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Pressure-Induced Order–Disorder Phase Transition of Spinel Single Crystals

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Abstract

The present study deals with single-crystal structure investigations by means of X-ray scattering of a pressure-induced phase transition of $Mg_{0.4}Al_{2.4}O_4$. The compressibility of the substance is very small, whereas the structural changes are surprisingly high. A non-identified high-pressure phase turns out to be reversible considering the existence of a spinel single crystal, but not reversible with regard to the ordering of the cations in the oxygen framework. The pressure-induced disordering of the cations is preserved on abrupt pressure decrease and can be detected in a recovered specimen.

1. Introduction

Representatives of the spinel group show a wide range of chemical compositions and high symmetry (space group $Fd\bar{3}m$). The common chemical formula is AB_2X_4, where A and B denote the tetrahedrally and octahedrally coordinated cations, respectively, and X denotes the anion (Hill *et al.*, 1979). These ternary compounds show a large variety of physical properties, which depend on the individual composition. Therefore, they seem to be ideal for investigating the interaction of the influence of structure and chemical composition on the response to external fields such as heat, pressure, magnetism *etc.* In addition, investigations of spinels under pressure are of geophysical interest, following the hypothesis of the layering of the earth's mantle, which is for the main part explained by the subsequent phase transitions of olivine-like compounds using the intermediate stage of spinels to result, on further increase of pressure and temperature, in a perovskite-like structure (Wood, 1989). Both these phase transitions, which are supposed to be of first order, are accompanied by an increase in density of several per cent. This difference in weight can explain the layered structure of the earth's mantle, which is predicted by seismic measurements of the earth's interior. As the mantle material should convect, the phase transitions in question are expected to be reversible. The spinel–perovskite phase transition is today mostly identified with a step in seismic velocities at a depth of ~670 km in the earth's interior. Powder diffraction experiments under high pressure and high temperature on $(MgFe)_2SiO_4$ spinel confirm the existence of the assumed phase transition to a perovskite-like phase under mantle conditions (Ito & Takahashi, 1989).

So far, experiments under pressure have mainly dealt with oxide spinels, but thiospinels have also been investigated. $ZnCr_2S_4$ shows no phase transition and few structural changes up to 12 GPa, except a macroscopic deterioration of the single crystals under consideration (Wittlinger, Werner & Schulz, 1997). $CuIr_2S_4$, however, shows a transition to a tetragonal phase at 2.5 GPa (Kagayama *et al.*, 1996). Equations of state have already been determined for several representatives of the spinel group (*e.g.* Hazen, 1993; Wilburn & Bassett, 1976). Single-crystal diffraction experiments on oxide spinels have not yet reached the relevant pressure regions to obtain information on phase transitions; only changes in lattice constants and the positional parameters could be observed (Finger *et al.*, 1977, 1986). A tendency seems to exist for all positional parameters under pressure to approach the value at which the cation packing would be an ideal f.c.c. (face-centred cubic) structure. The substance under consideration in this work is the prototype of the spinel group, simply termed 'spinel'. The ideal stoichiometry $MgAl_2O_4$ is very rare, as disorder is usual, especially in synthetic probes. Previous spectroscopic experiments revealed one phase transition at 11 GPa and a second at 19 GPa, which leads to an amorphous phase (Chopelas & Hofmeister, 1991). The phase transitions turned out to be reversible with regard to the observed spectra.

2. Considerations on the spinel structure

Spinels AB_2X_4 consist of an anion framework, where one-eighth of the tetrahedrally coordinated positions are occupied by a cation and the octahedrally coordinated positions are half-occupied. Oxygen and sulfur are the most common representatives of the anion framework, but other anions are also known to build spinel structures, such as selenium and halogenides. Thus, the formal charge of the ions is either A^{2+}, B^{3+} and X^{2-}, termed '2-3 spinels', A^{4+}, B^{2+} and X^{2-}, termed '4-2 spinels', or A^{2+}, B^{+} in the case of an X^{-} anion. The anion framework is an almost ideal f.c.c. structure. The space group allows only one positional parameter, commonly termed 'u', which describes the deviation of the anions from the ideal f.c.c. configuration. Throughout this paper we chose the origin of the coordinate system at the centre of inversion and so the parameter u of the f.c.c. structure is 0.25 (Finger *et al.*, 1986). It should be noted that other choices of origin are possible and common in other papers (Urusov, 1983). Therefore, here the deviation of u from 0.25 denotes the distortion of the anion sublattice. Usual spinels have values of u between 0.24 and 0.27, depending on the combination of cations and anions (Hill *et al.*, 1979).

