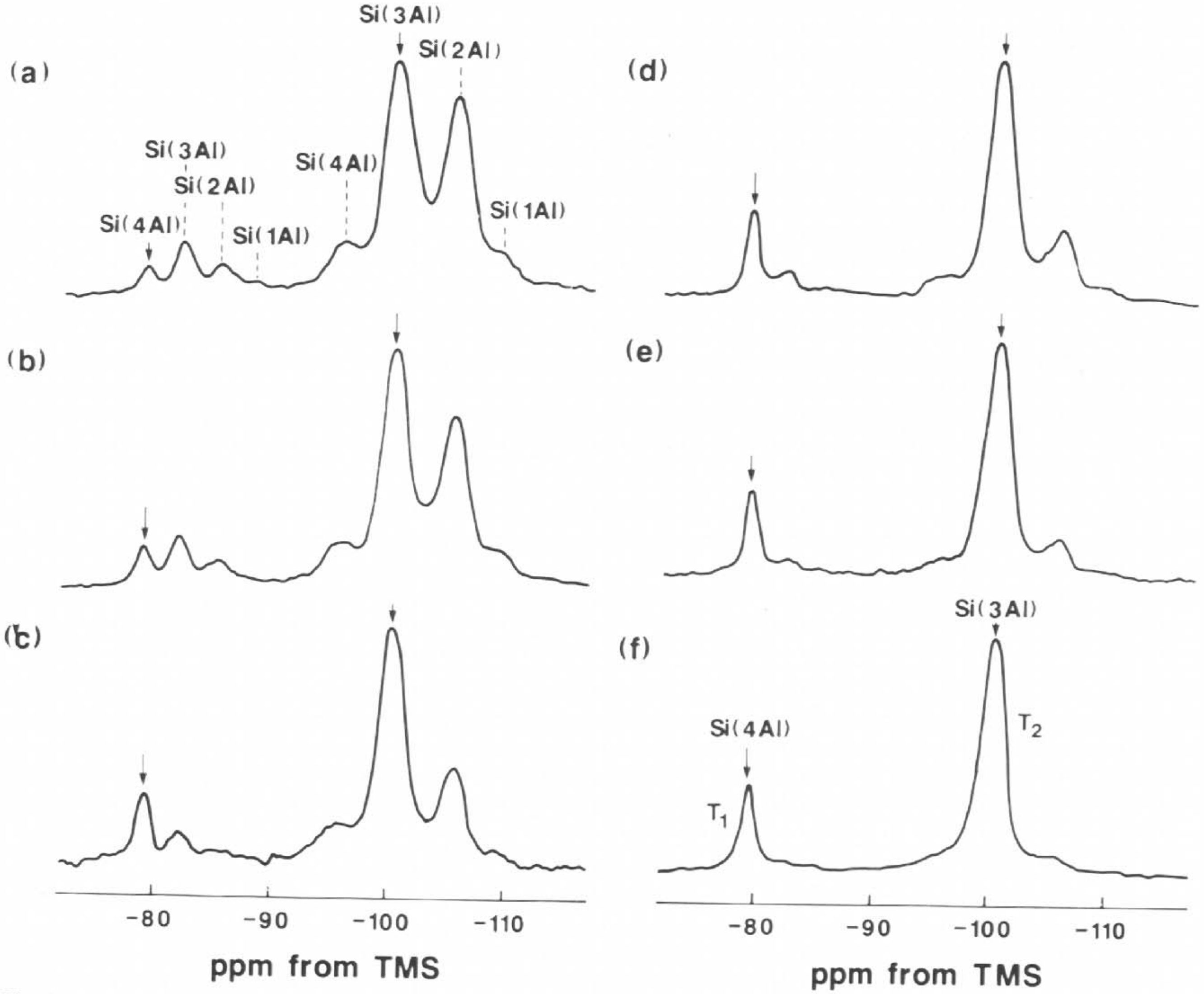

Fig. 4a–f. A sequence of ^{29}Si NMR spectra of synthetic cordierites isothermally annealed for increasing time. A similar sequence is observed at all temperatures studied here. In **(a)** the large number of Si(nAl) environments is due to the disorder in the first-formed hexagonal phase, while in **(f)** the orthorhombic cordierite is well ordered. For discussion of peak assignments see Putnis et al. (1985)

