

Study of cation order-disorder in MgAl₂O₄ spinel by in situ neutron diffraction up to 1600 K and 3.2 GPa

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ABSTRACT

The temperature-dependence of the cation distribution in synthetic spinel (MgAl₂O₄) was investigated using in situ time-of-flight neutron powder diffraction at ISIS, the pulsed-neutron source at the Rutherford Appleton Laboratory. Neutron diffraction patterns of stoichiometric MgAl₂O₄ were collected on heating from room temperature to ~1600 K at pressures of ~2.6 GPa. The cation distribution was determined directly from site occupancies obtained by Rietveld refinement. The equilibrium non-convergent ordering was analyzed using the O'Neill-Navrotsky (1983) thermodynamic model, which fits the observed behavior well over the temperature range of the measurements. Fitting the data between 790 and 1600 K yields $\alpha = 31(6)$ kJ/mol and $\beta = -20(13)$ kJ/mol in the expression for the free energy of ordering. The high-pressure temperature-dependent behavior, as compared to equivalent ambient-pressure behavior, demonstrates that disordering occurs to a much greater extent in MgAl₂O₄ at high pressure and that pressure favors disordering toward the inverse structure.

INTRODUCTION

The distribution of Mg and Al between the octahedrally and tetrahedrally coordinated sites in spinel (MgAl₂O₄) has attracted considerable attention over the years. This is a reflection, in part, of the importance of understanding this process in interpreting the stabilities of spinel down to depths of some 60 km or so in the mantle. Most spinels show some degree of disorder, with MgAl₂O₄ being close to the “normal” spinel configuration of ^{[4]A}[^{6]B}O₄. The alternative, inverse ordering scheme is expressed as ^{[4]B}[^{6]A}O₄. Typically, spinels will display some intermediate partly disordered state. This is particularly true as they re-equilibrate at high temperature; a partially ordered state may be expressed as a mix of the ordered (normal) and anti-ordered (inverse) states. This is described by the general formula ^{[4](A_{1-x}B_x)}[^{6](B_{2-x}A_x)}O₄, where x is the occupancy of cation B (in our case Al) at the tetrahedral site and is called the “inversion parameter.” The order-disorder process in spinel is termed “non-convergent,” since there is no symmetry change upon disordering and a completely disordered state is approached asymptotically with increasing temperature.

The importance of understanding cation ordering in MgAl₂O₄ has led to several experimental studies that have attempted to elucidate its high-temperature behavior. Because the X-ray scattering factors for Mg and Al are very similar, cation occupancies cannot be determined directly by X-ray methods, but instead rely on interpreting changes in average coordination radii in terms

of changes in site occupancies. Thus, changes in bond lengths were determined from XRD by Menegazzo et al. (1997), while ²⁷Al MAS-NMR was used to monitor changes in the Al environment (due to exchange between tetrahedral and octahedral sites) (Brun and Hafner 1962; Gobbi et al. 1985; Wood et al. 1986; Millard et al. 1992). Of the few high-temperature structural studies, Yamanaka and Takéuchi (1983) observed changes in the O atom coordinates and thermal expansion by X-ray diffraction, which can be understood in terms of order-disorder. In situ high-temperature neutron powder diffraction studies of synthetic MgAl₂O₄ were undertaken by Peterson et al. (1991) and Redfern et al. (1999), who exploited the relatively strong (40%) nuclear scattering contrast between Mg and Al to obtain absolute site occupancies (and hence the degree of long-range order) directly. The latter study enabled the characterization of the inversion process in terms of both thermodynamic and kinetic models for long-range ordering. The order-disorder properties of spinel as a function of pressure were studied by Pavese et al. (1999), who reported an increase in the degree of order with increasing pressure, based upon neutron powder diffraction of a sample held under pressure in a Paris-Edinburgh cell. Their results seem to indicate that cation ordering may be enhanced at high P to a greater extent than the volume decrease during the disordering process $\Delta V_{\text{disordering}}$ would imply. These results may be skewed by the fact that their sample was a non-stoichiometric (Mg_{0.94}Al_{2.04}O₄) synthetic spinel. Indeed, their results seem at odds with those of Hazen and co-workers (Hazen and Yang 1999; Hazen and Navrotsky 1996) who point to the reduced molar volume and increased compressibility of the inverse form of

