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Effects of cation substitution and order-disorder on *P-V-T* equations of state of cubic spinels

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ABSTRACT

The geometric simplicity of the cubic spinel structure allows prediction of equation-of-state parameters from cation-anion bond distances, bond compressibilities, and bond thermal expansivities, which can be estimated from crystal chemical systematics. We calculate effects of cation substitution and order-disorder reactions for phases of geological interest: $MgAl_2O_4$ (spinel), $MgFe_2O_4$ (magnesioferrite), Fe_3O_4 (magnetite), and Mg_2SiO_4 (ringwoodite). Compressibilities for normal vs. inverse variants of $A^{2+}B_2^{3+}O_4$ and $A^{4+}B_2^{2+}O_4$ spinels are predicted to differ by as much as 17%, and thermal expansivities by as much as 15%, as a result of the differential compressibilities or thermal expansivities of divalent, trivalent, and tetravalent cations in tetrahedral vs. octahedral coordination. These effects are unexpectedly large, and they suggest that care must be taken to document the state of cation order before and after any pressure-volume-temperature equation-of-state measurements on phases subject to a range of ordered states.

INTRODUCTION

Mineralogical models of Earth's deep interior are devised and constrained by comparing the elasticity of geochemically plausible mineral phases to observed seismic velocities (Weidner and Ito 1987; Ita and Stixrude 1992, 1993; Zhao and Anderson 1994; Angel 1997). Tabulations of mineral elastic constants typically record the structure type and major element composition of phases—a convention that implies that other compositional and structural variables are of secondary importance (Carmichael 1989; Ahrens 1995). Here, we demonstrate that this assumption may be invalid for some phases of geophysical interest.

Hazen and Navrotsky (1996) reviewed effects of pressure on order-disorder reactions, and demonstrated that many phases display a significant volume of disordering, $\Delta V_{dis} = V_{disordered} - V_{ordered}$. Silicates with Mg-Fe ordering commonly have ΔV_{dis} up to 0.5%, while values exceeding 2% obtain in some mixed-valence oxides and sulfides. In this study we analyze additional effects of cation ordering on compressibility and thermal expansion. The possibly significant role of cation ordering on equations of state (EOS) has long been recognized; Jackson et al. (1974) and Liebermann et al. (1977), for example, used velocity-density systematics to infer that cation ordering affects spinel elasticity.

Direct evidence for the influence of cation ordering on the EOS of a dense oxide was subsequently provided by Hazen and Yang (1997), who demonstrated that the bulk modulus of stoichiometric pseudobrookite-type $MgTi_2O_5$ varies by 6%, depending on the ordered state of Mg and Ti in two different octahedral sites. Such studies are usually difficult because they require a suite of compositionally identical crystals with a range of ordered states. The case of cubic spinels is special, however, because effects of cation substitution and order-disorder reactions on EOS can be calculated from geometrical arguments and well-established crystal chemical systematics. This study predicts effects of compositional variation and cation order-disorder reactions on the *P-V-T* equations of state of cubic spinels. Implications for other presumed mantle phases are discussed.

CUBIC SPINELS

Cubic spinel oxides with the structural formula AB_2O_4 (space group *Fd*3*m*) have two symmetrically distinct cation sites, with two octahedrally coordinated cations for each tetrahedrally coordinated cation. "Normal" spinels are fully ordered ($^{[4]}A^{[6]}B_2O_4$), while "inverse" spinels are disordered on the octahedral site only [$^{[4]}B^{[6]}(AB)O_4$]. Maximum disorder on both tetrahedral and octahedral sites is obtained for the intermediate form, $^{[4]}(A_{0.33}B_{0.67})^{[6]}(A_{0.67}B_{1.33})O_4$.

The spinel structure features tetrahedrally coordinated cations at (1/8,1/8,1/8), and octahedrally coordinated cations at (1/2,1/2,1/2). The oxygen atom also lies on the cube body diagonal at (u,u,u), where u is approximately 1/4. The cubic spinel structure thus has only two structural variables—the unit-cell edge a and the oxygen positional parameter u. The structure is completely determined, therefore, by its two independent cation-anion distances, designated d_T and d_O (Hill et al. 1979;

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O'Neill and Navrotsky 1983). For example, the unit-cell edge a is given by the expression:

$$a = \frac{40d_\mathrm{T} + 8\sqrt{33d_\mathrm{O}^2 \pm 8d_\mathrm{T}^2}}{11\sqrt{3}} \qquad (1)$$

or

$$a = \frac{8}{11\sqrt{3}}(5d_\mathrm{T} + A) \qquad (2)$$

where

$$A = \sqrt{33d_\mathrm{O}^2 - 8d_\mathrm{T}^2}\,. \qquad (3)$$

Any change in cation-oxygen bond distances, therefore, will alter unit-cell dimensions in a predictable way. A 1% increase in d_O, for example, results in approximately a +1% change in a, whereas a 1% increase in d_T results in approximately a +0.5% change in a.