Table 1. ^{29}Si peak areas (corrected for spinning side bands and normalized) for each of the four assigned Si(nAl) peaks in the T_1 and T_2 sites from NMR spectra of synthetic cordierite isothermally annealed for increasing time

Temp/Time	T_1 sites				T_2 sites				
	Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	N(Al−Al)
1290° C									
2 min	0.0469	0.0563	0.0338	0	0.0803	0.4557	0.2704	0.0563	1.226
20 min	0.0710	0.0539	0.0299	0.0138	0.0938	0.4737	0.2179	0.0456	1.008
120 min	0.0940	0.0371	0.0159	0.0088	0.0583	0.5587	0.1856	0.0412	0.876
250 min	0.1054	0.0410	0.0190	0.0140	0.1002	0.5555	0.1500	0.0146	0.554
1100 min	0.1267	0.0338	0	0	0.0642	0.6677	0.0986	0.0088	0.315
2880 min	0.1403	0.0311	0	0	0.0685	0.7088	0.0510	0	0.108
1400° C									
2 min	0.0524	0.0510	0.0437	0.0163	0.0892	0.4371	0.2653	0.0446	1.226
20 min	0.0749	0.0475	0.0309	0.0117	0.0668	0.5090	0.2057	0.0533	1.064
60 min	0.0898	0.0697	0.0290	0.0325	0.0732	0.4652	0.2051	0.0348	1.020
180 min	0.0967	0.0394	0.0241	0.0208	0.0794	0.5731	0.1588	0.0074	0.660
360 min	0.1112	0.0429	0.0085	0	0.0452	0.5720	0.1925	0.0275	0.751
1030 min	0.1144	0.0359	0.0188	0.0138	0.0440	0.5961	0.1389	0.0377	0.759
5300 min	0.1176	0.0424	0.0155	0.0118	0.099	0.5957	0.1120	0.0056	0.369