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MgAl₂O₄ over the normal form. This would imply that pressure should enhance disorder away from the normal configuration. More recently, computer simulations of the behavior of MgAl₂O₄ spinel have been reported by Lavrentiev et al. (2003) and Da Rocha and Thibaudeau (2003). The latter article, in particular, predicts significant effects of pressure on the high-temperature thermodynamic order-disorder behavior.

In situ neutron diffraction provides a particularly useful, and in several aspects unique, way to obtain detailed information about the crystal structure of minerals at high *P* and *T*. We have recently developed the ability to perform neutron diffraction measurements at simultaneous high pressures (7 GPa) and temperatures (1700 K) (Le Godec et al. 2001a), which allows us to obtain information about changes in the structure of minerals under these conditions. One application of this ability is the measurement of ordering at simultaneous high-*P/T* conditions to chart the effect of both *P* and *T* on processes and kinetics of cation ordering. Here we report the first results of this approach, adapted to the problem of cation disordering in spinel at high *P* and *T*.

EXPERIMENTAL METHODOLOGY

Sample synthesis

The spinel sample was synthesized from a 14 g stoichiometric mix of MgO (99.999%) and Al₂O₃ (99.99%) oxide powders and dried at 1370 K prior to weighing. The sample was then weighed and homogenized by grinding under acetone in an agate mortar. The oxide mix was pressed into several pellets using a 0.5 inch diameter tungsten carbide (WC) die. The pellets were sintered in air for a period of 42 h at 1770 K. The pellets were then drop-quenched from the furnace. XRD examination of a sintered chip from each of the pellets indicated single-phase spinel. The pellets were then annealed at 1070 K for 853 h and quenched by dropping the pellets from the furnace onto SiO₂ glass wool, which formed the lining of a previously evacuated metal beaker. As a cross-calibration, the cell parameter determined by Guinier X-ray diffraction, using NBS Si as an internal standard, was 8.0836(3) Å. The result of O'Neill (1997) indicated an MgO:Al₂O₃ ratio of 1:0.998(3), i.e., stoichiometric within the error of the cell parameter determination. Before neutron investigation, the spinel was mixed with a pressure calibrant (MgO) with a MgAl₂O₄:MgO ratio equal to 9:1 by mass. Pressure calibration was accomplished by using the well-known *P-T* dependence of the density of MgO (Anderson and Zou 1990; Chen et al. 1998; Martinez-Garcia et al. 2000; Raju et al. 2002).

Neutron diffraction procedures

The neutron diffraction experiments were performed at the High Pressure Facility on the PEARL beamline (HiPr) of the ISIS pulsed-neutron source at the Rutherford Appleton Laboratory. The principles of the time-of-flight neutron powder diffraction technique are summarized in Windsor (1981) and the experimental data collection and analysis conditions are summarized in Table 1 (PEARL/HiPr 1996). High pressure was obtained using a Paris-Edinburgh (PE) cell (Besson et al. 1992; Nelmes et al. 1993). There are technical advantages to using a time-of-flight neutron source with energy-dispersive measurements for high-pressure studies as compared to a steady-state source with angle-dispersive measurements. By using a small fixed range of scattering angles around 90°, any contaminant diffraction signals from the pressure cell can be removed completely if one uses tight collimation of both the incident and diffracted beam. In our case, the incident beam is reduced to a diameter of 3.5 mm, slightly smaller than that of the sample, by means of a boron nitride collimator fixed at the front of the cell (Le Godec et al. 2001a). The diffracted beam is collimated by covering the face of the anvils with neutron-absorbing cadmium and by boron-nitride collimators placed on the side of the cell to restrict the region seen by the detectors to that immediately around the sample. Corrections to the measured sample intensities take into account the wavelength-dependent attenuation due to the pressure cell materials that both incident and diffracted beam pass through.