In real spinel structures the distribution of the cations is often not as ideal as described here, as the stoichiometry is different and the cations are disordered on their sites. The disordering of the cations can be described by means of the parameter λ, leading to the more general formula $B_\lambda A_{1-\lambda}(A_\lambda B_{2-\lambda})X_4$, where the occupation of the octahedral position is noted in brackets. With $\lambda = 0$ the ideal distribution $A(B_2)X_4$ is obtained; with $\lambda = 1$ complete inversion can be described with the formula $B(AB)X_4$. An ideal stochastic distribution corresponds to the value $\lambda = \frac{2}{3}$ (Urusov, 1983).

In general, the configurational entropy of different cations on crystallographically identical positions is given by

$$S_{\text{conf}} = -R \sum_i \sum_s X_s^i \ln(X_s^i), \tag{1}$$

where X denotes the fractional part of the cations i on the position s (O'Neill & Navrotsky, 1983). In the special case of spinels this leads to

$$S_{\text{conf}} = -R\big[\lambda \ln \lambda + (1-\lambda)\ln(1-\lambda) + \lambda \ln(0.5\lambda) + (2-\lambda)\ln(1-0.5\lambda)\big]. \tag{2}$$

This function shows a maximum at $\lambda = \frac{2}{3}$, in agreement with the empirical considerations mentioned above (O'Neill *et al.*, 1991). Moreover, the configurational energy of the cation distribution on the two distinct positions is determined by the parameter u (O'Neill & Navrotsky, 1983). Thus, for 2-3 spinels, the normal cation distribution ($\lambda = 0$) should be favoured for $u > 0.2555$ and inverted ($\lambda = 1$) for $u < 0.2555$.

Bond lengths and volumes of the polyhedra are only a function of the lattice constant a and the positional parameter u, and are unequivocally fixed by these two variables (Yamanaka & Takeuchi 1983; Hill *et al.*, 1979),

$$(T\text{–}X) = 3^{1/2}a(u - 0.125) \tag{3}$$

$$(O\text{–}X) = a(3u^2 - 2u + 0.375)^{1/2} \tag{4}$$

$$V_{\text{tet}} = (8/3)a^3(u - 0.125)^3 \tag{5}$$

$$V_{\text{oct}} = (16/3)a^3u(u - 0.375)^2. \tag{6}$$

Here, T indicates the tetrahedral position, O the octahedral position and V the corresponding volume under consideration. Assuming known bond lengths of the anion–cation combinations in the tetrahedron (A_T, B_T) and the octahedron (A_O, B_O) and a linear dependence of the bond length on the ion concentration (Vegard's rule), the degree of inversion can be determined,

$$(T\text{–}X) = \lambda A_T + (1-\lambda)B_T \tag{7}$$

$$(O\text{–}X) = 0.5\lambda A_O + (1-0.5\lambda)B_O. \tag{8}$$

For the ratio of the octahedral and the tetrahedral bond lengths, termed R, we obtain a function dependent only on the inversion parameter λ,

$$R = (O\text{–}X)/(T\text{–}X) \tag{9}$$

$$R = [0.5\lambda A_O + (1-0.5\lambda)B_O]/[\lambda A_T + (1-\lambda)B_T] \tag{10}$$

$$u(R) = 0.25R^2 - (2/3) + [(11R^2/48) - (1/18)]^{1/2}/(2R^2 - 2). \tag{11}$$

So, λ and u are related by a rather simple function. Additionally, a relation between the two variables λ and u on the one side and the lattice constant a on the other can be obtained using the tetrahedral bond,

$$3^{1/2}a(u - 0.125) = \lambda A_T + (1-\lambda)B_T \tag{12}$$

$$a = [\lambda A_T + (1-\lambda)B_T]/[3^{1/2}(u - 0.125)]. \tag{13}$$

Using the octahedron an equivalent relation can be obtained,

$$a(3u^2 - 2u + 0.375)^{1/2} = 0.5\lambda A_O + (1-0.5\lambda)B_O \tag{14}$$

$$a = [0.5\lambda A_O + (1-0.5\lambda)B_O]/(3u^2 - 2u + 0.375)^{1/2}. \tag{15}$$

Now, if the different ideal anion–cation bond lengths of the spinel under consideration are known, the inversion parameter can be deduced only from the lattice constant. Whether the lattice constant increases or decreases with increasing inversion parameter cannot be said in general, but depends on the ratios A_T/A_O and B_T/B_O.