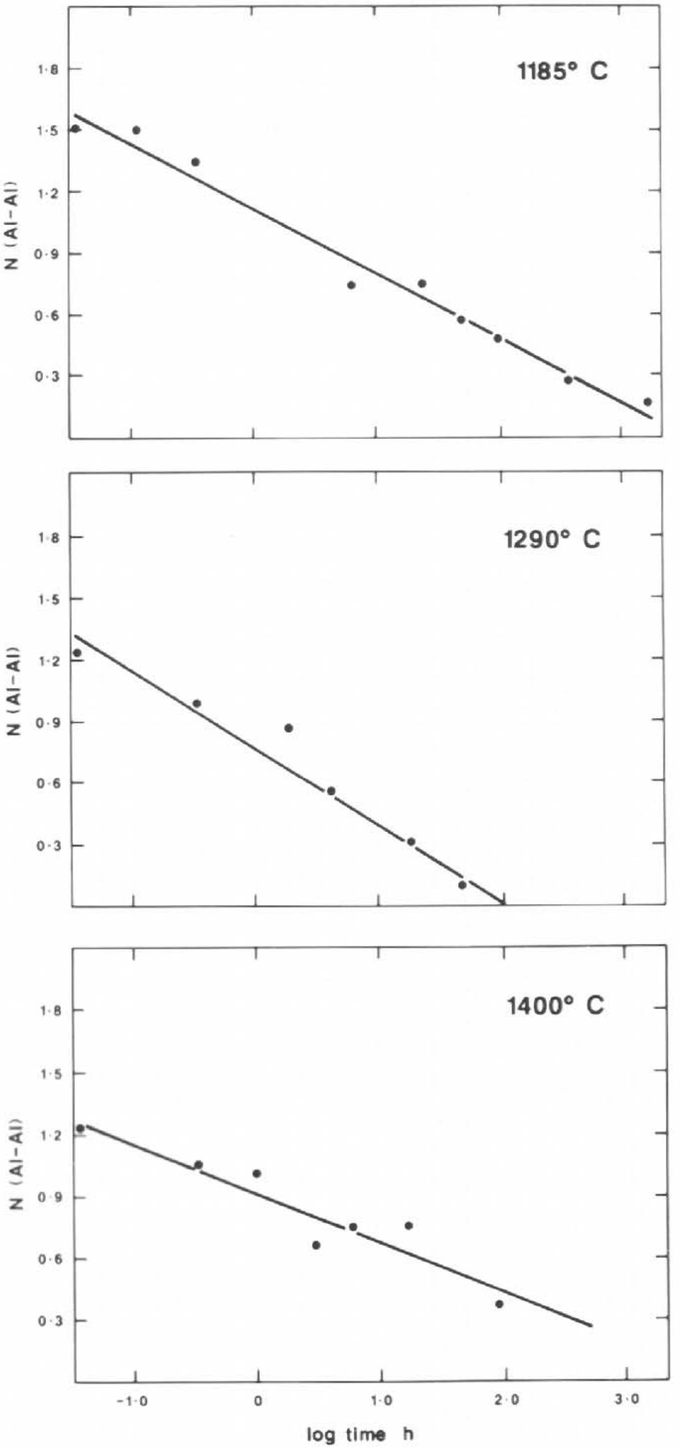

Fig. 5. The number of Al–O–Al bonds, $N(\mathrm{Al-Al})$, per formula unit plotted as a function of annealing time at three different temperatures

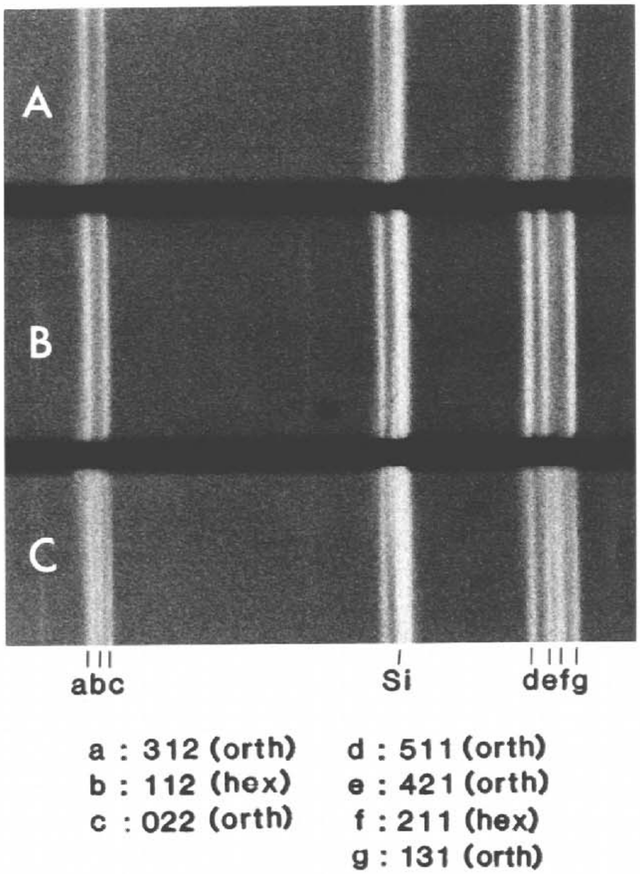

Fig. 6. Part of a set of Guinier X-ray powder photographs during a disordering sequence. (A) the well ordered orthorhombic starting material, (B) traces of hexagonal cordierite after 48 h annealing at 1455° C (C) hexagonal + orthorhombic cordierite after 72 h annealing at 1455° C. Note that the Δ index of the original orthorhombic cordierite has remained constant

ments were carried out to observe the mechanism of disordering of well-ordered orthorhombic cordierite which had been prepared by long annealing at 1400° C. The ordered cordierite was held at temperatures within the stability field of hexagonal cordierite for increasing periods of time and quenched. The products were examined using a Guinier X-ray camera and by transmission electron microscopy.