The design of the PE cell with internal heating is shown in Figure 1. The major improvement, as will be seen later, is the use of tantalum foil to determine the

TABLE 1. Experimental data collection and Rietveld refinement details

Instrumental details	
Diffractometer	PEARL/HiPr (neutron time-of flight powder diffractometer)
Moderator	100 K CH ₄
Flight paths	L ₁ = 12.6 m, L ₂ = 0.6 m (all detectors)
Scattering geometries	"transverse" (through-anvil) setting for access to the main detector bank covering 83° < 2θ < 97°
Data acquisition	Digital Personal Alpha Workstation (500 MHz)
Sample environment	
Equipment	Paris-Edinburgh pressure cell (version V4)
Pressure range	0–7 GPa using pseudo-conical profile tungsten carbide anvils
Initial sample volume	65 mm ³
Temperature range	See Table 2
Refinement details	
Phase	MgAl ₂ O ₄ MgO
Space group	<i>Fd</i> 3 <i>m</i> <i>Fm</i> 3 <i>m</i>
Z	8 4
Unit cell refinement	whole pattern
Observations	1900
Refined parameters	
Structural	13 2
Profile	2 1
Background	Cosine Fourier series with 8 terms
Phase fraction	1
Cell	1 1
Constraints	
Strict (equal <i>U</i> _{iso})	^[VI] Mg = ^[VI] Al, ^[VI] Mg = ^[VI] Al Mg = O
Strict (Σsite = 1.0)	^[VI] Mg + ^[VI] Al, ^[VI] Mg + ^[VI] Al
	^[VI] Mg + ^[VI] Mg = 1.0, ^[VI] Al + ^[VI] Al = 2.0
Agreement factors	See Table 2

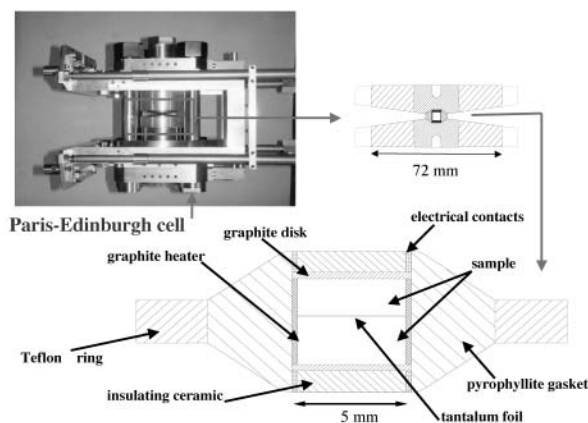


FIGURE 1. Design of the PE cell with internal heating and tantalum foil for in situ *T* measurements.

temperature in situ (Le Godec et al. 2001a). The PE cell achieves high pressures by confining a sample within a gasket between two opposed anvils. The standard arrangement consists of WC anvils with a hemispherical pressure chamber and metallic toroidal gaskets (Besson et al. 1992, 1995). A different shape of anvil is used here (pseudo-conical anvils) to maximize the volume of the sample (Le Godec et al. 2001b), the internal diameter of which is 4.5 instead of 3 mm (previously used for X-ray experiments). The anvils are made of WC supported by a maraging steel binding ring, which produces a radial stress of about 0.8 GPa. At the back, a recess 6 mm deep and 5 mm in diameter reduces attenuation of the incident neutron beam. To prevent pressure effects induced by increasing oil temperature in the PE cell, the anvils are equipped with collars in which water circulates (Le Godec et al. 2001b). The sample container, a graphite tube that serves as an electrical resistance heater and pressure medium, is located in a thermally treated pyrophyllite gasket (heated for 6 h at 1070 K to remove water of hydration). This ceramic material is used as both a thermal and electrical insulator. Heating is achieved by passing an electric

current from one anvil through the graphite heater and out through the opposite anvil. Temperature stability is achieved using a regulated power supply. During the experiment, the pressure applied to the gasket leads to extrusion as can be seen in Figure 2. This cross-section of the sample after the experiment clearly shows the bending of the graphite heater, but it also shows that the gasket shape remains well defined. A Teflon ring is used to limit the extrusion, to preserve the integrity of the gasket, and to improve the efficiency of the compression as well as the maximum pressure achieved (Le Godec et al. 2001b). The pressure is determined from the unit-cell volume of MgO, which has a well-known equation of state (Martinez-Garcia et al. 2000). The estimated error in pressure does not exceed 0.1 GPa.

