

# High-Pressure Crystal Chemistry of Spinel ( $\text{MgAl}_2\text{O}_4$ ) and Magnetite ( $\text{Fe}_3\text{O}_4$ ): Comparisons with Silicate Spinel

Larry W. Finger, Robert M. Hazen, and Anne M. Hofmeister

Geophysical Laboratory, Carnegie Institution of Washington, 2801 Upton St., NW, Washington, DC 20008, USA

**Abstract.** High-pressure crystal structures and compressibilities have been determined by x-ray methods for  $\text{MgAl}_2\text{O}_4$  spinel and its isomorph magnetite,  $\text{Fe}_3\text{O}_4$ . The measured bulk moduli,  $K$ , of spinel and magnetite (assuming  $K' = 4$ ) are  $1.94 \pm 0.06$  and  $1.86 \pm 0.05$  Mbar, respectively, in accord with previous ultrasonic determinations. The oxygen  $u$  parameter, the only variable atomic position coordinate in the spinel structure ( $Fd\bar{3}m$ ,  $Z = 8$ ), decreases with pressure in  $\text{MgAl}_2\text{O}_4$ , thus indicating that the magnesium tetrahedron is more compressible than the aluminum octahedron. In magnetite the  $u$  parameter is unchanged, and both tetrahedron and octahedron display the 1.9 Mbar bulk modulus characteristic of the entire crystal. This behavior contrasts with that of nickel silicate spinel ( $\gamma\text{-Ni}_2\text{SiO}_4$ ), in which the  $u$  parameter increases with pressure because the silicon tetrahedron is relatively incompressible compared to the nickel octahedron.

## Introduction

Spinel-type  $\text{AB}_2\text{O}_4$  oxides are associated with many geological environments, from aluminates, ferrites, and chromites in metamorphic, sedimentary, and igneous rocks of the earth's crust, to high-pressure forms of orthosilicates in the earth's mantle. The versatile spinel structure may accommodate cations of +1, +2, +3, or +4 valence in either tetrahedral or octahedral coordination, thus leading to stable compounds over a wide range of temperature, pressure, and composition.

Recent studies on the high-pressure crystal chemistry of isomorphous compounds, such as  $\text{ABO}_4$  scheelites (Hazen et al. 1985) and  $\text{A}_2\text{BO}_4$  silicate olivines and chrysoberyl (Hazen 1986), demonstrate the extreme variability of physical properties that may result from mixed-valence substitutions of the type  $\text{Ca}^{2+}\text{W}^{6+} - \text{La}^{3+}\text{Nb}^{5+}$  or  $\text{Mg}^{2+}\text{Si}^{4+} - 2\text{Al}^{3+}$  in a given structure type. The objectives of the present study of spinel and magnetite are to (1) determine equation-of-state parameters for end-member samples of these minerals, (2) document atomic structure changes that accompany crystal compression, and (3) compare these results with the previous high-pressure structure data of Finger et al. (1979) on silicate spinels.

## Experimental

### Specimen Description

A nearly colorless, gem-quality crystal of natural spinel from South East Asia was provided by G.R. Rossman (California Institute of Technology). Microprobe analysis showed the sample to be nearly pure  $\text{MgAl}_2\text{O}_4$ , containing 28.77 weight percent MgO, 70.08 weight percent  $\text{Al}_2\text{O}_3$ , 0.33 weight percent FeO, 0.33 weight percent ZnO, 0.05 weight percent  $\text{TiO}_2$ , and 0.02 weight percent  $\text{SiO}_2$ . Oxides of Cr and Mn, if present, were below the detection limit of approximately 0.02 weight percent. The structural formula of this natural spinel, assuming 4 oxygens per formula unit, is  $\text{Mg}^{\text{IV}}(\text{Al}_{1.97}\text{Mg}_{0.02}\text{Fe}_{0.005}\text{Zn}_{0.005})^{\text{VI}}\text{O}_4$ .

