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

F. Nestola, T. Boffa Ballaran, T. Balic-Zunic, F. Princivalle, L. Secco, and A. Dal Negro

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, \( K_0 \), and its first pressure derivative, \( K'_0 \), were simultaneously refined using a third-order Birch-Murnaghan equation of state, giving the following coefficients: \( V_0 = 529.32(2) \, \text{Å}^3 \), \( K_0 = 193(1) \, \text{GPa} \), \( K'_0 = 5.6(3) \) for the ordered sample and \( V_0 = 528.39(2) \, \text{Å}^3 \), \( K_0 = 192(1) \, \text{GPa} \), \( K'_0 = 5.4(3) \) 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

Spinelns, 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 located at 1/8,1/8,1/8, while the octahedral cation at 1/2,1/2,1/2.

Intermediate cation distributions are very common and a general formula can be written as \( x^A(A_{1-x}B)^x(O_{3x}) \), 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:

\[
u = 0.2651 - 0.0123x\]  
(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...
and room temperature up to 4 GPa of a synthetic spinel with composition \( \text{MgAl}_2\text{O}_4 \) 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 \( \text{MgAl}_2\text{O}_4 \) and concluded that the change in \( u \) with pressure was on the order of their uncertainties. More recently, Medunic 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 \( \text{MgAl}_2\text{O}_4 \) 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\(_2\)O\(_4\) is less compressible than recent theoretical study based on density functional theory, Li et al. (2007) in a single-crystal investigation on ringwoodite \( \text{MgAl}_2\text{O}_4 \) 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 \( \text{MgAl}_2\text{O}_4 \).

**EXPERIMENTAL METHODS**

**Sample characterization**

Two fragments of a pale pink gem quality crystal of \( \text{MgAl}_2\text{O}_4 \) (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 \( \mu \)m) as sample A or ordered sample and to the experimentally disordered fragment (size 200 × 90 × 50 \( \mu \)m) 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 in 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\(_2\)O\(_3\) for Al, Cr\(_2\)O\(_3\) for Cr, Zn\(_2\)S for Zn, and Fe\(_2\)O\(_3\) for Fe were used as standards. The results of microprobe analyses are reported in Table 1 and are consistent with an extremely pure \( \text{MgAl}_2\text{O}_4 \) composition.

**X-ray diffraction at ambient conditions**

X-ray data of the two crystals were collected using an automated KUMA-KM4 (Kappa-geometry) diffractometer (MoK\(_\alpha\) monochromatized by a flat graphite crystal). Intensity data were collected up to 110 °2θ in the \( \omega \)-2θ step-scan mode, with peak-base width of 1.8 °2θ, which increased with the 2θ 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 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 \( \text{Fd}_3\text{m} \) space group with origin at 3m, 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 \( R \), \( wR \), and \( GooF \) in all sin2θ/\( \lambda \) 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:

\[
F(\bar{X}) = \sum (|I| - C(\bar{X}))/\sigma(\bar{X})^2
\]

where \( O \) 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, \( \sigma \) are their standard deviations. The variables \( \bar{X} \) are the cation fractions Mg(T), A1(T), Mg(M), and Al(M), related by the inversion parameter \( x \) that are used to calculate the quantities \( C \), which enter into the minimization procedure. Such function was restricted to Mg\(_2\)Al\(_2\)O\(_4\) 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), A1(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 \( \mu \)m in diameter. A T301 gasket preindented to 100 \( \mu \)m, with a hole of 300 \( \mu \)m 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

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxide wt%*</th>
<th>Cation partitioning from crystal-structure refinements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Disordered</td>
</tr>
<tr>
<td>MgO</td>
<td>28.2(2)</td>
<td>T site Mg</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>71.5(1)</td>
<td>Al</td>
</tr>
<tr>
<td>Cr(_2)O(_3)</td>
<td>0.111(3)</td>
<td>M site Al</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.17(9)</td>
<td>FeO</td>
</tr>
<tr>
<td>FeO</td>
<td>0.271(5)</td>
<td>Mg</td>
</tr>
<tr>
<td>Sum</td>
<td>99.98</td>
<td></td>
</tr>
</tbody>
</table>