PREDICTED COMPRESSIBILITY AND THERMAL EXPANSION OF CUBIC SPINEL

Differentiating Equation 1 with respect to pressure (or temperature) yields an expression for the dimensional change in unit-cell edge:

$$\frac{\partial a}{\partial P} = \frac{\partial a}{\partial T} = \frac{8}{11\sqrt{3}}\left[5d_\mathrm{T}' + \frac{33d_\mathrm{O}d_\mathrm{O}' - 8d_\mathrm{T}d_\mathrm{T}'}{A}\right] \qquad (4)$$

where $d' = \partial d/\partial P$ or $\partial d/\partial T$, as appropriate. Dividing Equation 4 by Equation 2 yields an exact expression for the linear compressibility (or thermal expansion) of a in terms of bond distances, d_T and d_O, and their P (or T) derivatives:

$$\left.\begin{aligned} -\beta &= \frac{\partial a}{a\partial P} \\ \alpha &= \frac{\partial a}{a\partial T} \end{aligned}\right\} = \frac{5d_\mathrm{T}'}{5d_\mathrm{T} + A} + \frac{33d_\mathrm{O}d_\mathrm{O}' - 8d_\mathrm{T}d_\mathrm{T}'}{(5d_\mathrm{T} + A)A} \qquad (5)$$

Cation-anion bond distances, d_T and d_O, are known to ±1% from spinel refinements and from tabulations of bond distances. Approximate values of the derivatives d_T' and d_O', are constrained by high-pressure or high-temperature structure studies or from comparative crystal chemical systematics (e.g., Hazen and Finger 1982), although additional studies of spinel structures at nonambient conditions would be welcome. Table 1 lists values for these parameters for six cations that are common in natural spinels: Mg^{2+}, Fe^{2+}, Al^{3+}, Fe^{3+}, Si^{4+}, and Ti^{4+}.

Table 2 uses Equations 2 and 5 and the information in table 1 to predict unit-cell volume, bulk modulus, and linear thermal expansivity for the normal and inverse ordered variants of five cubic spinels. Values in Table 1 were lineraly interpolated for spinels with mixed cations on a given site. This assumption is well documented for bond distances (e.g., Smith and Bailey 1963; Lindsley 1976; Brown 1982), but will require further testing for bond compressibilities and thermal expansivities. Note, however, that a linear relation is observed in the case of Mg-Ti octahedral volumes and site compressibilities in pseudobrookite-type $\mathrm{MgTi_2O_5}$, in which octahedral sites display a range of occupancies from pure Ti to pure Mg (Yang and Hazen 1998, 1999).

The calculated unit-cell volumes are within ±1%, of the observed values (summarized in Table 2); whereas the calculated isothermal bulk moduli are within ±3% of observed values. Calculated linear thermal expansion coefficients (averaged

TABLE 1. Tetrahedral and octahedral bond distances and their pressure and termperature derivatives, for cubic spinels

Bond	d_T (Å)	d_O (Å)	ref.*	$\partial d_T/\partial P$ 10^4 Å/GPa	$\partial d_O/\partial P$ 10^4 Å/GPa	ref.†	$\partial d_T/\partial T$ 10^6 Å/°C	$\partial d_O/\partial T$ 10^6 Å/°C	ref.†
$\mathrm{Mg^{2+}}$-O	1.96	2.08	1–3	46	47	2, 11	19	29	12
$\mathrm{Fe^{2+}}$-O	2.01	2.13	2, 4–8	49	47	2	19	28	6
$\mathrm{Al^{3+}}$-O	1.77	1.91	2, 8, 9	27	25	2	2	17	12
$\mathrm{Fe^{3+}}$-O	1.89	2.00	2, 5	33	29	2	3	18	
$\mathrm{Si^{4+}}$-O	1.65	1.79	1, 4, 6–7, 10	13	19	4	0	10	4, 6
$\mathrm{Ti^{4+}}$-O	1.80	1.98	3, 5	14	25	3, 11	0	14	

Notes:
1 = Sasaki et al. (1982);
2 = Finger et al. (1986);
3 = Wechsler and Von Dreele (1989);
4 = Finger et al. (1979);
5 = Sedler et al. (1994);
6 = Yamanaka (1986);
7 = Yagi et al. (1974);
8 = Hill (1984);
9 = Yamanaka and Takeuchi (1983);
10 = Hazen et al. (1993a);
11 = Yang and Hazen (1999);
12 = Takeuchi et al. (1984).