Crystals of pure, synthetic magnetite were provided by Harold Harrison (Materials Science Council, Purdue University) from material grown by the skull melter method (Harrison and Aragon 1978). The material is free from exsolved wüstite or iron and is close to the ideal  $\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$ , in composition, as determined with x-ray diffraction, wet chemical, and reflected light measurements by Harrison and Aragon. Crystal fragments employed in the present high-pressure study were obtained as chips from equant synthetic single crystals that exceed 1 cm in length.

### Data Collection

Room-pressure unit-cell parameters and crystal structures of spinel and magnetite were determined on samples in the pressure cell in order to facilitate comparisons between room- and high-pressure data. Flat, plate-like crystals approximately  $100 \times 100 \times 40 \mu\text{m}$  were mounted in a diamond-anvil pressure cell for x-ray diffraction, with an alcohol mixture of 4:1 methanol:ethanol as the hydrostatic pressure medium and several 5 to 10  $\mu\text{m}$  chips of ruby as an internal pressure calibrant. Pressure-cell design, loading, operation, and calibration were as described by Hazen and Finger (1982). Special care was taken to avoid x-ray shielding by the gasket portions of the diamond cell. A large gasket hole approximately 400  $\mu\text{m}$  in diameter was employed, and the crystal was observed to remain centered in the hole throughout the experiments.

Spinel and magnetite unit cell parameters at room pressure and at four high pressures (Table 1) were refined from diffractometer angles of twelve to fifteen reflections by the

Table 1. Refinement conditions and refined positional and thermal parameters of spinel and magnetite

Pressure (kbar)	Spinel, MgAl <sub>2</sub> O <sub>4</sub>				Magnetite, Fe <sub>3</sub> O <sub>4</sub>				
	10	20	30	40	0.001	13	26	39	45
No. of Obs. <sup>a</sup>	45	46	43	45	57	58	53	59	66
R (%) <sup>a</sup>	3.7	3.9	3.0	4.1	1.6	2.0	2.4	2.3	4.3
wR (%) <sup>b</sup>	3.2	2.6	2.3	3.5	1.6	2.1	2.6	2.2	4.0
a (Å)	8.0898 (9)	8.0776 (5)	8.0515 (6)	8.034 (1)	8.3778 (5)	8.3578 (8)	8.339 (4)	8.3199 (7)	8.3153 (7)
V (Å <sup>3</sup> )	529.4 (4)	527.0 (2)	522.0 (2)	518.5 (4)	588.0 (1)	583.8 (2)	579.9 (2)	575.9 (1)	574.9 (1)
Extint. (cm × 10 <sup>5</sup> )	12 (2)	10 (2)	20 (2)	5 (1)	1.7 (3)	2.0 (3)	1.4 (4)	1.1 (3)	2.7 (7)
<i>A</i> (Tetrahedral) Site at (1/8,1/8,1/8)									
<i>B</i> (Å <sup>2</sup> )	0.90 (2)	0.61 (3)	0.65 (3)	0.88 (3)	0.60 (2)	0.61 (3)	0.51 (4)	0.57 (3)	0.50 (5)
$\beta_{1,1} = \beta_{2,2} = \beta_{3,3}$	0.0033 (3)	0.0023 (3)	0.0037 (4)	0.0034 (4)	0.0022 (2)	0.0023 (3)	0.0018 (4)	0.0021 (3)	0.0018 (5)
$\beta_{1,2} = \beta_{1,3} = \beta_{2,3} = 0$									
rms amplitude (Å)	0.107 (1)	0.088 (1)	0.091 (2)	0.106 (2)	0.087 (1)	0.088 (2)	0.080 (3)	0.085 (2)	0.080 (4)
<i>B</i> (Octahedral) Site at (1/2,1/2,1/2)									
<i>B</i> (Å <sup>2</sup> )	0.87 (3)	0.61 (2)	0.72 (3)	0.81 (2)	0.70 (2)	0.69 (3)	0.61 (4)	0.64 (3)	0.58 (5)
$\beta_{1,1} = \beta_{2,2} = \beta_{3,3}$	0.0035 (3)	0.0023 (2)	0.0028 (2)	0.0031 (3)	0.0025 (1)	0.0025 (1)	0.0022 (1)	0.0023 (1)	0.0021 (2)
$\beta_{1,2} = \beta_{1,3} = \beta_{2,3}$	-0.0001 (2)	-0.0001 (2)	-0.0002 (1)	0.0001 (2)	0.0001 (1)	0.0001 (1)	0.0002 (1)	0.0002 (1)	-0.0001 (1)
rms amplitudes (Å)									
Parallel [111]	0.109 (2)	0.090 (1)	0.099 (3)	0.100 (2)	0.092 (1)	0.091 (2)	0.083 (4)	0.085 (4)	0.086 (3)
Perpendicular [111]	0.104 (2)	0.083 (3)	0.088 (3)	0.105 (3)	0.099 (3)	0.098 (3)	0.096 (5)	0.099 (3)	0.083 (6)
Oxygen site at ( <i>u</i> , <i>u</i> , <i>u</i> )									
<i>u</i>	0.2633 (3)	0.2627 (3)	0.2632 (4)	0.2627 (3)	0.2550 (2)	0.2549 (2)	0.2547 (4)	0.2549 (3)	0.2551 (5)
<i>B</i> (Å <sup>2</sup> )	1.07 (3)	1.10 (2)	0.85 (2)	1.00 (3)	0.73 (4)	0.78 (5)	0.69 (7)	0.70 (5)	0.62 (8)
$\beta_{1,1} = \beta_{2,2} = \beta_{3,3}$	0.0041 (3)	0.0042 (3)	0.0033 (2)	0.0039 (3)	0.0026 (1)	0.0028 (2)	0.0025 (2)	0.0025 (2)	0.0022 (3)
$\beta_{1,2} = \beta_{1,3} = \beta_{2,3}$	-0.0001 (3)	-0.0002 (3)	0.0000 (4)	-0.0006 (3)	0.0001 (2)	0.0002 (3)	0.0001 (4)	-0.0004 (3)	0.0008 (4)
rms amplitudes (Å)									
Parallel [111]	0.118 (2)	0.105 (2)	0.103 (5)	0.120 (2)	0.094 (5)	0.095 (6)	0.091 (9)	0.101 (13)	0.070 (12)
Perpendicular [111]	0.113 (3)	0.104 (3)	0.112 (5)	0.095 (4)	0.101 (9)	0.108 (10)	0.098 (15)	0.080 (6)	0.117 (15)

