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Comparative compressibility and structural behavior of spinel $MgAl_2O_4$ at high pressures: The independency on the degree of cation order

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Abstract

The equation of state and the crystal structure evolution with pressure were determined for two single crystals of pure natural $MgAl_2O_4$ spinels with different degrees of order. The two samples studied were cut from a larger single crystal and one of them was experimentally disordered at high temperature. The two crystals, showing an inversion parameter x of 0.27 and 0.15 at ambient conditions, were loaded together in a diamond anvil cell and their unit-cell edge was measured up to about 7.5 GPa at 14 different pressures. The unit-cell volume, V_0, the bulk modulus, K_{T0}, and its first pressure derivative, K', were simultaneously refined using a third-order Birch-Murnaghan equation of state, giving the following coefficients: V_0 = 529.32(2) Å^3, K_{T0} = 193(1) GPa, K' = 5.6(3) for the ordered sample and V_0 = 528.39(2) Å^3, K_{T0} = 192(1) GPa, K' = 5.4(3) for the disordered one. Complete intensity data were collected at 0, 0.44, 2.92, 7.34, and 8.03 GPa in a separate experiment. For the ordered and disordered samples the oxygen atomic coordinate u remains practically unchanged inside the investigated pressure range with an average value of 0.2633(5) and 0.2614(2), respectively. As a consequence, the polyhedral compressibilities are similar and are not influenced by the Mg/Al distribution over the two crystallographic sites. This also suggests that pressure has little or no influence on the degree of order in the $MgAl_2O_4$ spinel.

Keywords: X-ray single-crystal diffraction, spinel, cation ordering, high pressure

Introduction

Spinels, with general chemical formula AB_2O_4 (in common 2-3 spinels A is a divalent cation and B a trivalent), are among the most studied oxide phases in the Earth sciences, because they can be used as petrogenetic indicators (Princivalle et al. 1989, 1999; Sack 1982; Sack and Ghiorso 1991) as well as a structural model for minerals stable at pressure/temperature conditions of the Earth's mantle (e.g., ringwoodite, Sasaky et al. 1982; Hazen 1993). Spinels show a simple crystal structure (space group $Fd\bar{3}m$) characterized by two symmetrically distinct polyhedra: an octahedron, M, and a tetrahedron, T, occupied by divalent and trivalent cations. The number of occupied octahedral sites is twice that of the tetrahedral ones. The tetrahedral cation is located at 1/8,1/8,1/8, while the octahedral cation at 1/2,1/2,1/2. The oxygen has coordinates u,u,u [when u = 0.25 oxygen atoms are arranged in ideal cubic closest packing (eutaxy)]. Cation distribution among the octahedral and tetrahedral sites may vary. In "normal" spinels, the A cations occupy the tetrahedral sites (AB_2O_4), whereas "inverse" spinels have formula $^{IV}B^{VI}(AB)O_4$ with A and B randomly distributed among the octahedral sites. Intermediate cation distributions are very common and a general formula can be written as $^{IV}(A_{1-x}B_x)^{VI}(A_xB_{2-x})O_4$, where x is the inversion parameter and is usually taken as the fraction of B cation on the tetrahedral site. There is no change in symmetry associated with this cation order-disorder process as it involves non-equivalent sites, and therefore it is considered non-convergent and can be described by the inversion parameter x, which approaches asymptotically the value of 2/3 corresponding to a completely random distribution, i.e., complete disorder (Sack and Ghiorso 1991).

Spinel sensu stricto, $MgAl_2O_4$ ss, is one of the most common spinels, and both its high-temperature and high-pressure behavior have been extensively investigated (Finger et al. 1986; Redfern et al. 1999; Hazen and Yang 1999; Pavese et al. 1999; Carbonin et al. 2002; Levy et al. 2003; Martignago et al. 2003). Andreozzi et al. (2000) suggested a linear relationship between x and u according to the expression:

$$u = 0.2651 - 0.0123x \quad (1)$$

Several works have shown that cation disordering increases with temperature, in contrast the influence of pressure is still a matter of controversy. Finger et al. (1986) investigated a single-crystal of natural spinel up to about 4 GPa at room temperature, and concluded that u decreases slightly with pressure. Pavese et al. (1999) in a neutron powder diffraction study at high pressure