* Tetrahedral and octahedral cation-oxygen bond distances are taken from Shannon (1976), O'Neill and Navrotsky (1983), Smyth and Bish (1988), and from structure refinements of dense oxides and silicates, as numbered. When more than one reference is cited, the tabulated values of d_T and d_O represent average values. The range of observed values is typically within ±2% of the average.

† Variations of cation-oxygen bond distances with pressure and temperature, $\partial d/\partial P$ and $\partial d/\partial T$, are taken from Hazen and Finger (1982; Tables 6–3 and 7–2), or from structure refinements as numbered. When more than one reference is listed, the tabulated values represent an average. The range of observed values is typically within ±10% of the average. Note that these values are related to bond compressibilities, β, and bond thermal expansivities, α, as follows:

$$-\beta = \frac{1}{d}\left(\frac{\partial d}{\partial P}\right), \qquad \alpha = \frac{1}{d}\left(\frac{\partial d}{\partial T}\right).$$

TABLE 2. Calculated and observed unit-cell volumes (Å^3), bulk moduli (GPa), and linear thermal expansivities (×10^6 Å/°C^{-1}) for normal (N) and inverse (I) cubic spinels

Composition	Unit-cell volume		Bulk modulus		Thermal expansion coeff.		Reference
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	
$MgAl_2O_4$ (N)	530.0	528.1	199	194	9.2	9.1	1,2
$MgAl_2O_4$ (I)	528.9	–	196	–	8.0	–	
$MgFe_2O_4$ (N)	580.6	584.3	190	–	9.2	–	3
$MgFe_2O_4$ (I)	582.0	–	183	–	8.0	–	
$FeFe_2O_4$ (N)	595.7	–	187	–	9.1	–	
$FeFe_2O_4$ (I)	592.9	591.4	184	186	8.0	8.8	1, 4
Mg_2SiO_4 (N)	528.4	524.6	187	184	9.4	9.0	5, 6
Mg_2SiO_4 (I)	546.9	–	174	–	9.8	–	
Mg_2TiO_4 (N)	575.9	–	198	–	9.3	–	
Mg_2TiO_4 (I)	598.0	601.2	169	–	10.1	–	7

Notes: Calculations are based on Equations 1 and 5, using values for d_T, d_O, $\partial d/\partial P$, and $\partial d/\partial T$ from Table 1. Observed values are from Smyth and Bish (1988), Ahrens (1995), and numbered references.

1 = Finger et al. (1986);
2 = Takeuchi et al. (1984);
3 = Hill et al. (1979);
4 = Skinner (1966);
5 = Hazen (1993);
6 = Suzuki et al. (1979);
7 = Liebermann et al. (1977).

from 20° to 500 °C) are within ±5% of observed values for spinel and ringwoodite, but underestimate the thermal expansion of magnetite. Note, however, that magnetite has anomalous thermal expansion below the 570 °C Curie point (Skinner 1966); the average observed thermal expansion coefficient between 20° and 500 °C is approximately 12.0×10^{-6} °C^{-1}, compared to the predicted value of 8.0×10^{-6} °C^{-1}.

In all five examples (Table 2) the calculated unit-cell volumes, compressibilities, and thermal expansivities of normal and inverse spinels differ. We predict maximum effects for the thermal expansivity of $MgAl_2O_4$ and $MgFe_2O_4$ (the normal spinels are predicted to be 15% more expansible than the inverse variant), and for the compressibility of Mg_2TiO_4 (inverse magnesium titanate is predicted to be 17% more compressible than the normal variant). Predicted effects of order-disorder reactions on EOS differ systematically for $A^{2+}B_2^{3+}O_4$ (2-3) spinels, compared to $A^{4+}B_2^{2+}O_4$ (4-2) spinels. The normal variants of spinel, magnesioferrite, and magnetite, all examples of 2-3 spinels, are predicted to have similar unit-cell volumes, but significantly greater coefficients of thermal expansion, than inverse variants. The differences in thermal expansion result primarily because the thermal expansivity of tetrahedral R^{2+}-O bonds is much greater than that of tetrahedral R^{3+}-O bonds, whereas octahedral bond expansivities are similar for R^{2+}-O and R^{3+}-O bonds (Table 1). Normal 2-3 spinels are also predicted to be slightly less compressible than inverse variants, but these differences are modest because the tetrahedral and octahedral compressibilities of divalent and trivalent cations are similar.