<sup>a</sup>  $I > 2\sigma$ <sup>b</sup>  $R = \sum |F_o| - |F_c| / \sum |F_o|$ <sup>c</sup>  $wR = [\sum w(F_o^2 - F_c^2) / \sum wF_o^2]^{1/2}$

method of Hamilton (1974), as modified by King and Finger (1979), in order to correct for errors in crystal centering and diffractometer alignment. The reflections selected for these measurements ranged from 35° to 40° 2θ for Mo radiation. The same reflections were used for both room-pressure and high-pressure determinations to reduce any systematic errors in comparison of these data (Swanson et al. 1985). Each set of angular data was first refined without constraint, and the resultant "triclinic" cell was examined for conformity with the expected cubic spinel symmetry. Unit-cell angles were 90° within two standard deviations and the cubic constraint that  $a_1 = a_2 = a_3$  also obtained at all pressures studied. Final lattice constants were obtained with the program of Ralph and Finger (1982) with the cell geometry constrained to be cubic.

Intensity data for three-dimensional structure refinements were collected at 0.001, 10, 20, 30, and 40 kbar for spinel and at 0.001, 13, 26, 39, and 45 kbar for magnetite (all high pressures  $\pm 1$  kbar). All accessible reflections with  $(\sin \theta)/\lambda \leq 0.7$  were measured by an automated, four-circle diffractometer with MoK $\alpha$  radiation ( $\lambda = 0.7093$  Å). The fixed- $\phi$  mode of data collection (Finger and King 1978) was used to optimize reflection accessibility and minimize attenuation by the diamond cell. Corrections were made for Lorentz and polarization effects, crystal absorption, and x-ray absorption by the diamond and beryllium components of the pressure cell (Hazen and Finger 1982). Omega step scans with 0.025° step increments and 4 second counting time per step were used. Digitized step data were integrated by the method of Lehmann and Larsen (1974). Tabulated observed and calculated structure factors for spinel and magnetite at several pressures are available from the authors on request. Refinement conditions, refined isotropic extinction coefficients (Zachariasen 1967), refined structural parameters and anisotropic temperature parameters, and the magnitudes of thermal vibration ellipsoids for spinel and magnetite at room conditions are given in Table 1.