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and room temperature up to 4 GPa of a synthetic spinel with composition $Mg_{0.94}Al_{2.04}O_4$ suggested that pressure strongly increases the cation ordering. Also these authors reported that the *u* coordinate decreases with pressure. Using X-ray powder diffraction with synchrotron radiation, Levy et al. (2003) performed a study up to 30 GPa and room temperature on a synthetic $MgAl_2O_4$ and concluded that the change in *u* with pressure was on the order of their uncertainties. More recently, Meducin et al. (2004) performed a combined high-pressure and high-temperature study (from room temperature up to 1600 K at 2.6 GPa) again by means of neutron powder diffraction and suggested that for $MgAl_2O_4$ the effect of pressure at high temperature is to increase the cation disorder. Hazen and Yang (1999) calculated on the basis of a polyhedral model that normal 2-3 spinels are slightly less compressible than their inverse variants. In a very recent theoretical study based on density functional theory, Li et al. (2007) show that inverse $MgAl_2O_4$ is less compressible than ordered spinel, however, for small degree of disorder the bulk modulus decreases slightly before increasing. Finally, Kudoh et al. (2007) in a single-crystal investigation on ringwoodite spinel found an increase in *u* with increasing the pressure; this could mean that pressure has some effect on the degree of order of spinels.

In this study, we performed a comparative in-situ study at high pressures on two natural single crystals of pure and stoichiometric $MgAl_2O_4$ with different degrees of order, loaded into the same diamond-anvil cell. The aim of our work was to clarify the effect of the Mg/Al distribution on the high-pressure crystal-structure behavior and on the equation of state of $MgAl_2O_4$.

Experimental methods

Sample characterization

Two fragments of a pale pink gem quality crystal of $MgAl_2O_4$ (2 mm in diameter) from gem gravels of Sri Lanka, kindly provided by the "Museo di Mineralogia e Petrografia" of the Department of Earth Science of Trieste University, was used in this study. One of the fragments was annealed at 1000 °C for 24 h to obtain a more disordered sample. To this end, the fragment was sealed in a thin-wall quartz tube in air, because oxidation problems were not expected for this composition, and the heating-quenching run was performed at room pressure. No change in crystal color or transparency was observed at the end of the thermal run. The duration of annealing time was chosen on the basis of a previous equilibrium study (Andreozzi et al. 2000). The temperature was measured by means of a calibrated Pt/Pt-Rh thermocouple located near the sample with an estimated uncertainty of ±5 °C. At the end of the run the sample was quenched by dropping the quartz tube into cold water (20 cm of free fall), with cooling time down to 400 °C estimated to be less than 0.5 s (Molin et al. 1991; Della Giusta et al. 1996). Hereafter we will refer to the natural fragment (size 95 × 80 × 50 μm^3) as sample A or ordered sample and to the experimentally disordered fragment (size 200 × 90 × 50 μm^3) as sample B or disordered sample.

Chemical analysis was carried out on the polished surface of the fragment from which the two crystals were taken for the high-pressure single-crystal X-ray investigation, using a Cameca/Camebax Microbeam electron microprobe at the Istituto di Geoscienze e Georisorse, CNR Padova. Analyses were performed at 15 kV and 15 nA sample current by the wavelength-dispersive method (WDS). X-ray counts were converted into oxide weight percentages using the PAP correction program supplied by CAMECA. MgO for Mg, Al_2O_3 for Al, Cr_2O_3 for Cr, ZnS for Zn, and Fe_2O_3 for Fe were used as standards. The results of microprobe analyses are reported in Table 1 and are consistent with an extremely pure $MgAl_2O_4$ composition.