Measurement of temperature using neutron absorption resonance radiography

The neutron radiography method (Neutron Absorption Resonance Radiography — NARR) is used to measure the temperature in situ. It is a non-invasive technique that provides an alternative to the use of thermocouples (Fowler and Taylor 1987). With this method, an epithermal-energy (~ 10 eV) neutron absorption resonance line is measured from a thin metallic foil embedded in the sample. The width of the resonance increases with temperature by the Doppler effect from the thermal motion of the atoms in the foil (Mayers et al. 1989; Frost et al. 1989). If a simple metal is used, the phonon frequencies will be relatively low, and for temperatures above the Debye temperature θ_D the vibrational amplitudes will be given by classical equipartition and will be independent of the force constants. As a result, the width of the resonance should be independent of pressure, provided that the generally increased θ_D , seen as a function of P , does not violate $T > \theta_D$. We used a tantalum foil disk (50 μm) with a useful resonance at 10.34 eV and corresponding wavelength at 8.9 μm as can be seen on Figure 3 (obtained at 1600 K). This absorption profile was fitted by a Gaussian function and a sixth-order polynomial background. The signal to noise ratio was limited in comparison with previous experiments (Le Godec et al. 2001a, 2001b) through improved electronics. High

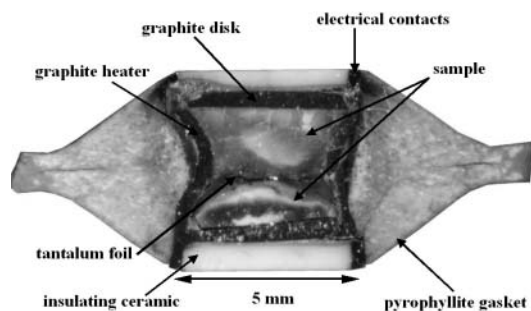


FIGURE 2. Cross section of the sample after the experiment showing the deformation of the graphite furnace and the sustained pyrophyllite gasket integrity.

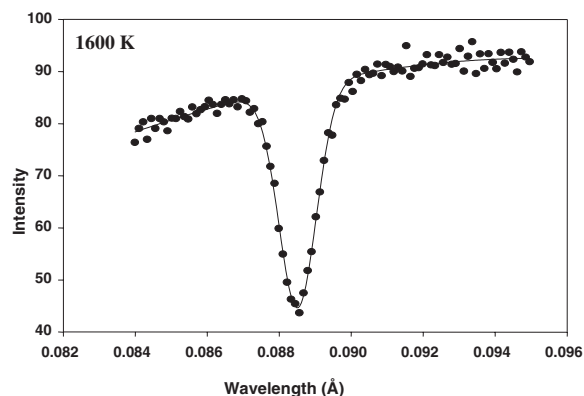


FIGURE 3. Ta^{181} 10.34 eV neutron absorption resonance spectrum at 1600 K (improved electronics detection).

temperature is achieved by adjusting the power applied through the anvils based on a calibration curve. Three separate calibration experiments in which the Ta foil was accompanied by a thermocouple were performed with quartz, alumina, and zirconia. The squares of the fitted width, σ^2 , are shown in Figure 4 as a function of temperature. The data was fitted by a straight line that was used for the current experiment (accuracy ± 20 K).