## Results

### Structure Refinements

The spinel-type structure consists of a cubic close-packed arrangement of oxygens in which one half of the octahedral sites and one eighth of the tetrahedral interstices are occupied by cations. In spinel the tetrahedral and octahedral cations are Mg<sup>2+</sup> and Al<sup>3+</sup>, respectively. In magnetite the tetrahedral position is fully occupied by Fe<sup>3+</sup>, whereas the disordered octahedral site contains half Fe<sup>2+</sup> and half Fe<sup>3+</sup>. In silicate spinels, on the other hand, the tetrahedral and octahedral cations are Si<sup>4+</sup> and R<sup>2+</sup>, respectively.

The ideal spinel structure is cubic with space group  $Fd\bar{3}m$  and  $Z = 8$  (e.g., Hill et al. 1979). The commonly used setting with an inversion center at the origin, the tetrahedral cation at (1/8,1/8,1/8) and the octahedral cation at (1/2,1/2,1/2) was employed. The oxygen parameter in this setting is at  $u,u,u$  ( $u \approx 0.25$ ). Note, however, that other settings are possible. The tetrahedral and octahedral cation positions may be defined as (3/8,3/8,3/8) and (0,0,0), respectively, in which case the oxygen positional coordinate is  $u' = 1/2 - u$ . Furthermore, the origin may be shifted by (1/4,1/4,1/4) to a point with  $\bar{4}3m$  symmetry. It is necessary to identify the choice of both origin and fixed cation coordinates prior to any comparison of spinel structures.

Table 2. Selected bond distances (Å), bond angles (°), polyhedral volumes (Å<sup>3</sup>), and polyhedral distortion indices for spinel and magnetite

Pressure (kbar)	Spinel, MgAl <sub>2</sub> O <sub>4</sub>					Magnetite, Fe <sub>3</sub> O <sub>4</sub>				
	0.001	10	20	30	40	0.001	13	26	39	45
A <sup>IV</sup> -O	1.937 (1)	1.934 (1)	1.923 (2)	1.928 (1)	1.916 (1)	1.887 (3)	1.880 (4)	1.873 (5)	1.872 (4)	1.873 (7)
O-O (IV)	3.164 (3)	3.159 (3)	3.141 (4)	3.148 (3)	3.129 (3)	3.081 (5)	3.070 (6)	3.059 (8)	3.058 (6)	3.059 (11)
Vol A <sup>IV</sup> O <sub>4</sub>	3.731 (7)	3.715 (7)	3.652 (9)	3.678 (9)	3.610 (7)	3.448 (5)	3.410 (6)	3.374 (8)	3.369 (6)	3.374 (7)
B <sup>VI</sup> -O	1.921 (2)	1.918 (2)	1.919 (3)	1.912 (2)	1.912 (2)	2.054 (2)	2.050 (2)	2.046 (3)	2.041 (2)	2.037 (4)
O-O (unshared)	2.8682 (2)	2.8639 (4)	3.8583 (4)	2.8546 (2)	2.8478 (5)	2.964 (1)	2.956 (1)	2.949 (1)	2.943 (1)	2.940 (1)
O-O (shared)	2.557 (3)	2.553 (3)	2.561 (4)	2.545 (3)	2.552 (3)	2.844 (5)	2.840 (6)	2.837 (9)	2.827 (6)	2.821 (11)
Vol B <sup>VI</sup> O <sub>6</sub>	9.28 (1)	9.24 (1)	9.26 (2)	9.15 (2)	9.16 (2)	11.52 (1)	11.45 (1)	11.40 (2)	11.31 (1)	11.25 (2)
Quad. elongation	1.012 (1)	1.012 (1)	1.011 (1)	1.012 (1)	1.011 (1)	1.002 (1)	1.002 (1)	1.001 (1)	1.002 (1)	1.002 (2)
Angle variance	47	47	43	47	43	6.1	5.7	5.4	5.8	6.3
O-B-O	83.4 (1)	83.8 (1)	83.7 (1)	83.4 (1)	83.7 (1)	87.6 (1)	87.7 (1)	87.7 (1)	87.7 (1)	87.6 (2)
O-B-O	96.6 (1)	96.2 (1)	96.3 (1)	96.6 (1)	96.3 (1)	92.4 (1)	92.3 (1)	92.2 (2)	92.3 (1)	92.4 (2)
A-O-B	120.7 (1)	120.7 (1)	120.9 (1)	120.7 (1)	120.9 (1)	123.6 (2)	123.7 (1)	123.7 (2)	123.6 (1)	123.6 (1)
B-O-B	96.2 (1)	96.2 (1)	96.0 (1)	96.2 (1)	95.9 (1)	92.4 (2)	92.3 (1)	92.2 (2)	92.3 (1)	92.3 (1)