X-ray diffraction at ambient conditions

X-ray data of the two crystals were collected using an automated KUMA-KM4 (Kappa-geometry) diffractometer (Mo$K\alpha$ monochromatized by a flat graphite crystal). Intensity data were collected up to 110 °2θ in the ω-2θ step-scan mode, with peak-base width of 1.8 °2θ, which increased with the θ angle. Counting times ranged from 30 to 120 s, according to peak standard deviation, with background measured from both sides of the peak for a total of half peak-time. Because the psi-scan curves were flat, an empirical correction for absorption was not applied. Twenty-four equivalents of the 12 8 4 reflection (ca. 82 °2θ) were accurately centered at positive and negative values of 2θ and used for cell parameter determination. Structure factors tables are available from the authors on request.

Structural refinements, performed with the SHELX-97 program (Sheldrick 1997), were carried out in the $Fd\bar{3}m$ space group with origin at $\bar{3}m$, without chemical constraints. No violations of this symmetry were detected. Refined parameters were: scale factor, secondary extinction coefficient, oxygen positional parameter (*u*), Mg and Al occupancy in T and M sites, respectively, and anisotropic displacement parameters for all atoms. The scattering factors for partially oxidized oxygen (70%) and neutral cations were used (see Andreozzi et al. 2000 for details). This gave the best values of the statistical descriptors R_1, wR_2, and GooF in all $\sin\theta/\lambda$ shells, as well as a total mean atomic number (m.a.n.) corresponding to that expected from stoichiometry within ±1σ. All the crystal structure refinement details at ambient conditions are reported in Table 2.

The inversion parameter *x* (fraction of Al at the T site) was calculated according to the bond-length method, following Carbonin et al. (1996) and using the ionic radii from Lavina et al. (2002). This method determines cation distribution by minimizing the following function, which takes into account structural data as well as soft chemical constraint:

$$F(X_i) = \Sigma_j \{[O_j - C_j(X_i)]/\sigma_j\}^2 \quad (2)$$

where O_j are observed quantities, i.e., T-O and M-O bond lengths, m.a.n. of T and M sites, and atomic proportions obtained from microprobe analysis, σ_j are their standard deviations. The variables X_i are the cation fractions Mg(T), Al(T), Mg(M), and Al(M), related by the inversion parameter *x* that are used to calculate the quantities C_j, which enter into the minimization procedure. Such function was restricted to $MgAl_2O_4$ stoichiometry, according to the microprobe analyses. Results were considered acceptable when the differences between observed and calculated parameters were within 2σ of each observed quantity. The cation fractions Mg(T), Al(T), Mg(M), and Al(M) and the corresponding inversion parameters are reported in Table 1 for both A and B samples. These are in good agreement with the inversion parameters calculated according to Equation 1, using simply the atomic position *u* of the oxygen atoms.

X-ray diffraction at high pressure

Sample A and B were loaded together in a BGI (Bayerisches Geoinstitut) diamond anvil cell (DAC), with diamond culets of 600 μm in diameter. A T301 gasket preindented to 100 μm, with a hole of 300 μm in diameter was used. A mixture of methanol:ethanol:water with ratio 16:3:1 was used as pressure transmitting medium. Together with the two samples, a single crystal of quartz was loaded into the DAC as pressure internal standard (Angel et al. 1997).

X-ray intensity data were collected from series of exposures on a CCD-

Table 1. Chemical data for the spinel fragment from which the two single crystals were selected and cation distributions of the single crystals

Oxide wt%*		Cation partitioning from crystal-structure refinements			
				Disordered	Ordered
MgO	28.2(2)	T site	Mg	0.725(8)	0.851(9)
Al_2O_3	71.5(1)		Al	0.272(4)	0.145(4)
Cr_2O_3	0.11(3)				
ZnO	0.17(9)	M site	Al	1.727(9)	1.853(9)
FeO	–		Mg	0.271(5)	0.145(4)
Sum	99.98				
Cations on basis of 4 O atoms					
Al	1.998(5)	Inversion parameter *x*		0.272(5)†	0.145(4)†
Cr	0.002(1)				
Mg	0.997(5)				
Zn	0.003(2)				
Sum	3.000				

Note: The stoichiometric formula is $Mg_{0.997}Al_{1.998}Cr_{0.002}Zn_{0.003}O_4$.
* Average of 10 electron microprobe analyses; standard deviations are in parentheses.
† The standard deviation is relative to 2σ.