For our NARR experiment, a high-efficiency neutron monitor was used (Le Godec et al. 2001a). The active scintillation element is a ^6Li -enriched glass, with dimensions 7×7 mm in cross-section and 25 mm deep in the direction of the neutron beam. One of the long faces is viewed by a ten-stage linear photomultiplier tube. The photomultiplier tube and scintillation block are surrounded by a thin (50 μm) cylindrical aluminum foil reflector to enhance light collection. The detector exhibits good pulse height resolution, and to a first approximation, the neutron detection efficiency is close to the neutron absorption efficiency, which was calculated to be 75% at 10 eV.

Rietveld refinement details

High-temperature/pressure structures were refined from our powder data using the GSAS Rietveld refinement software (Larson and Von Dreele 1994). Total site occupancies were constrained to stoichiometric values completely describing the Mg-Al distribution. The background was modeled using an eight-term cosine Fourier series. The crystallographic variables were the unit-cell parameter, the coordinates of the O atom, and the occupancies of the tetrahedral and octahedral sites. The isotropic temperature factors were first refined and their evolution against the temperature was modeled as a monotonically increasing function, to reduce any weighting to site occupancies from correlation with temperature factors. The values found with this calibration curve were then used in further refinements. In the same manner, the absorption was first refined at around 2.6 GPa and an average value determined, which was then used in subsequent refinements.

RESULTS AND DISCUSSION

The good agreement found between the temperature estimated from the applied power and the temperature determined by NARR calibration is demonstrated in Figure 5. However, because the calibration curve between the power and the temperature reached was performed with a different arrangement, some differences may appear. The accuracy of the NARR method leads to a great improvement in the temperature determination (Le Godec et al. 2001b).

A typical neutron diffraction pattern is shown, together with the fit from the refinement, in Figure 6. The pattern given is the one obtained for the most extreme pressure and temperature conditions (1600 K and 3.2 GPa). Tickmarks are shown below the pattern for both MgO and MgAl_2O_4 . The results of the high-temperature structural refinements for MgAl_2O_4 are given in Table 2. In particular, the evolution of the spinel lattice param-

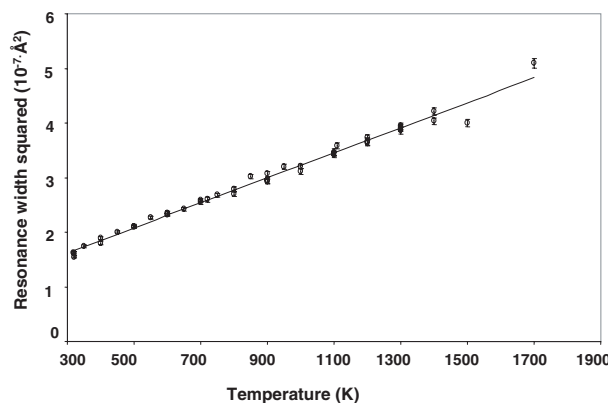


FIGURE 4. Calibration curve of the measured width of the Ta^{181} 10.34 eV neutron absorption resonance vs. thermocouple temperature.

TABLE 2. Structural data

T (K)	P (GPa)	Spinel lattice parameter (Å)	O atom position u	Inversion parameter x	U_{80} (oxy)	U_{80} (tet)	U_{80} (oct)	R_p
289(4)	0	8.0834(4)	0.26211(17)	0.320(38)	0.0045(8)	0.0050(7)	0.0092(5)	0.1192
571(5)	0.4(1)	8.0727(8)	0.26206(23)	0.262(50)	0.0046(8)	0.0109(7)	0.0183(5)	0.1117
789(7)	0.4(1)	8.0874(8)	0.26175(24)	0.292(51)	0.0038(8)	0.0154(7)	0.0261(5)	0.1150
1061(9)	1.5(1)	8.1104(7)	0.26204(24)	0.386(53)	0.0070(8)	0.0185(7)	0.0330(5)	0.1091
1254(10)	2.0(1)	8.1274(5)	0.26179(23)	0.453(50)	0.0111(8)	0.0148(7)	0.0399(5)	0.1032
1436(11)	2.8(1)	8.1350(4)	0.26211(22)	0.571(49)	0.0124(8)	0.0244(7)	0.0316(5)	0.1043
1591(12)	3.2(1)	8.1452(4)	0.26199(23)	0.633(50)	0.0156(8)	0.0231(7)	0.0440(5)	0.1015
1106(9)	1.9(1)	8.1171(4)	0.26159(21)	0.524(49)	0.0101(8)	0.0103(7)	0.0311(5)	0.1076
912(7)	1.7(1)	8.1050(4)	0.26181(20)	0.509(47)	0.0086(8)	0.0128(7)	0.0213(5)	0.1045
390(4)	0.5(1)	8.0800(4)	0.26136(20)	0.365(47)	0.0059(8)	0.0043(7)	0.0116(5)	0.1174