The present room-pressure structure refinement of magnetite is in agreement with the previous study of Fleet (1981). The  $u$  parameter of spinel ( $u=0.2633 \pm 0.0003$ ) reported here for a natural specimen, however, is significantly larger than the  $0.2623 \pm 0.0001$  value for a synthetic sample studied by Ishii et al. (1982) and Yamanaka et al. (1984). The smaller  $u$  parameter of the synthetic sample is consistent with a small degree of Mg–Al disorder in that material, compared to the fully-ordered natural specimen. Selected bond distances, angles, and cation polyhedral volumes and distortion indices appear in Table 2. The tetrahedron (point symmetry  $\bar{4}3m$ ) is constrained to be regular, with four equal T–O distances and O–T–O angles of  $109.5^\circ$ . The octahedron (point symmetry  $\bar{3}m$ ) is close to regular, with all six cation-anion distances equal and observed oxygen-cation-oxygen angles deviating by less than  $10^\circ$  from the ideal  $90^\circ$  value. Six of the twelve octahedral edges in spinels are shared between adjacent octahedra. In spinel and magnetite these shared edges are significantly shorter than the unshared edges; a condition that is true of all spinels in which  $u > 0.25$ . Note that in silicate spinels stable at high pressures for which  $u < 0.25$ , octahedral shared edges are longer than unshared edges.

Each oxygen atom (point symmetry  $3m$ ) is coordinated to one tetrahedral cation and three octahedral cations. Cation-oxygen-cation angles deviate by less than  $15^\circ$  from the ideal value (Table 2).

The thermal vibration ellipsoid of the tetrahedral cation is constrained to be isotropic, whereas those of the octahedral cation and oxygen are uniaxial. Observed vibration ellipsoids in spinel and magnetite are nearly isotropic for all atoms, thus reflecting the regular coordination of these atoms.

### Bulk Moduli

The bulk moduli,  $K$ , of spinel and magnetite were calculated by least-squares fit of pressure-volume data to a Birch-Murnaghan equation of state. If  $K'$ , the pressure derivative of  $K$ , is assumed to be 4, then  $K$  for spinel is  $1.94 \pm 0.06$  Mbar, in close agreement with the 1.95 Mbar ultrasonic value determined by Wang and Simmons (1972). Magnetite bulk modulus is observed to be  $1.86 \pm 0.05$  Mbar if  $K'$  is assumed to be 4 and  $1.83 \pm 0.05$  if  $K'$  is assumed to be 5.6. These values are consistent with previous static x-ray measurements of Mao et al. (1974) of  $1.83 \pm 0.10$  ( $K'=4$ ) and the ultrasonic determination of Manghnani (pers. commun)  $1.96 \pm 0.2$  Mbar ( $K'=5.6$ ).