3. Experimental

The samples were small chips taken from a piece of spinel. Before the start of the high-pressure experiments, great care was taken to characterize the probes. For every individual sample rocking curves were investigated to obtain information on the mosaicity of the sample and, in addition, the existence of twin domains following the spinel law were excluded.

The high-pressure experiments were performed with single-crystal diamond anvil cells, which allow a maximum pressure of more than 30 GPa and show an opening angle transparent to X-rays of 100° on both sides (Werner *et al.*, 1996). Thus, for cubic structures in most positions of the crystal in the cell, complete data sets can be collected up to $\sin\theta/\lambda = 0.8$ or more. The culet size was between 0.4 and 0.6 mm and the pressure chamber had a height of 90 μm and a diameter between 150 and 300 μm, depending on the culet used in the individual high-pressure run. Typical sample sizes were ~30 μm in height and 40 μm in diameter. The pressure-transmitting medium was either argon, which was loaded cryogenically (Wittlinger, Fischer *et al.*, 1997), or an alcohol mixture. Argon was used in the experiments which were dedicated to reaching pressures which exceeded the solidus of the alcohol mixture. Pressure was measured *in situ* by the ruby fluorescence method, using a small single crystal of ruby which was introduced in the pressure chamber (Ross *et al.*, 1986). All experiments were performed on a CAD-4 four circle diffractometer with kappa geometry equipped with a sealed tube, using Mo $K\alpha$ radiation. Only one set of data (p = 1.9 GPa) was obtained at HASYLAB (Hamburg, Germany) at beamline D3 (λ = 0.6 Å). To centre the cell on the diffractometer the profile of the primary beam was used, which can provide an accuracy comparable to the sphere of confusion of the diffractometer (Wittlinger, 1997). In general, the lattice constants were obtained by centring 12 or more reflections at $2\theta > 10°$, mostly at four positions ($\pm\theta, \pm\chi$). Intensity data were collected with ω scans and of every set of symmetry-dependent reflections at least three different ones were taken.

Data were reduced with the program *REDA*, dedicated to handle high-pressure data. Herein, an empirical absorption correction of the reflections, normalization of the intensities to the primary-beam monitoring system (not available for CAD-4 data) and a Lorentz–polarization correction could be performed. Additionally, this program allows the integration of the reflections automatically and graphic display of the results of the integration, showing all (maximum number 9) symmetry-equivalent reflections simultaneously. It is also possible to set the integration limits manually in an interactive procedure. This is only necessary for weak reflections [$I/\sigma(I) < 2$], where the automatic integration procedure, which follows the seed–skewness method, obviously fails (Bolotovsky *et al.*, 1995).

Structure refinements were all performed with *SHELXL*93 (Sheldrick, 1993).

4. Results

4.1. *Sample characterization*

The characterization of the substance at ambient conditions shows a lattice constant a = 7.9780 (4) Å and a positional parameter u = 0.2580 (1), whereas the corresponding values for a stoichiometric spinel would be approximately a = 8.0898 Å and u = 0.2633 (Finger *et al.*, 1986). As Mg^{2+} and Al^{3+} have almost the same scattering power, only the overall site occupation factor of the individual positions can be deduced by means of X-ray scattering and the distribution of the cations on the two symmetrically distinct sites has to be calculated with the aid of the assumption of the localization of the Mg^{2+} cations on the tetrahedral site (Lucchesi & Della Giusta, 1994). The occupation of the octahedral site is 91%. Thus, in $Mg_xAl_{1-x}(Al_{1.8})O_4$, assuming the global neutrality of the substance, x is calculated to be 0.4. $Mg_{0.4}Al_{0.6}(Al_{1.8})O_4$ is a realistic chemical formula. Previous extensive work carried out on non-ideal spinels showed a dependence of the cation distribution on the lattice constant and the positional parameter (Lucchesi & Della Giusta, 1994). Introducing the present values for a and u in the formalism leads to 61% $Al_{8/3}\square_{1/3}O_4$ and 39% $MgAl_2O_4$. □ denotes a vacancy. These considerations and the site occupation factors obtained from the structure refinement agree well. Our results can be explained by a typical disordering of the Al cations on the two different sites of the structure and an ordering of the Mg ions on the tetrahedral site. Symmetry implications of the space group of the structure lead to the fact that the tetrahedron always shows an ideal geometry, whereas the bond angles of the octahedron are dependent on the positional parameter u (Hill *et al.*, 1979). At the value u = 0.25, the octahedron would be perfectly symmetric with bond angles Al—O—Al = 90°. Here, the octahedron is squeezed along its threefold (111) axis.