The time-scale for disordering was substantially greater than that reported by Smart and Glasser (1977). As the incongruent melting point of cordierite is only about 10° C higher than the reported disordering temperature only a small amount of superheating is possible and annealing times in excess of 48 h at 1460° C were needed to detect the appearance of the hexagonal phase. The discrepancy between these annealing times and those reported by Smart and Glasser (1977) may be due to the fact that both the apparent transition temperature and the time to nucleate the hexagonal phase will depend on the degree of order in the orthorhombic starting material. In the present experiments the starting material was virtually completely ordered. The intergrowth of orthorhombic and hexagonal phases is well resolved on Guinier photographs. Figure 6 shows a part of three Guinier photographs of the disordering sequence. No measurable change in the Δ index of the orthorhombic cordierite could be detected during annealing prior to the appearance of the hexagonal phase.

Lattice parameter measurements of orthorhombic and hexagonal cordierites show that

$$\frac{\Delta a}{a_0} = -\frac{\Delta b}{b_0} = 6\cdot 9 \times 10^{-3}$$

where Δa and Δb are the differences between the a and b lattice parameters of the orthorhombic phase and the hexagonal phase (defined with an equivalent orthorhombic cell, with parameters a_0 and b_0).

No modulated structures were observed in the cordierite by transmission electron microscopy during disordering. The hexagonal phase grows by a classical nucleation and growth process, with a curved interface separating the two phases. Electron diffraction patterns across such interfaces show split reflections consistent with a hexagonal + orthorhombic intergrowth.

The Structural States of Cordierite

We can see from the above data that the temperature-time evolution of the cordierite structure is defined by two parameters. First, the degree of Al, Si order and second, the tendency for the cordierite structure to distort to orthorhombic symmetry. It is clear that while these two parameters are related, the relationship is by no means linear. Within the hexagonal structure a considerable degree of local Al, Si order can exist – the $N(\mathrm{Al-O-Al})$ for total statistical disorder would be 3.3 per formula unit (Putnis and Angel 1985), compared with less than half that number in the hexagonal cordierites described here (Fig. 5). Similarly the degree of order in the orthorhombic phase depends on the temperature, as described above.

To treat this problem it is convenient to separate the two effects and consider the way in which they interact. The theoretical basis for this is discussed in Part II of this paper (Salje 1987). The effects of Al, Si ordering and the lattice distortion are each described by an order parameter. The number of Al–O–Al bonds per formula unit, N, (normalized to 1 for complete order, and 0 for complete disorder) defines the order parameter as $Q_{od}=\left\langle 1-\frac{N}{3\cdot 3}\right\rangle^{\frac{1}{2}}$. The lattice distortion is defined by an order parameter Q which is determined by the spontaneous strain e_1 (Salje et al. 1985). The distortion of the cordierite structure is described by two strain parameters e_1 and e_2 with $e_2=0$ in the orthorhombic phase (Salje 1987). The line splitting between the 2θ values of the *(131)*, *(421)* and *(511)* reflections is proportional to the structural deformation between the a and b axes in the orthorhombic phase. In hexagonal cordierite the relation between the equivalent axes is $b_0=\sqrt{3}\,a_0$. With $e_2=0$, $\gamma=90°$ and $a_0=b_0/\sqrt{3}\approx\frac{1}{2}a+\frac{1}{2}b/\sqrt{3}$ the strain parameter can be expressed by the orthorhombic lattice constants alone:

$$e_1=\frac{a-\dfrac{b}{\sqrt{3}}}{a+\dfrac{b}{\sqrt{3}}},\qquad e_2=0.$$

The spontaneous strain is therefore proportional to the splitting of the above mentioned powder lines and is also proportional to the distortion index Δ. Thus the Δ index, normalized to 1 for $\Delta=0.25$ (the maximum distortion) may be used as the order parameter Q. As the splitting between each pair of powder reflections is proportional to the spontaneous strain it is irrelevant which pair of peaks or any combination of differences between scattering angles (such as the Δ index) is chosen to display the temperature evolution of the spontaneous strain. The experimental data show that all possible differences in the 2θ values of the three powder lines are exactly proportional to each other. In other words, the ratio between the line splittings:

$$\frac{2\theta_{131}-2\theta_{511}}{2\theta_{511}-2\theta_{421}}$$

is identical for all samples of orthorhombic cordierite, because all individual differences in scattering angles are exactly proportional to each other. Here we use the distortion index as the order parameter Q as it is a familiar parameter in the cordierite literature.