### Discussion

#### Comparison with Silicate Spinel

Hill et al. (1979), in their analysis of 149  $AB_2O_4$  oxide spinels, noted a close relationship between the oxygen  $u$  parameter and the relative size of  $A$  and  $B$  cations. In particular, the ratio  $R$  of the octahedral to tetrahedral cation-oxygen bond lengths is related to  $u$  by the exact expression:

$$u = \frac{\frac{R^2}{4} - \frac{2}{3} + \left\{ \frac{11R^2}{48} - \frac{1}{18} \right\}^{0.5}}{2R^2 - 2}$$

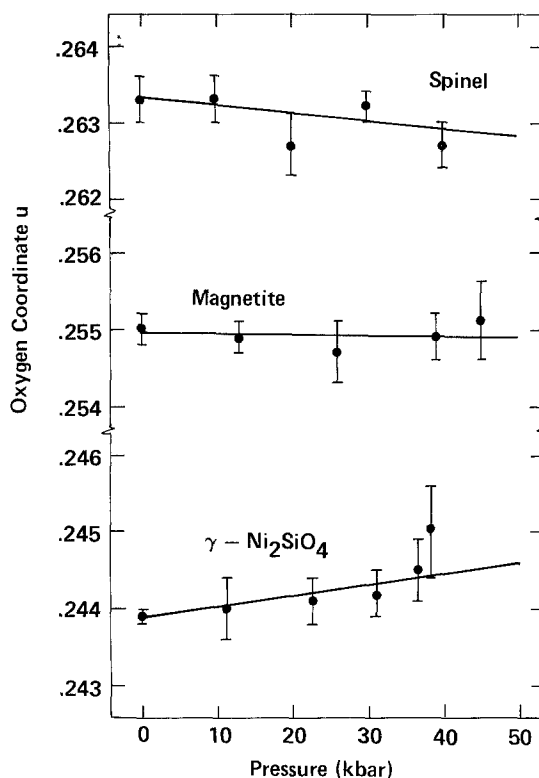


Fig. 1. The variation of the oxygen  $u$  parameter in spinel, magnetite, and nickel silicate spinel. Increasing  $u$  with pressure indicates that the octahedron is more compressible than the tetrahedron; decreasing  $u$  with pressure indicates that the tetrahedron is more compressible

Hill et al. concluded that standard ionic radii account for most of the observed range of oxygen  $u$  parameter in spinels; other factors such as electronic structure are not significant in cubic spinels.

Hazen and Finger (1979) demonstrated that the compressibilities of cation coordination polyhedra are proportional to polyhedral volume and inversely proportional to cation formal valence. In some circumstances differences in octahedral and tetrahedral compression may lead to systematic variation of  $u$  with pressure. In this regard, it is instructive to compare the high-pressure behavior of spinel and magnetite to that of  $\gamma$ -Ni<sub>2</sub>SiO<sub>4</sub> (Finger et al. 1979). The  $u$  parameter of magnesium aluminate spinel decreases slightly with pressure, thus indicating that the tetrahedron compresses more than the octahedron (Fig. 1). Magnetite  $u$  parameter is unchanged with pressure and so the structure simply scales with pressure. In nickel silicate spinel, on the other hand, the  $u$  parameter increases with pressure, as a consequence of the relative incompressibility of the silicon tetrahedron compared to the nickel octahedron. The slopes of these curves are not significant relative to the uncertainties in the individual points; however, the variations for magnesium aluminate and nickel silicate spinels are monotonic with pressure.

All three spinel-type compounds have bulk moduli of about 2 Mbar, yet the individual cation polyhedral moduli differ greatly (Table 3). Divalent magnesium tetrahedra in spinel are twice as compressible as tetravalent silicon tetrahedra in  $\gamma$ -Ni<sub>2</sub>SiO<sub>4</sub>, whereas trivalent ferric iron tetrahedra in magnetite have an intermediate compressibility. Divalent nickel octahedra in the silicate spinel are 50 percent more

**Table 3.** Cation polyhedral bulk moduli,  $K$ , and cation valences,  $Z$ , for  $\gamma$ - $\text{Ni}_2\text{SiO}_4$ , magnetite, and spinel

Compound	Octahedron		Tetrahedron	
	$Z$	$K(\text{Mbar})$	$Z$	$K(\text{Mbar})$
$\gamma$ - $\text{Ni}_2\text{SiO}_4$	+2	1.7(1)	+4	> 2.5
$\text{Fe}_3\text{O}_4$	+2.5	1.9(2)	+3	1.9(2)
$\text{MgAl}_2\text{O}_4$	+3	2.6(4)	+2	1.2(2)

compressible than trivalent aluminum octahedra in magnesium aluminate, and the mixed  $\text{Fe}^{2+} - \text{Fe}^{3+}$  octahedra of magnetite with an average valence of 2.5 are again intermediate in compressibility. In both octahedral and tetrahedral polyhedra, therefore, the inverse relationship between cation formal charge and compressibility is evident.