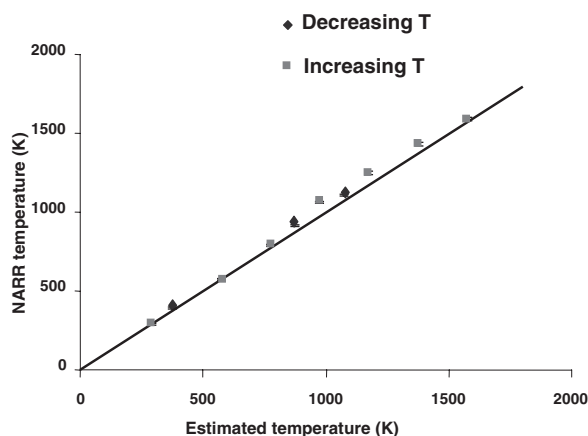


FIGURE 5. Comparison of the temperature estimated from the power applied through the anvils to that determined by NARR. The filled diamonds show the values obtained while decreasing temperature and the filled squares on increasing temperature. The solid line identifies the condition where parity is achieved between the estimated temperature and that determined by NARR.

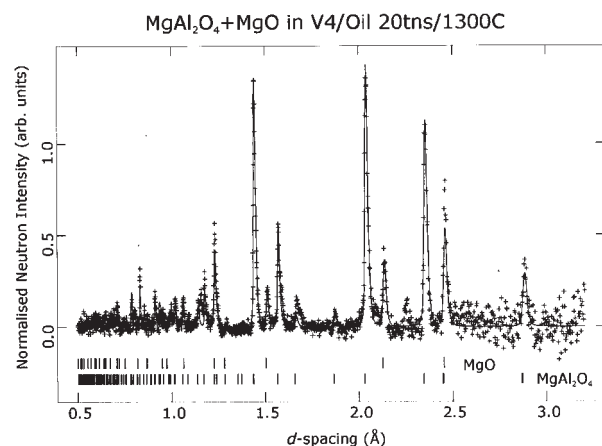


FIGURE 6. Diffraction pattern of MgAl_2O_4 :MgO (9:1) at 1600 K and 3.2 GPa.

eter is shown as a function of the temperature in Figure 7. The PE device allows us to maintain a constant force to the anvils (and therefore the sample volume); the pressure then varies with temperature due to additional thermal pressure. The pressure, determined from the equation of state of MgO, is given in GPa for each temperature in Figure 7.

The essential feature of the structural response at temperatures and pressures of interest to us is the exchange of metal cations between the tetrahedral and octahedral sites, which is given by

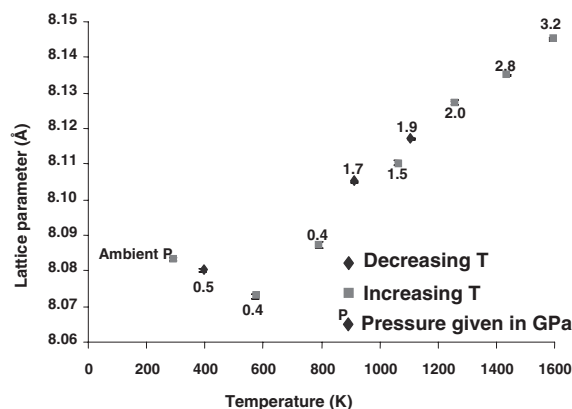


FIGURE 7. Evolution of MgAl_2O_4 lattice parameter with temperature. The filled diamonds show the values obtained while decreasing temperature and the filled squares on increasing temperature.