Table 2. Details of structure refinements at ambient and high pressure for the two spinels investigated in the present study

P (GPa)	0.0001*	0.0001†	0.44(5)	2.92(5)	7.34(5)	8.03(5)
Ordered sample						
a (Å)	8.0888(1)	8.0961(2)	8.0864(4)	8.0494(4)	7.9996(3)	7.9921(5)
u	0.26332(5)	0.2630(3)	0.2637(5)	0.2634(3)	0.2629(4)	0.2633(4)
M-O (Å)	1.9205(4)	1.924(2)	1.918(4)	1.911(2)	1.902(3)	1.898(3)
T-O (Å)	1.9379(7)	1.935(4)	1.942(7)	1.929(4)	1.911(5)	1.914(6)
V_T (Å^3)	3.735(1)	3.710(5)	3.769(10)	3.676(5)	3.564(6)	3.600(8)
V_M (Å^3)	9.270(2)	9.352(10)	9.202(20)	9.143(10)	9.047(13)	8.945(15)
U_{eq} (O) (Å^2)	0.0049(2)	0.0051(9)	0.0100(17)	0.0074(10)	0.0087(12)	0.0100(14)
U_{eq} (M) (Å^2)	0.0037(2)	0.0036(8)	0.0068(16)	0.0060(10)	0.0068(11)	0.0094(13)
U_{eq} (T) (Å^2)	0.0047(2)	0.0053(9)	0.0070(18)	0.0067(10)	0.0081(14)	0.0097(14)
Unique refl.	118	26	22	26	24	19
R_1	2.04	2.26	3.20	3.10	2.92	2.25
GooF	1.39	1.31	1.39	1.05	1.10	1.15
R_{int}	3.03	3.34	4.93	3.55	9.11	2.61
wR_2	3.88	5.49	7.97	6.06	6.42	5.94
Disordered sample						
a (Å)	8.0849(1)	8.0899(2)	8.0801(3)	8.0451(3)	7.9928(3)	7.9874(3)
u	0.26166(6)	0.2614(2)	0.2615(2)	0.2614(2)	0.2612(2)	0.2613(2)
M-O (Å)	1.9316(4)	1.935(1)	1.932(2)	1.924(2)	1.913(1)	1.911(2)
T-O (Å)	1.9137(8)	1.912(3)	1.910(3)	1.900(3)	1.886(3)	1.886(3)
V_T (Å^3)	3.597(1)	3.588(3)	3.579(4)	3.523(4)	3.444(3)	3.445(4)
V_M (Å^3)	9.474(2)	9.516(7)	9.475(9)	9.369(8)	9.206(7)	9.174(8)
U_{eq} (O) (Å^2)	0.0078(2)	0.0094(7)	0.0110(9)	0.0094(9)	0.0081(7)	0.0094(7)
U_{eq} (M) (Å^2)	0.0041(2)	0.0051(6)	0.0060(7)	0.0063(8)	0.0043(6)	0.0051(6)
U_{eq} (T) (Å^2)	0.0038(2)	0.0050(7)	0.0062(8)	0.0056(9)	0.0038(7)	0.0041(7)
Unique refl.	120	41	34	42	39	36
R_1	1.99	2.53	2.71	3.50	2.50	2.08
GooF	1.36	1.29	1.33	1.22	1.23	1.20
R_{int}	3.07	3.14	4.99	4.03	4.63	4.39
wR_2	4.52	5.60	5.26	7.15	5.63	5.64

* Crystal in air measured using a point detector.
† Crystal in DAC measured using a CCD detector. U_{eq} for the high-pressure measurements are actually U_{iso} since they were refined as isotropic.