4.2. *Lattice constants and equation of state*

As already revealed in previous experiments, the bulk modulus of spinel is very big and thus the relative volume change under pressure is small (Finger *et al.*, 1986). This leads to considerable relative errors in the determination of the lattice constants used for the calculation of the equation of state. As no systematic difference in the individual high-pressure runs nor a dependence of the results on the use of different pressure media (alcohol or argon) could be observed, all data obtained were used to determine one averaged Birch–Murnaghan equation of state (Bass *et al.*, 1981). The pressure range is limited owing to a phase transition at a pressure between 10.5 and 11 GPa (Fig. 1). Above the phase transition no lattice constants could be obtained, because the signals vanished and the reflections broadened abruptly. The square in Fig. 1 denotes the lattice constant of a sample which had been recovered from a high-pressure run up to a maximum pressure of 13 GPa, which exceeded the phase boundary.

The equation of state agrees within error with previous experiments, which were carried out to *ca* 4 GPa on a nearly stoichiometric, natural sample (Finger *et al.*, 1986). Thus, no dependence of the compressibility of the substance on the disordering of the cations can be observed. In comparison with other oxide spinels investigated under pressure so far, it can be stated that most of the bulk moduli only show small differences which are hardly beyond the reported errors (see Table 2; Hazen, 1993; Wilburn & Bassett 1976). The point marked by the square, representing the sample recovered from the high-pressure region, shows that the phase transition is in some aspects irreversible (see below for details).

Comparison with a recently investigated quenchable high-pressure phase of $MgAl_2O_4$ with a calcium ferrite-type structure shows that the form with the calcium ferrite-type structure has a compressibility ~20% smaller (K = 241 GPa) than spinel, but has a higher density.

4.3. *Pressure dependence of the structure*

Despite the small change in volume, the structural changes of spinel under pressure are considerable and show some interesting features. The positional parameter u approaches 0.25, but not with a linear pressure dependence, as could be concluded from previous studies (Finger *et al.*, 1986). Here, the compression seems to be almost isotropic up to 5 GPa and with further pressure increase the slope changes rapidly. Between 10.5 and 11 GPa, the value of u = 0.255 is reached and the structure undergoes a phase transition to a phase which shows no single-crystal reflections.

The volumes of the coordination polyhedra depend both on the lattice constant and on the positional parameter. The results for the octahedron and the tetrahedron are shown in Fig. 4. Obviously, the compressibility of the octahedron is the same over the whole pressure range considered and also almost the same as for the tetrahedron up to 5 GPa. At higher pressures the tetrahedron shows a higher compressibility, leading to a considerably larger volume decrease compared with the octahedron. Despite the small change in volume, pressure has a strong influence on the shape of the octahedron. The bond angle of the octahedron shows a rapid change above 5 GPa (Fig. 5). The pressure dependence can be described with an exponential function of the type

$$\alpha(p) = w_0 + w_1 \exp(w_2 p),$$

with the fitting parameters w_0 = 86.09°, w_1 = 5.1572 × $10^{-3\circ}$ and w_2 = 0.6699 GPa.

4.4. *Phase transition at 11 GPa*

In our experiments a phase transition occurred at a pressure of ~10.7 GPa. The reflections broaden suddenly and on further pressure increase no single-crystal reflections could be detected by photographic or scintillation counter techniques. As a representative, the pressure dependence of the average half-width of five {844} reflections can be seen in Fig. 2. At the onset of the phase transition, the overall volume of the structure corresponds to 97% of the initial volume, whereas the volume reduction of the two coordination polyhedra differs significantly (see Table 1, Fig. 4). The positional parameter u shows a value close to 0.255, which corresponds to the break-even of the configurational energy for the cation ordering and disordering on the different sites of the structure (O'Neill *et al.*, 1991). On complete