In the thermodynamic states of cordierite between the hexagonal and the fully ordered orthorhombic structure we may expect to find a uniquely defined relation between both parameters. Such a relation can be worked out theoretically for cordierite in thermodynamic equilibrium (Salje 1987). This solution however does not necessarily account for kinetic effects as described in this paper. This raises the question of how far the Al, Si ordering in cordierite, described by Q_{od}, is involved in the structural phase transition, described by Q: Does Q_{od} drive the phase transition or, alternatively, does a critical degree of Al, Si order only "trigger" the structural transformation which then follows a different transformation pattern than Q_{od}?

In order to answer this question we have to investigate the correlation between Q and Q_{od} for all structural states which could be observed in our experiments. For each annealing time and temperature the order parameters Q, determined from the X-ray spectra and Q_{od} determined from the NMR data are plotted on an order parameter vector diagram (Fig. 7). It has been shown by Salje (1987) that in the case of Q_{od} being the driving order parameter on which Q responds linearly, this diagram would show the dashed straight line.

Our experimental results show that this linear relation holds within experimental error for all samples with orthorhombic symmetry. As a consequence of this observation we expect the critical temperature at which cordierite would be fully disordered ($T_c^{Q_{od}}$) and the extrapolated critical temperature at which the orthorhombic phase would transform to hexagonal (if there was no intervention of a modulated state, or melting etc.) should be identical. This linear relation, however, is broken by the abrupt breakdown of the orthorhombic form into modulated cordierite with decreasing Q_{od}. This strongly first order transformation between the orthorhombic phase and the hexagonal modulated form is not equivalent to the theoretical phase transition between an orthorhombic phase and the totally disordered hexagonal phase with $Q_{od}=0$ and $Q=0$. In none of our experiments has this ideal hexagonal state ever been observed because each hexagonal modification of cordierite either contains a very high degree of short range order or it appears as a modulated structure (in either case $Q_{od}>0.8$).

Discussion

The structural phase transition between modulated hexagonal and orthorhombic cordierite is characterized by a spontaneous increase in Q. The order parameter Q_{od}, on the other hand, does not reveal any singularity at the phase transition point. Both order parameters Q and Q_{od} show a strong correlation in the orthorhombic phase which follows exactly the theoretical predictions of a bilinear coupling process.

As this correlation breaks down in the hexagonal form, the phase transition can indeed be looked upon as being "triggered" by a certain threshold value of Q_{od} where no