equipped (Smart 1000) Bruker-AXS four-circle diffractometer utilizing graphite-monochromatized Mo$K\alpha$ radiation (Geological Institute of Copenhagen). One 1 atm and six high-pressure data sets, each consisting of 1800 exposures, 0.2° ω-rotation apart and covering the accessible angular range up to sinθ/λ = 0.68, were collected at 298 K. The data collection strategy ensured a collection of nearly all accessible reflections, avoiding at the same time shaded regions on the detector surface. Although a significantly lower number of unique reflections could be collected compared to the measurement without DAC, the average redundancy was relatively high (around 7) ensuring a good determination of intensities. For intensity integration, data reduction and correction the Bruker-AXS software (SAINT+ and SADABS), which utilize a three-dimensional extraction of intensities, and the method of spherical harmonics for empirical absorption correction, was used. The final unit-cell parameters were obtained from a least-squares refinement of positions of 250 to 260 reflections with $I > 10\sigma_I$ obtained through the integration process. The complete intensity data collections were performed at 0, 0.440, 2.409, 7.342, and 8.027 GPa. No violations of symmetry were observed throughout the pressure range investigated. For the ordered sample a smaller number of unique reflections were collected with respect to the disordered crystal, probably due to the smaller crystal size and to its orientation. The crystal structure parameters at high-pressure were refined using the SHELXL program (Sheldrick 1997) starting from the atomic coordinates of the ambient conditions data, using only isotropic displacement factors. For the ordered crystal, the m.a.n. of the tetrahedral and octahedral sites was softly constrained to the values obtained from the refinement of the data collected at ambient conditions. This refinement strategy is suggested by the limited number of independent reflections collected at high pressure due to the DAC angular limitation, which strongly influences the reliability of the occupancy and displacement parameters. Refinement details and crystal data relative to the high-pressure measurements are reported in Table 2.

The crystals were recovered after the HP data collection measurements and reloaded in the same DAC to measure accurate lattice parameters to determine the equation of state (EoS) of $MgAl_2O_4$ spinel. Unit-cell parameters were determined as a function of pressure using a Huber four-circle single-crystal diffractometer at the Bayerisches Geoinstitut. Full details of the instrument and the peak centering algorithms are provided by Angel et al. (2000). The eight-position centering method (King and Finger 1979) was used to minimize the effects of crystal offsets and diffractometer aberrations on the refined peak positions. The crystals were investigated up to ~7.4 GPa, at which pressure the experiment was stopped due to gasket failure. Symmetry constrained unit-cell parameters for both ordered and disordered spinels were obtained by vector-least-square refinements (Ralph and Finger 1982) and are within one standard deviation with respect to the unconstrained cell parameters. The unit-cell edges and volumes of both samples collected at the different pressures are reported in Table 3.

Results

Equation of State

The evolutions of the unit-cell edges of ordered and disordered $MgAl_2O_4$ spinel crystals are shown in Figure 1 as a function of pressure. The data do not indicate any evidence of phase transition in the pressure range investigated. The two samples behave under pressure exactly in the same way with a unit-cell volume variation of 3.4% to the maximum pressure reached. The *P*-*V* data were fitted with a third-order Birch-Murnaghan EoS (Birch 1947), using the EOSFIT 5.2 program (Angel 2002). The unit-cell volume, V_0, the bulk modulus, K_{T0}, and its first pressure derivative, K', were simultaneously refined. The resulting EoS parameters are: V_0 = 529.32(2) Å^3, K_{T0} = 193(1) GPa, K' = 5.6(3), and V_0 = 528.39(2) Å^3, K_{T0} = 192(1) GPa, K' = 5.4(3) for the ordered and disordered samples, respectively. The bulk moduli obtained are in a good agreement with previous works (Finger et al. 1986; Pavese et al. 1999; Levy et al. 2003); however, the accuracy of the present data resulted in the possibility of refining simultaneously all three EoS coefficients.

Crystal structure at high-pressure

The only independent position parameter in this spinel structure is the oxygen atomic coordinate *u*. The *u* coordinate at ambient conditions is 0.26332(5) for the ordered sample and 0.26166(6) for the disordered one (Table 2; row 2). In Figure 2, the coordinate *u* is plotted for both samples as a function of

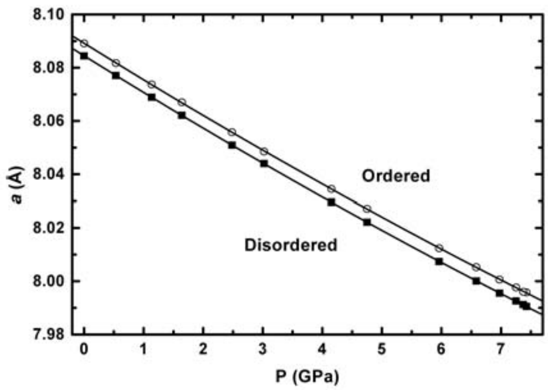

FIGURE 1. Evolution of the unit-cell edge with pressure for ordered (open circles) and disordered (filled squares) spinels studied in this work. The standard deviations are smaller than the symbols used. The solid curves are the third-order Birch-Murnaghan EoS fits to the observed *P*-*V* data.