Cations on basis of 4 O atoms

<table>
<thead>
<tr>
<th>Element</th>
<th>P [Å]</th>
<th>Inversion parameter x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.00(2)</td>
<td>0.272(5)†</td>
</tr>
<tr>
<td>Mg</td>
<td>0.99(5)</td>
<td>1.45(4)†</td>
</tr>
<tr>
<td>Zn</td>
<td>0.003(2)</td>
<td>0.145(4)†</td>
</tr>
</tbody>
</table>

* Average of 10 electron microprobe analyses; standard deviations are in parentheses.
† The standard deviation is relative to 2θ.
Table 2. Details of structure refinements at ambient and high pressure for the two spinnels investigated in the present study

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>0.0001*</th>
<th>0.0001†</th>
<th>0.44(5)</th>
<th>2.92(5)</th>
<th>7.34(5)</th>
<th>8.03(5)</th>
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<tr>
<td>Ordered sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>8.088(1)</td>
<td>8.096(2)</td>
<td>8.086(4)</td>
<td>8.049(4)</td>
<td>7.999(3)</td>
<td>7.992(5)</td>
</tr>
<tr>
<td>u</td>
<td>0.2632(5)</td>
<td>0.2630(3)</td>
<td>0.263(5)</td>
<td>0.2634(3)</td>
<td>0.2629(4)</td>
<td>0.263(4)</td>
</tr>
<tr>
<td>M-O (Å)</td>
<td>1.920(4)</td>
<td>1.924(2)</td>
<td>1.918(4)</td>
<td>1.911(2)</td>
<td>1.902(3)</td>
<td>1.898(3)</td>
</tr>
<tr>
<td>T-O (Å)</td>
<td>1.937(9)</td>
<td>1.935(4)</td>
<td>1.942(7)</td>
<td>1.929(4)</td>
<td>1.911(5)</td>
<td>1.914(6)</td>
</tr>
<tr>
<td>Vio (Å)</td>
<td>3.735(1)</td>
<td>3.710(5)</td>
<td>3.769(10)</td>
<td>3.676(5)</td>
<td>3.564(6)</td>
<td>3.600(8)</td>
</tr>
<tr>
<td>Vo (Å)</td>
<td>9.270(2)</td>
<td>9.352(10)</td>
<td>9.202(20)</td>
<td>9.143(10)</td>
<td>9.047(13)</td>
<td>8.945(15)</td>
</tr>
<tr>
<td>Uoo(O) (Å)</td>
<td>0.004(2)</td>
<td>0.005(19)</td>
<td>0.010(17)</td>
<td>0.007(14)</td>
<td>0.008(12)</td>
<td>0.0100(14)</td>
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<tr>
<td>Uoo(M) (Å)</td>
<td>0.003(2)</td>
<td>0.0036(8)</td>
<td>0.0068(16)</td>
<td>0.0060(10)</td>
<td>0.0068(11)</td>
<td>0.0094(13)</td>
</tr>
<tr>
<td>Uoo(T) (Å)</td>
<td>0.004(2)</td>
<td>0.0053(9)</td>
<td>0.0070(18)</td>
<td>0.0067(10)</td>
<td>0.0081(14)</td>
<td>0.0097(14)</td>
</tr>
<tr>
<td>Unique refl.</td>
<td>118</td>
<td>26</td>
<td>22</td>
<td>26</td>
<td>24</td>
<td>19</td>
</tr>
<tr>
<td>R₁</td>
<td>2.04</td>
<td>2.26</td>
<td>3.20</td>
<td>3.10</td>
<td>2.92</td>
<td>2.25</td>
</tr>
<tr>
<td>Goof</td>
<td>1.39</td>
<td>1.34</td>
<td>1.39</td>
<td>1.05</td>
<td>1.10</td>
<td>1.15</td>
</tr>
<tr>
<td>Rₑₑ</td>
<td>3.03</td>
<td>3.49</td>
<td>4.93</td>
<td>3.55</td>
<td>9.11</td>
<td>2.61</td>
</tr>
<tr>
<td>wRₑₑ</td>
<td>3.88</td>
<td>5.49</td>
<td>7.97</td>
<td>6.06</td>
<td>6.42</td>
<td>5.94</td>
</tr>
<tr>
<td>Disordered sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
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<td>8.0899(2)</td>