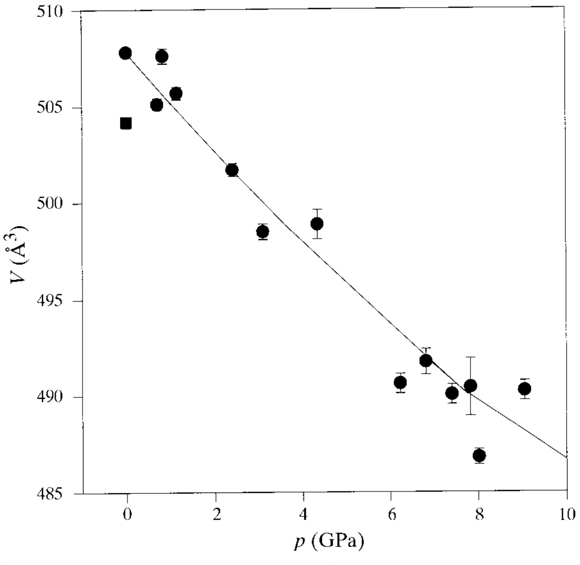

Fig. 1. Pressure dependence of the unit-cell volume of $Mg_{0.4}Al_{2.4}O_4$. Around 11 GPa a phase transition occurs. The fitted line is a Birch–Murnaghan equation of state. The square denotes a value originating from the sample bearing a maximum pressure of more than 13 GPa for several hours.

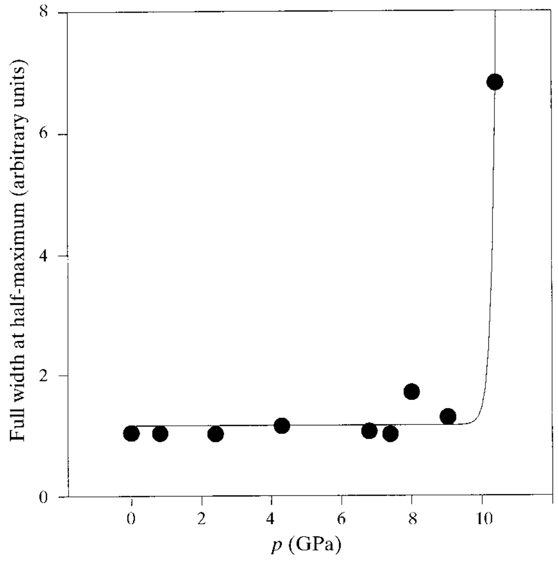

Fig. 2. The width of the reflections is shown *versus* pressure (p). At the onset of the phase transition around 10.5 GPa, the reflections broaden suddenly and cannot be detected after a further pressure increase.

Table 1. *Details of the structure refinements of* $Mg_{0.4}Al_{2.4}O_4$

Site occupation factors (s.o.f.) are kept fixed throughout the refinements, except the first at ambient pressure. The values of an ideal spinel would be 0.166, 0.04166 and 0.0833 for the anion, the tetrahedral (Mg) and the octahedral (Al) cation, respectively. The last column gives values from the refinement of data from a crystal recovered from a high-pressure experiment. The structure refinement at 1.9 GPa was performed with isotropic displacement parameters, owing to the small number of independent reflections. GOF = goodness-of-fit, u = positional parameter of the anion, U^{ij} = displacement parameter.

Pressure (GPa)	0	1.9	4.32	7.13	8.26	0
Lattice constant (Å)	7.9780 (4)	7.9543 (6)	7.9310 (8)	7.8838 (7)	7.8662 (8)	7.9736 (3)
No. of reflections	775	130	364	283	326	553
No. of average reflections	139	31	77	75	72	139
GOF	1.3	1.3	1.2	1.7	1.7	1.2
wR (σ)	0.053	0.072	0.093	0.127	0.173	0.156
U^{11}(Mg) (Å^2)	0.0055 (5)	0.007 (2)	0.010 (1)	0.009 (2)	0.007 (3)	0.0137 (9)
U^{11}(Al) (Å^2)	0.0088 (5)	0.017 (2)	0.0129 (9)	0.020 (2)	0.020 (3)	0.023 (1)
U^{12}(Al) (Å^2)	−0.0003 (2)		−0.0008 (7)	0.002 (1)	0.005 (2)	0.001 (1)
u(O)	0.2580 (1)	0.2582 (4)	0.2580 (4)	0.2569 (5)	0.255 (1)	0.2569 (2)
U^{11}(O) (Å^2)	0.0114 (6)	0.010 (2)	0.014 (1)	0.016 (2)	0.033 (3)	0.0139 (8)
U^{12}(O) (Å^2)	0.0010 (3)		0.0004 (10)	−0.001 (1)	−0.004 (4)	0.000 (1)
O—Al—O (°)	86.1 (1)	86.1 (3)	86.2 (2)	86.7 (2)	87.4 (5)	87.1 (2)
O—Mg (Å)	1.838 (2)	1.835 (7)	1.827 (6)	1.801 (7)	1.78 (1)	1.810 (6)
O—Al (Å)	1.931 (1)	1.925 (4)	1.921 (3)	1.918 (4)	1.925 (8)	1.946 (3)
s.o.f. (O)	0.1666					
s.o.f. (Mg)	0.043 (1)					
s.o.f. (Al)	0.076 (1)					