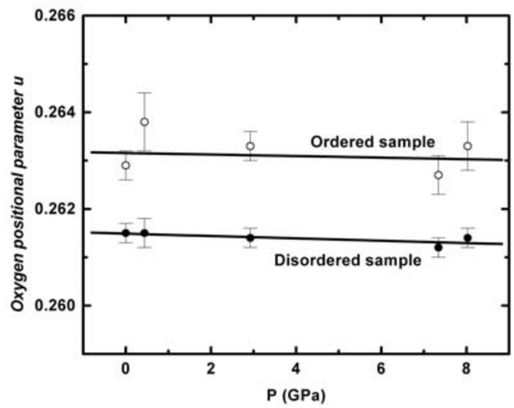

FIGURE 2. The oxygen coordinate *u* as a function of pressure for ordered (ord) and disordered (dis) spinels investigated in this study. Symbols as in Figure 1. The solid lines are weighted linear fits through the data resulting in the following equations: $u_{(ord)} = 0.2634(3) - 0.00004(1)$ P (GPa) and u(dis) = 0.2614(1) – 0.00002(1) P (GPa).

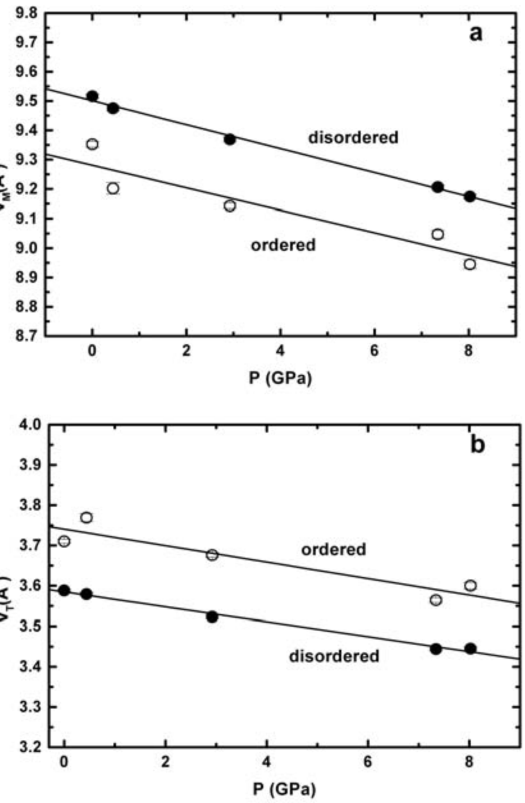

FIGURE 3. Evolution of the octahedral (**a**) and tetrahedral (**b**) volumes with pressure for the ordered and disordered spinels studied in this work. Symbols as in Figure 1. The size of symbols corresponds approximately to two standard deviations.

pressure. For both crystals, this parameter does not change with pressure by more than one standard deviation from the value at 1 atm (see also Table 2). The linear fits predict a very small decrease in the value of *u* suggesting a slightly more compressible tetrahedral coordination (see Appendix). However, given the uncertainties, the change in *u* may also be negligible (the slopes of the weighted regression are practically zero for both the samples: –0.00004 and –0.00002 for the A and B samples, respectively) and, if this is the case, according to the mathematical relationships reported in the appendix, octahedron and the tetrahedron are compressing at the same rate.