the inversion parameter (equal to the occupancy of Al at the tetrahedral site). The temperature and pressure dependence of the inversion parameter is shown in Figure 8. The filled squares and crosses show the values obtained with increasing temperature and the filled diamonds with decreasing temperature. The behavior takes the same form as that now observed in several minerals undergoing cation ordering, including other spinels and olivines, in which relaxation is seen below some kinetically controlled freezing temperature, and thermodynamic equilibrium is followed above this temperature (Redfern et al. 1996, 1997, 1999; Harrison et al. 1998). The initial degree of inversion measured at room temperature and pressure corresponds to the degree of order achieved by quenching the sample during the initial synthesis. The value we observe for our sample is slightly higher than that found in previous work (Redfern et al. 1999), which simply implies that this sample may have been quenched faster and has not maintained equilibrium ordering on cooling. During heating the sample begins to move toward its equilibrium state, which is a more ordered state. The process begins when the temperature becomes high enough to allow exchange of Mg and Al between the tetrahedral and octahedral sites. By 650 K, the sample has ordered on heating to a maximum degree of order (minimum x) with $x \approx 0.25$, at which point it is essentially in equilibrium; further heating of the sample results in progressive disordering down the equilibrium pathway. It is interesting to note that the maximum degree of order is attained faster and is lower under pressure than that achieved at room pressure (Redfern et al. 1999). The results for cooling indicate that the sample did not remain at equilibrium while cooling. The degrees of order found with decreasing T are lower than those found with increasing

T. The errors on structural parameters determined in this study are greater than those determined in previous ambient-pressure high-temperature studies (e.g., Redfern et al. 1999) due to the lower signal-to-noise and smaller sample volumes employed in the PE cell. The O atom positional parameter shows no variation beyond the error across the measured *P/T* range. This parameter is sensitive to both the site occupancies of the tetrahedral and octahedral sites, as well as the relative compressibilities and expansivities of each site. In the case of our experiments, the variations in positional parameter due to occupancy variations are counterbalanced by the combined changes due to compression and thermal expansion across the *P/T* trajectory of our experiment (which is not strictly isobaric).

The equilibrium non-convergent ordering can be analyzed using the O'Neill-Navrotsky (1983) thermodynamic model, which fits the observed behavior well over the temperature range of the measurements (solid line). The dashed line in Figure 8 represents the evolution of the order parameter with temperature at room pressure (Redfern et al. 1999). This model expresses the enthalpy of a spinel with an intermediate cation distribution (relative to the same spinel with the normal cation distribution) as a quadratic function of the inversion parameter previously defined ($\Delta H = \alpha x + \beta x^2$). The free energy of ordering is then given by combining this excess enthalpy with the configurational entropy of the intermediate cation distribution (Redfern et al. 1999). Noting that our data are not isobaric, the use of this equation for a *P/T* experiment such as we have employed must be conducted with caution. It does, nonetheless, allow an approximate comparison with low-pressure results. For example, if we fit the data between 790 and 1600 K (filled squares) using the O'Neill-Navrotsky thermodynamic model we obtain $\alpha = 31(6)$ kJ/mol and $\beta = -20(13)$ kJ/mol (Figure 8). This suggests that the sign of the β coefficient in MgAl_2O_4 is a function of pressure, because the ambient pressure data were described by a small positive value of β (Redfern et al. 1999). The data themselves show that the effect of pressure at high temperature appears to produce more disorder. In particular, the highest temperature data, which cor-

respond to pressures of more than 2.6 GPa, are significantly more disordered than samples studied at the same temperature but at ambient pressure.