pressure release, reflections from a sample which bore 13 GPa maximum pressure for several hours can be detected again, but with smaller intensities than the initial reflections (I_0/I = 5) and a half-width which is increased by a factor of 1.5 on a CAD-4 diffractometer. Thus, the single crystal, at least partially, seems to be reconstructed. A structure refinement of intensity data reveals that the value of u is not completely reversible, but remains at a point which corresponds to ~5 GPa on the initial pressure scale (Table 1). The corresponding lattice constant is slightly smaller than the initial one. As explained above, the positional parameter u is dependent on the cation ordering or disordering. Therefore, the change in u can be explained by a change in the cation distribution. Before the high-pressure experiment, the Mg^{2+} cations are ordered on the tetrahedral sites and this ordering corresponds to u = 0.2580. After the high-pressure experiment, the value of u = 0.2569 (2) corresponds to a partial disordering on the different polyhedron sites. Before the experiment, the octahedron was only occupied by Al cations with a bond distance of d_{oct} = 1.931 (1) Å. An octahedral Mg—O bond would have a distance of d_{oct} = 1.946 Å (Yamanaka & Takeuchi, 1983). According to (15), the degree of disordering can be described with λ = 0.17 (2). So, after the phase transition to the high-pressure phase, the cations change their positions in the oxygen framework and, at least partially, keep this position after pressure release. The slight decrease of the lattice constant also indicates that the crystal is in a state which is different from the initial one. Comparison of this disordered phase with high-temperature investigations of $MgAl_2O_4$ (Yamanaka & Takeuchi, 1983; Wood, Kirkpatrick & Montez, 1986) shows that a comparable effect of disordering can also be observed at high temperatures. For other spinel-type compounds with various cations the dependency of the cation ordering on the growing conditions could be observed (Hazen *et al.*, 1993) and this disordered state could be at least partially quenched to room-temperature conditions. Obviously, the same happens on abrupt pressure decrease and a metastable state with a disordered configuration of the cations is the result. Reports of high-temperature structure investigations and theoretical studies of spinel order–disorder phase transitions give contradictory results for the increase or decrease of the lattice constants on disordering. A theoretical work revealed a decrease in the

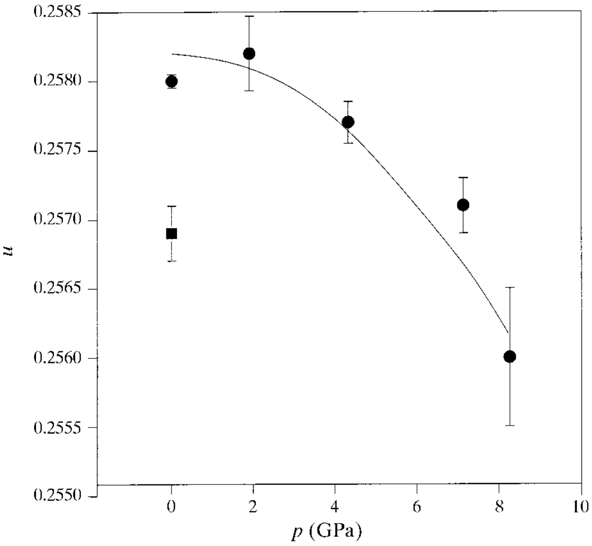

Fig. 3. Pressure dependence of the positional parameter u. The square denotes a value obtained from a specimen recovered from a high-pressure run. The line serves as a guide to the eye.

lattice constant (O'Neill & Navrotsky, 1983), which is in agreement with this experiment, whereas other experimental results show a slight increase (Wood, Kirkpatrick & Montez, 1986) hardly beyond error. Therefore, no final conclusion can be drawn on the dependency of the lattice constants at room conditions on the degree of inversion, although it is easier to understand that there is a decrease of the lattice constant owing to a disordering at high pressures rather than an increase. The results remain contradictory and it only can be stated that there is a relation between the lattice constant and the cation distribution.