The volumes of the octahedron and tetrahedron for both ordered and disordered samples are plotted against pressure in Figures 3a and 3b. Their evolution can be described with linear regressions, which have practically the same slope regardless of the type of polyhedron and of the degree of order. The values of the volume compressibilities, obtained by the weighted linear regression, are: $\beta_M = -0.0041(4)$ GPa^{-1} and $\beta_T = -0.0053(3)$ GPa^{-1} for the ordered sample and $\beta_M = -0.0043(2)$ GPa^{-1} and $\beta_T = -0.0050(2)$ GPa^{-1} for the disordered one. The slightly larger compressibility of the tetrahedron with respect to the octahedron for both crystals is in accordance with the observed small decrease of the *u* parameter with pressure.

DISCUSSION

Whereas the effect of temperature on cation ordering has been well characterized for many minerals, just a few studies have been focused on how pressure affects the cation distribution (e.g., Hazen and Navrotsky 1996; Hazen and Yang 1999; Angel and Seifert 1999). A general conclusion of these works is that pressure has only a minor effect on the degree of order. An exception may be relative to those minerals for which ΔV_{dis}, (defined as $\Delta V_{dis} = V_{disordered} - V_{ordered}$), is significant and does not decrease with increasing pressure (Angel and Seifert 1999). Since ordered $MgAl_2O_4$ spinels have larger volumes than those disordered, one would expect that the effect of pressure, if any, would be that of stabilizing more disordered state, in contrast to that observed by Pavese et al. (1999). This has actually been observed by Meducin et al. (2004) whose data indicate that the effect of pressure at high-temperature appears to produce more disorder. The similar behavior of the ordered and disordered samples observed in this study, however, suggests that pressure only (i.e., at room temperature) has a negligible effect on the cation distribution of spinels ss.

Table 3. Variation with pressure of the unit-cell edges and volumes for the disordered and the ordered $MgAl_2O_4$ spinels studied in this work

P (GPa)	*a* (Å)	*V* (Å^3)	*a* (Å)	*V* (Å^3)
	disordered sample		ordered sample	
0.00010(1)	8.0844(1)	528.38(2)	8.0891(1)	529.30(2)
0.535(4)	8.0770(1)	526.93(2)	8.0817(1)	527.84(3)
1.136(5)	8.0688(1)	525.33(2)	8.0737(2)	526.28(3)
1.642(5)	8.0621(1)	524.01(2)	8.0670(1)	524.97(2)
2.484(5)	8.0509(1)	521.83(2)	8.0557(1)	522.78(3)
3.023(6)	8.0440(2)	520.48(3)	8.0485(2)	521.37(4)
4.153(6)	8.0296(3)	517.70(6)	8.0345(1)	518.65(3)
4.752(7)	8.0221(1)	516.26(2)	8.0272(1)	517.24(2)
5.961(7)	8.0074(1)	513.42(2)	8.0124(1)	514.38(2)
6.584(7)	8.0001(1)	512.02(2)	8.0053(1)	512.98(2)
6.975(8)	7.9955(1)	511.14(2)	8.0006(1)	512.12(2)
7.253(9)	7.9926(1)	510.57(3)	7.9977(1)	511.55(2)
7.374(10)*	7.9912(1)	510.31(2)	7.9960(1)	511.24(3)
7.427(10)	7.9905(1)	510.17(3)	7.9958(1)	511.19(2)

Notes: Standard deviations are in parentheses. The data were measure using a Huber single-crystal diffractometer equipped with a point-detector.
* Data measured during decompression.