<td>8.08013</td>
<td>8.0451(3)</td>
<td>7.992(3)</td>
<td>7.9874(3)</td>
</tr>
<tr>
<td>u</td>
<td>0.26166(6)</td>
<td>0.2614(2)</td>
<td>0.2615(2)</td>
<td>0.2614(2)</td>
<td>0.2612(2)</td>
<td>0.2613(2)</td>
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<tr>
<td>M-O (Å)</td>
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<td>1.935(1)</td>
<td>1.932(2)</td>
<td>1.924(2)</td>
<td>1.913(1)</td>
<td>1.911(2)</td>
</tr>
<tr>
<td>T-O (Å)</td>
<td>1.9137(8)</td>
<td>1.9123(3)</td>
<td>1.910(3)</td>
<td>1.900(3)</td>
<td>1.886(3)</td>
<td>1.886(3)</td>
</tr>
<tr>
<td>Vio (Å)</td>
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<td>3.588(3)</td>
<td>3.579(4)</td>
<td>3.523(4)</td>
<td>3.444(3)</td>
<td>3.445(4)</td>
</tr>
<tr>
<td>Vo (Å)</td>
<td>9.474(2)</td>
<td>9.517(6)</td>
<td>9.475(9)</td>
<td>9.369(8)</td>
<td>9.206(7)</td>
<td>9.174(8)</td>
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<tr>
<td>Uoo(O) (Å)</td>
<td>0.007(8)</td>
<td>0.0094(7)</td>
<td>0.0110(9)</td>
<td>0.0094(9)</td>
<td>0.0081(7)</td>
<td>0.0094(7)</td>
</tr>
<tr>
<td>Uoo(M) (Å)</td>
<td>0.004(2)</td>
<td>0.0051(6)</td>
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<td>0.0045(6)</td>
<td>0.0051(6)</td>
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<td>Uoo(T) (Å)</td>
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<td>0.0050(7)</td>
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<td>0.0041(7)</td>
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<td>34</td>
<td>42</td>
<td>39</td>
<td>36</td>
</tr>
<tr>
<td>R₁</td>
<td>1.99</td>
<td>2.53</td>
<td>2.71</td>
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</tr>
<tr>
<td>Goof</td>
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<td>1.29</td>
<td>1.33</td>
<td>1.22</td>
<td>1.23</td>
<td>1.20</td>
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<tr>
<td>Rₑₑ</td>
<td>3.07</td>
<td>3.14</td>
<td>4.99</td>
<td>4.03</td>
<td>4.63</td>
<td>4.39</td>
</tr>
<tr>
<td>wRₑₑ</td>
<td>4.52</td>
<td>5.60</td>
<td>5.26</td>
<td>7.15</td>
<td>5.63</td>
<td>5.64</td>
</tr>
</tbody>
</table>

* Crystal in DAC measured using a CCD detector. Uoo for the high-pressure measurements are actually Uoo since they were refined as isotropic.
† Crystal in DAC measured using a point detector.

Equation of State

The evolutions of the unit-cell edges of ordered and disordered MgAl₂O₄ 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, Vₒ, the bulk modulus, Kₒ, and its first pressure derivative, K′, were simultaneously refined. The resulting EoS parameters are: Vₒ = 529.32(2) Å³, Kₒ = 193(1) GPa, K′ = 5.6(3), and Vₒ = 528.39(2) Å³, Kₒ = 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

Table of values for M-O, T-O, and M-O distances and displacement factors.