It is an intriguing feature of the polyhedral data in Table 3 that the observed crystal bulk modulus for these three spinels are simply the averages of the tetrahedral and octahedral bulk moduli. In magnesium aluminate, for example,  $(2.6 + 1.2)/2 = 1.9$  Mbar, which is the observed value. Similarly, for the nickel silicate,  $(1.7 + 2.5)/2 = 2.1$  Mbar, which is close to the observed 2.2 Mbar value of Finger et al. (1979). Such behavior is in sharp contrast to other binary oxide compounds, including olivine-type and scheelite-type materials, in which tetrahedral bulk moduli have little effect on macroscopic crystal compression, whereas crystal bulk modulus is controlled by the larger cation polyhedra. Compression studies of such exotic spinel-type materials as  $\text{LiV}_2\text{O}_4$  and  $(\text{LiAl})\text{SiO}_4$  could provide additional evidence for the relationship between crystal bulk modulus and that of average polyhedra.

If spinel octahedra and tetrahedra contribute equally to crystal compression, then it is probable that *all* oxide spinels have a similar bulk modulus of about 2 Mbar. Any increase in octahedral compressibility that results from cations of lower valence will be offset by the decrease in tetrahedral compressibility of higher-valence cations. This behavior would, again, contrast sharply with that of scheelite-type  $\text{ABO}_4$  oxides, which vary in compressibility by more than a factor of 4 as a result of mixed valence cation substitutions. It is evident that additional high-pressure research on a variety of spinel-type compounds is required to test these speculative observations.

#### Comparison of High-Pressure and High-Temperature Structures

Finger et al. (1979) reported the crystal structure of  $\text{Ni}_2\text{SiO}_4$  at  $700^\circ\text{C}$ , and Yamanaka and Takeuchi (1983) described high-temperature structures of  $\text{MgAl}_2\text{O}_4$  to  $1,700^\circ\text{C}$ . At temperatures to about  $700^\circ\text{C}$  structure changes are opposite to those observed with increasing pressure. In nickel silicate spinel a one percent decrease in volume leads to a 0.0005 unit increase in oxygen fractional coordinate  $u$ , whether that volume reduction is caused by compression or by cooling. Similarly, in  $\text{MgAl}_2\text{O}_4$  spinel a one percent volume decrease is accompanied by a 0.0003 unit increase in  $u$  with either compression or cooling. These spinels thus conform to the "inverse relationship" of structural response to temperature and pressure.

In magnesium aluminate the inverse relationship fails dramatically above about  $700^\circ\text{C}$ , owing to disordering of

Mg and Al. As aluminum enters the tetrahedral cation positions and magnesium occupies octahedral cation positions, the  $u$  parameter displays a sharp decrease. This decrease corresponds to the decrease in average tetrahedral cation-anion bond distance and increase in octahedral cation-anion distance. Yamanaka and Takeuchi (1983) observed irreversible lowering of the  $u$  parameter in spinels that were rapidly quenched from high temperature, thus providing further evidence for cation disorder at elevated temperature.

Silicate spinels in the earth's interior may be subject to considerable cation disorder, which may alter the stability and transport properties of these important mantle rock-forming minerals. On the basis of the site compressibility evidence of the present study, however, the 2-Mbar bulk moduli of these phases should be little affected by the degree of ordering.

*Acknowledgments.* The authors thank H. Harrison (Purdue) and G.R. Rossman (Caltech) for providing samples, and R.J. Hemley, J. Jephcoat, and H.S. Yoder, Jr. for their constructive reviews of the manuscript. This work was supported in part by National Science Foundation Grants EAR83-19209 and EAR84-19982.

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Received December 27, 1985