The studies reported by Finger et al. (1986) on a natural ordered $MgAl_2O_4$ and by Pavese et al. (1999) on a synthetic spinel show that *u* decreases with pressure, indicating a larger compressibility of the tetrahedron with respect to that of the octahedron. Even considering the linear fits in Figure 2, the variation of *u* for our samples is one order of magnitude smaller than that of the cited studies and is in agreement with the results reported by Levy et al. (2003), which conclude that *u* remains practically constant over a large pressure range. Thus, in spinel ss, as in magnetite (Finger et al. 1986) the polyhedral compressibilities of the tetrahedral and octahedral cation sites are similar. The discrepancy with the two earlier studies cannot be ascribed to different cation order of the different samples used, since our results show clearly that the behavior of the ordered and disordered samples are the same. Instead a reason may be the relatively small pressure range covered by Finger et al. (1986) and Pavese et al. (1999) (both to approximately 4 GPa). In the latter study, powder rather than single-crystal diffraction methods were used, which may have resulted in a lower accuracy for the refined atomic positional parameters. Concerning the equation of state, our data indicate clearly that there are no differences in the unit-cell volume compressibility between the ordered and disordered samples (Fig. 1). The bulk moduli of the two samples are practically the same with values of 193(1) and 192(1) GPa for ordered and disordered samples, respectively. Moreover, the first pressure derivatives also do not depend on the degree of order. The bulk moduli reported in this work are in a very good agreement with previous studies and are in agreement with the suggestion of Li et al. (2007) who calculated a slight decrease in bulk modulus with increasing disorder. However, our first pressure derivatives (K' = 5.4–5.6) are smaller than that reported by Levy et al. (2003) (K' = 6.8). This difference is very likely related to the different experimental techniques, and hence to the hydrostaticity (our experiments) vs. quasi-hydrostaticity (powder diffraction) conditions. Also we cannot exclude that the presence of structural vacancies in the synthetic sample used by Levy et al. (2003) may affect the compressional behavior of spinel ss. In a recent theoretical study of Li et al. (2007), and two earlier studies where the value of K' for spinel also was determined (Chang and Barsch 1973; Kruger et al. 1997), even smaller values, ranging from 3.84 to 4.85, were obtained. The K' values reported in this study are very close to that of natural gahnite $ZnAl_2O_4$ [K' = 4.8(3), Reichmann and Jacobsen 2006] and natural magnetite Fe_3O_4 [K' = 5.2(4), Reichmann and Jacobsen 2004]. It appears therefore that for the spinel structure the K' values are only slightly larger than 4, at least for stoichiometric samples.

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APPENDIX

In the following, a_0 is the lattice parameter of a spinel, and Δu is the absolute displacement (in Å) of the O atom from the ideal site in the cubic eutaxy along one of the crystal axes. $\Delta u = (u - 0.25)a_0$. The octahedral coordination in spinel is slightly distorted, and conforms to $\bar{3}2/m$ symmetry. It is elongated along one of the threefold axes, and has six shorter and six longer edges, with all center-to-vertex distances equal. The volume can be divided in eight equal-volume pyramids with apices meeting at the center of the octahedron and bases at each of the octahedral faces. The length of the edge at the base of the pyramid is: $s = o - 2\sqrt{2}\Delta u$ where o represents the edge length of an ideal non-distorted octahedron (u = 0.25). The height of the pyramid is $h = \frac{\sqrt{6}}{6}o + \frac{\sqrt{3}}{3}\Delta u$. The volume of a pyramid is $V = Fh/3$ where F represents the area of the pyramid base, and because the edge of an ideal octahedron is $o = \frac{\sqrt{2}}{4}a_0$ the volume of the pyramid in question is

$$V = \frac{a_0^3}{384} - \frac{a_0^2\Delta u}{32} + \frac{2\Delta u^3}{3}.$$

As there are eight equal pyramidal volumes in one octahedron:

$$V_{oct} = a_0^3\left(\frac{16u^3}{3} - 4u^2 + \frac{3u}{4}\right).$$

The tetrahedral coordination is regular. The length of an edge is

$$t = \frac{a_0}{2\sqrt{2}} + 2\sqrt{2}\Delta u.$$

Using the general formula for the volume of a pyramid, and because the height of a tetrahedron is

$$h = \frac{\sqrt{2}}{\sqrt{3}}t.$$

The final formula for the volume of the tetrahedron in spinel is obtained as $V_{tet} = \frac{a_0^3}{192}(8u-1)^3$. As can be seen from these two expressions, if the u parameter remains constant, for any change of a_0 the relation between the octahedral and tetrahedral volumes remains constant. For $u = 0.25$ $V_{oct}/V_{tet} = 4$ as expected for an eutaxy. The analysis of the two functions shows that for $u < 0.25$ $V_{oct}/V_{tet} > 4$, and for $u > 0.25$ $V_{oct}/V_{tet} < 4$. If a change of u is observed on compression, an increase shows that the octahedron has a larger compressibility than the tetrahedron, and a decrease results in the opposite behavior.