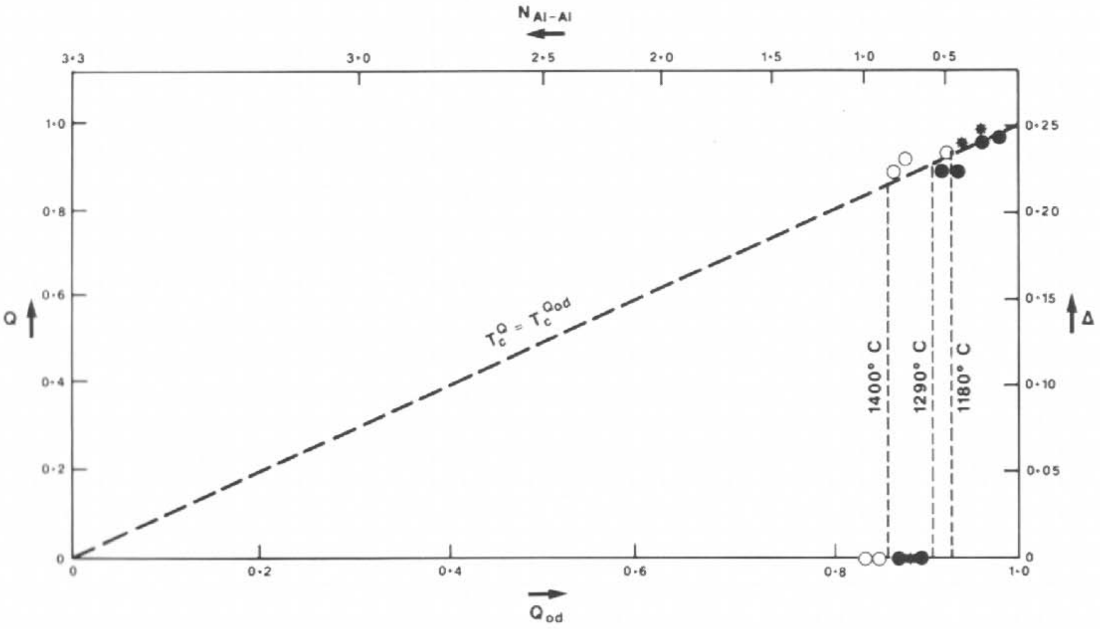

Fig. 7. The experimentally determined variation of the order parameter Q, defined by the Δ index, plotted against the order parameter Q_{od}, defined as a function of $N(\mathrm{Al-Al})$ during the annealing sequence at three different temperatures (data points: open circles – 1400° C; closed circles – 1290° C; stars – 1180° C). The short-dashed lines show the experimentally determined discontinuities in Q. The long-dashed straight line shows the expected theoretical relations between Q and Q_{od} for a bilinear coupled process for which the critical temperatures for Al, Si ordering ($T_c^{Q_{od}}$) and the structural phase transition (T_c^Q) are equal. See Salje (1987) for more details

hexagonal cordierite exists for higher values. The fact that this threshold value depends on the annealing temperature at which the kinetic experiments are performed is likely to be understood as due to a temperature dependence of the elastic constants as predicted theoretically (Salje 1987). The threshold value of the phase transition itself is a direct consequence of the appearance of the modulated form of cordierite. Whenever the orthorhombic phase of cordierite appears in an annealing sequence such as described here we would expect Q and Q_{od} to follow the quasi-equilibrium line in the order-parameter vector space. If we now consider the fact that any deviation of Q_{od} from its zero value (i.e. any Al – Si ordering) has to destroy the hexagonal symmetry at least locally, then we must expect the correlation between Q and Q_{od} to hold up to the stability point of fully disordered cordierite with $Q_{od}=0$ and $Q=0$. Experimentally, this would mean that under most experimental conditions we have to observe a phase mixture of hexagonal and orthorhombic cordierite where the degree of order in the orthorhombic phase corresponds exactly to its Δ-index (i.e. Q). This is in complete disagreement with our experimental findings, which could therefore not be understood without the explicit consideration of the modulated form of hexagonal cordierite and hexagonal cordierite with considerable amount of short-range order ($Q>0$).

Modulated cordierite has hexagonal symmetry and is characterized by the order parameter Q_{od} and the wavelength of the modulation. It is however, not characterized by the order parameter Q, which is necessarily zero in this form. This means that the correlation between Q and Q_{od} is spontaneously broken at the very point of the transition between the modulated and the orthorhombic form of cordierite. It must be broken in such a way that Q has to disappear at the point of transformation to the modulated form and has to obey the correlation with Q_{od} in the orthorhombic form. This implies that there must be a jump of Q at the transformation point. The degree of Al, Si order, as described by Q_{od} on the other hand, is a continuous variable of the kinetic process and either no singularity or only a small one is expected in the Q_{od} versus *ln* time plot. The stepwise behaviour of Q is therefore a consequence of the appearance of modulated cordierite and does not mean that there is a stepwise behaviour in the time evolution of the Al, Si ordering.

Another important conclusion of our experiments is that we can now answer the question of how far the kinetic behaviour of cordierite is influenced by symmetry changes and displacive movements as described by Q. The strongly non-linear relationship between Q and Q_{od} allows one to distinguish between those thermally activated processes which reduce the free energy due to Al, Si ordering or the elastic energy by their time dependence. Only that quantity which drives the phase transition varies, by a simple dissipation function, with time. In experimental terms, this means that the decision must be made in favour of that parameter which follows a continuous dependence on *ln* time. The present experiments show clearly that this relation holds well for Q_{od} but not for Q. Consequently, the transformation processes from hexagonal to modulated to orthorhombic are clearly driven by the increasing degree of Al, Si order in an annealing experiment, whereas the influence of the correlated lattice distortions is comparatively small.

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