<table>
<thead>
<tr>
<th>M-O (Å)</th>
<th>8.088(1)</th>
<th>8.096(2)</th>
<th>8.086(4)</th>
<th>8.049(4)</th>
<th>7.999(3)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>T-O (Å)</td>
<td>1.937(9)</td>
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<td>1.929(4)</td>
<td>1.911(5)</td>
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<td>9.047(13)</td>
<td>8.945(15)</td>
</tr>
</tbody>
</table>

Equation of state coefficients for MgAl₂O₄ spinel.

Kₒ = 193(1) GPa, K′ = 5.6(3) for the ordered sample and Kₒ = 192(1) GPa, K′ = 5.4(3) for the disordered sample.
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 $\Delta V_{\text{dis}}$, (defined as $\Delta V_{\text{dis}} = V_{\text{disordered}} - V_{\text{ordered}}$), is significant and does not decrease with increasing pressure (Angel and Seifert 1999). Since ordered MgAl$_2$O$_4$ 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.
The studies reported by Finger et al. (1986) on a natural ordered MgAl₂O₄, and by Pavese et al. (1999) on a synthetic spinel show that the unit cell 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 unit cell for our samples is one order of magnitude smaller than that of the cited studies and in agreement with the results reported by Levy et al. (2003), which conclude that the unit cell 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 is 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 garnet ZnAl₂O₄ (K′ = 4.8(3), Reichmann and Jacobsen 2006) and natural magnetite Fe₃O₄ (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.

**References cited**


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Finger, L.W., Hazen, R.M., and Hofmeister, A.M. (1986) High pressure crystal chemistry of spinel (MgAl₂O₄) and magnetite (Fe₃O₄)–comparison with silicate spinels. Physics and Chemistry of Minerals, 13, 215–220.


Note: Standard deviations are in parentheses. The data were measure using a Huber single-crystal diffractometer equipped with a point-detector.
The volume of a pyramid is \( \frac{1}{3} \) \( \text{length} \times \text{width} \times \text{height} \). As can be seen from these two expressions, if the \( a_0 \) parameter remains constant, for any change of \( \Delta u \) the relation between the octahedral and tetrahedral volumes remains constant. For \( u = 0.25 \), \( V_{\text{oct}}/V_{\text{tet}} = 4 \) as expected for an eutaxy. The analysis of the two functions shows that for \( u < 0.25 \), \( V_{\text{oct}}/V_{\text{tet}} > 4 \), and for \( u > 0.25 \), \( V_{\text{oct}}/V_{\text{tet}} < 4 \). 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.

**APPENDIX**

In the following, \( a_0 \) is the lattice parameter of a spinel, and \( \Delta u \) 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 \( \overline{2}m \) 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: \( s = a - 2\sqrt{2}\Delta u \) where \( a \) represents the edge length of an ideal non-distorted octahedron (\( u = 0.25 \)). The height of the pyramid is \( h = \frac{\sqrt{2}}{2} a + \frac{\sqrt{2}}{2}\Delta u \). 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 \( a = \frac{2}{\sqrt{3}} a_0 \), the volume of the pyramid in question is

\[
V = \frac{a_0^4}{384} a_0^3 \Delta u \left( \frac{2\Delta u^3}{3} \right).
\]

As there are eight equal pyramidal volumes in one octahedron:

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

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 \( V_{\text{tet}} = \frac{a_0^4}{192} (192u - 1) \). 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 \( u = 0.25 \), \( V_{\text{oct}}/V_{\text{tet}} = 4 \) as expected for an eutaxy. The analysis of the two functions shows that for \( u < 0.25 \), \( V_{\text{oct}}/V_{\text{tet}} > 4 \), and for \( u > 0.25 \), \( V_{\text{oct}}/V_{\text{tet}} < 4 \). 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.