The stability of the structure at high temperature may also be related to the changing of the volume as was previously observed at ambient pressure (Redfern et al. 1999). Several processes take place simultaneously. The increasing temperature yields an increasing cell parameter, as seen in Figure 7. At the same time, the cation exchange between the tetrahedral and octahedral sites has competing effects. First, the tetrahedral site tends to decrease in size with increasing temperature, when an equilibrium degree of order exists, as the occupancy of the smaller Al^{3+} cation at that site increases. Meanwhile, the octahedral site becomes larger as a result of thermal expansion and the increasing occupancy of that site by the larger Mg^{2+} cation.

It is interesting to compare our results with predictions from the most recent computational study of order-disorder effects in MgAl_2O_4 reported by Da Rocha and Thibaudau (2003). They discussed the influence of *P* on the inversion parameter behavior in terms of additional contribution to the free energy of ordering through the work of external pressure ($P\Delta V$). The volume modification associated with ordering was expressed as $\Delta V = \mu x + \nu x^2$, where *x* is the inversion parameter, so that the effective constants in the O'Neill-Navrotsky model become $\alpha' = \alpha + P\mu$ and $\beta' = \beta + P\nu$. Both μ and ν are found to be negative, and for disordered spinel the cell volume decreases most rapidly upon increasing pressure at low pressure. Da Rocha and Thibaudau (2003) were able to calculate equilibrium order-disorder pathways for *x* as a function of *P* and *T*, and their results are shown together with ours in Figure 9. Our experimental data highlight the conclusion that pressure, especially in the temperature range between 750 and 1500 K, has a significant impact on the expected degree of order in spinel.

Our results demonstrate the feasibility of high-*P/T* neutron powder diffraction for the in situ study of cation ordering under real Earth interior conditions and provide the first experimental indications of significant deviations in thermodynamic behav-

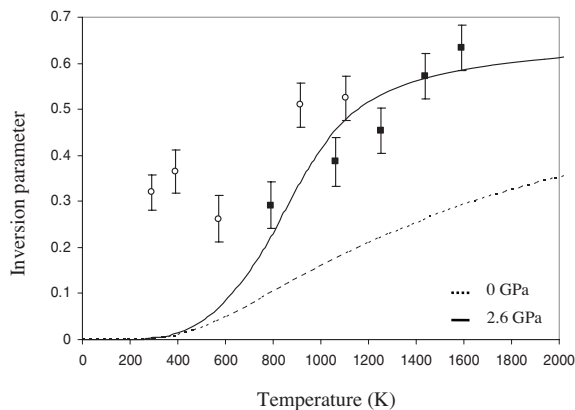


FIGURE 8. Evolution of MgAl_2O_4 inversion parameter with temperature and pressure. Solid data points represent equilibrium data, open points are data that have fallen off the equilibrium curve. The fit to the data at 2.6 GPa is shown by the solid line, and the equivalent 0 GPa fit is given by the dotted line.

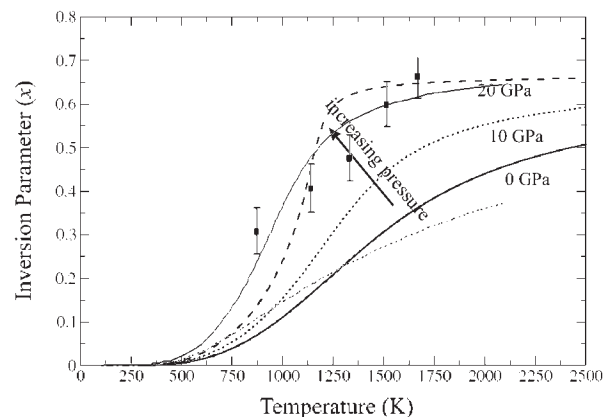


FIGURE 9. Comparison of our experimental data with computational predictions for the temperature dependence of the inversion parameter at 0, 10, and 20 GPa (from Da Rocha and Thibaudau 2003).

ior of order-disorder under combined P and T , compared with results from the same material investigated solely as a function of P or T .

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