5. Discussion

Bulk moduli of various oxide spinels have been collected in the past, mostly motivated by the desire to reveal new aspects of the earth's mantle constitution. Most of these studies are limited to a pressure range below 8 GPa. Less work has been carried out on thiospinels or others (Wittlinger, Werner & Schulz, 1997; Kagayama *et al.*, 1996). All oxide spinels show compressibilities between 180 and 230 GPa, depending on the cation combination of the individual sample (Finger *et al.*, 1986; Wilburn & Bassett, 1976; Hazen, 1993). The values for the derivative K' are hardly greater than the errors and are between 4 and 6. In contrast, the spinel-type compounds with sulfur anions show values of compressibility around 80–100 GPa. Independently of the cations, the anions seem to restrict a range of compressibility of the individual compounds.

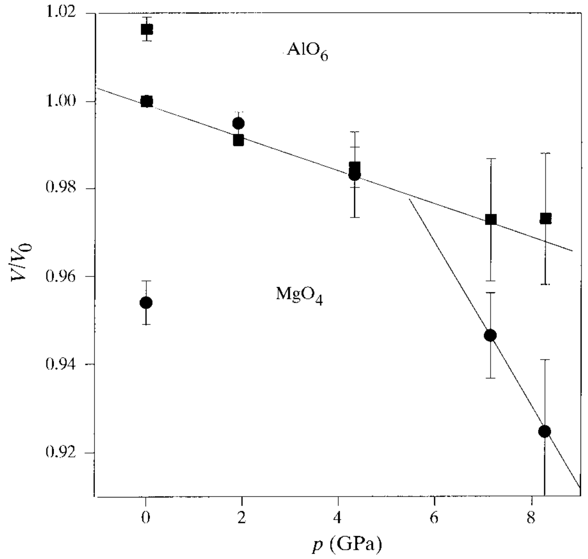

Fig. 4. The changes of the polyhedral volumes under pressure are similar to the change of the unit-cell volume up to a pressure of ~4 GPa. At higher pressures, considerable structural changes occur. The values at 1 bar deviating from 1 originate from a specimen recovered after a high-pressure run.

Table 2. *Comparison of bulk moduli of different spinel structures*

All oxide spinels have comparable overall bulk moduli, whereas the thiospinel is much more compressible.

Compound	Fe_3O_4 [(a)]	Ni_2SiO_4 [(a)]	$MgAl_2O_4$ [(b)]	$ZnCr_2S_4$ [(c)]
K (GPa)	183 (5)	220	212 (5)	94 (9)
K'	5.6	4	6.3 (1.5)	4
K_{tet} (GPa)	190 (20)	> 250	110 (25)	107 (17)
K_{oct} (GPa)	190 (20)	170 (10)	330 (40)	127 (17)

References: (*a*) Finger *et al.* (1986); (*b*) this work; (*c*) Wittlinger, Werner & Schulz (1997).

Comparison of the structure determinations with other results for spinel under pressure suggests that all representatives of the spinel group have a tendency to approach a value of $u = 0.25$, independently of the nature of the constituents or the starting value of u, which can be lower or higher than 0.25. Magnetite, which shows a value of $u = 0.255$ at ambient pressure, compresses with hardly any structural changes. Following this, the f.c.c. configuration of the anions seems to be the favoured configuration under the influence of pressure. The change in u towards 0.25 results in a difference in the compressibility of the symmetrically distinct coordination polyhedra. At the same time it implies a change in the shape of the octahedron, which is squeezed along the (111) axis at room conditions and approaches its ideal cubic symmetry, while the overall anionic configuration tends towards the ideal f.c.c. packing. The response of the structure to the applied pressure is a tendency to reach a configuration with the highest possible density and at the same time the spinel structure approaches a configuration with higher symmetry. This is also known for other structures under pressure. In particular, SiO_2 and related compounds show a tendency to approach a close-packed configuration (Sowa, 1991). The non-linear dependency of the positional parameter u of $MgAl_2O_4$ on the applied pressure is a feature rarely observed for spinels. Experiments on Ni_2SiO_4 indicate comparable behaviour, but unfortunately the maximum pressure reached in those experiments was too low to obtain the required information clearly (Finger *et al.*, 1977). All other structure investigations did not reach the pressure regions required to observe a non-linear behaviour of the positional parameter. Structure determinations on $ZnCr_2S_4$, which reached comparable pressure regions, show no phase transition or unexpected behaviour of the positional parameter, only a small structural change and a compressibility which is twice as high as that of spinel (Wittlinger, Werner & Schulz, 1997). The response to the applied pressure is, in contrast to $MgAl_2O_4$, mainly an isotropic compression of the ionic bonds. Obviously, the bond lengths are relatively soft, owing to the sulfur anion which shows a compressibility comparable to that of other high-pressure investigations of sulfur compounds (Wittlinger, Werner & Schulz, 1997).

The existence of a structural phase transition of $MgAl_2O_4$ at room temperature and high pressure was predicted by quantum mechanical calculations at almost the correct pressure value (Catti *et al.*, 1994). However, the expected division of spinel into Al_2O_3 and MgO is incompatible with the restructuring of the single crystal on pressure release found here. To undergo this transition, the single crystal should locally divide up into two different compounds, both of which form the new nucleus of a crystal. This would destroy the single crystal completely because of the change in stoichiometry. It is hard to imagine that on pressure release there would be a restructuring of the single crystal after the constitution of such a high-pressure phase. The high-pressure phase must, in contrast, preserve in some way the original ordering of the atoms, to keep the possibility of resulting in a new single crystal on pressure release. Independently of the calculations, spectroscopic experiments showed a phase transition at 11 GPa and amorphization at 19 GPa, but these experiments were carried out with alcohol as the pressure medium and the point of the first phase transition was suspected to be the solidus of the pressure medium. Now, the existence of the transition can be confirmed with our experiments. On the other hand, as the spectra did not vanish, but only changed their pressure dependence at 11 GPa, this supports the fact, deduced from the recovery of the single crystal, that the phase transition is only some destruction of a long-range order. The X-ray experiment shows amorphization, but the remaining short-range order can be further observed in the spectroscopic experiments. At pressure release, this short-range order can help to reconstruct the single crystal.

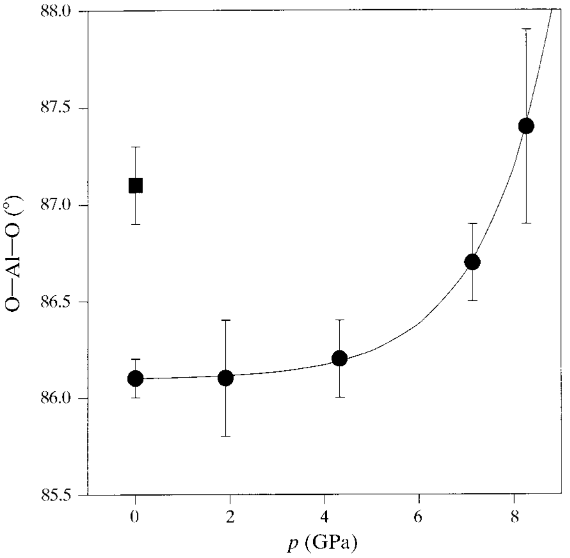

Fig. 5. Pressure dependence of the angle O—Al—O in the octahedron. Whereas the volume of the octahedron seems to be resistant to the applied pressure, the shape of the polyhedron suddenly begins to change above 4 GPa. The square denotes a value obtained from a specimen recovered from a high-pressure run. The fitted exponential function serves as a guide to the eye.

In contrast, if the pressure had been raised to a value of more than 19 GPa, where the spectroscopic signals also vanished, it should be expected that the crystal undergoes a phase transition to a substance which is unable to reconstruct a single crystal on pressure release. Although the phase transition appeared reversible in that experiment, the high-pressure phase is observed as a compound which is completely disordered and so no short-range ordering remains which could preserve information on the reconstruction of a single crystal. A polycrystalline compound of small nuclei would be expected rather than one crystal.

A change in the lattice constant of a recovered specimen is also known for $ZnCr_2S_4$, but the effect is even greater and is heavily dependent on the individual sample. For $ZnCr_2S_4$ the resulting lattice constants correspond to values which are reached at several GPa in the initial high-pressure run, whereas here the effect is hardly detectable. Unfortunately, no structure refinement of the recovered thiospinel probes was carried out, so the lattice constants can only be used as an indication that a comparable effect of pressure-induced cation exchange reactions might happen. Based on crystal-field stabilization energy calculations, the stability of $ZnCr_2S_4$ should not be considerably higher than that of $MgAl_2O_4$ (Glidewell, 1976), so it is not hard to imagine that at comparable pressures the ions also begin to exchange their sites in the spinel. On the other hand, the process of disordering in $MgAl_2O_4$ can be explained with the aid of the uncharacterized high-pressure phase, but in $ZnCr_2S_4$ the effect is also observed in specimens that remained in pressure regions where no phase change was observed. So, either the disordering of the cations can also happen indirectly *via* a high-pressure modification or the reduced lattice constant of $ZnCr_2S_4$ has a different explanation which may be revealed by a successful structure refinement of a recovered specimen.

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