By contrast, the inverse variants of 4-2 titanate and silicate spinels are predicted to have significantly greater unit-cell volumes and to display significantly greater compressibilities and expansivities than their normal spinel counterparts. These differences result from the relative stiffness of tetrahedral R^{4+}-O bonds compared to tetrahedral R^{2+}-O bonds.

IMPLICATIONS FOR EOS OF MANTLE MINERALS

Experimental pressure-volume data for both ordered and disordered variants are not yet available for any presumed mantle mineral. The effects of ordering on EOS can be illustrated, however, by using the crystal chemical systematics for cubic spinels developed above to calculate unit-cell volumes and bulk moduli for ordered and partially disordered variants of ringwoodite, Mg_2SiO_4. Synthetic silicate spinels quenched from high temperature and pressure are typically ordered, with Si in tetrahedral coordination and divalent cations (Mg, Fe, Co, and Ni) in octahedral coordination. Disordering with up to 4% Si in octahedral coordination, however, has been reported for synthetic Mg_2SiO_4 rapidly quenched from 1400 °C (Hazen et al. 1993a). Consider, therefore, the contrasting EOS for a fully ordered and a hypothetical 10% disordered magnesium silicate spinel (a plausible extreme for conditions at the lower transition zone).

Applying Equation 2 and values from Table 1, we estimate room-pressure unit-cell volumes for fully ordered Mg_2SiO_4 and a disordered variant with 10% Si in octahedral coordination $[(Mg_{1.8}Si_{0.2})(Mg_{0.2}Si_{0.8})O_4]$ to be 528.4 and 531.4 Å^3, respectively—a 0.6% difference that arises primarily because disordered Mg cations enlarge d_T. Similarly, Equation 5 yields bulk moduli of 187.2 and 184.5 GPa, respectively, for the normal and 10% disordered variants. The slightly disordered silicate spinel is predicted to be 1.5% more compressible than the normal end member—an effect on EOS that is three times greater than that of a 10% Fe^{2+} substitution for Mg (Hazen 1993).

Although details of order-disorder and minor compositional variations are more difficult to predict for non-cubic mantle minerals than for cubic spinels, the present study suggests that the largest effects are to be expected for changes involving mixed-valence and/or mixed-coordination substitutions—Mg-Si disordering, for example, or substitution of Mg + Si for 2Al (Finger and Hazen 1991). Table 3 lists possible minor cation

TABLE 3. Minor cation substitutions and order-disorder variants that might affect EOS of mantle minerals

Mineral and composition	Cation substitutions	Order-disorder	References
Olivine $(Mg,Fe)_2SiO_4$	Ca, Fe^{3+}	Mg-Fe	1, 2
Wadsleyite $(Mg,Fe)_2SiO_4$	Fe^{3+}, H	Mg-Fe	3, 4
Spinel $(Mg,Fe)_2SiO_4$	Fe^{3+}, Ti	Mg-Si	5
Pyrope $(Mg_3Al_2Si_3O_{12})$	Ca, Fe, MgSi—2Al	Mg-Si; Ca-Mg	6
Majorite $(Mg,Fe)SiO_3$	Ca, Al, Fe^{3+}	Mg-Al-Fe^{3+}-Si; Ca-Mg	6–8
Clinopyroxene $(Mg,Fe,Ca)SiO_3$	Na, K, Al, Fe^{3+}, Ti	Mg-Al-Fe^{3+}-Ti-Si; Ca-K-Na	9–11
Orthopyroxene $(Mg,Fe)SiO_3$	Ca, Al, Fe^{3+}	Mg-Al-Fe^{3+}-Ca	12, 13
Perovskite $(Mg,Fe)SiO_3$	Ca, Al, Fe^{3+}	Mg-Al-Fe^{3+}-Si	7, 14–16
Anhydrous B $(Mg,Fe)_{14}Si_5O_{24}$	Al, Fe^{3+}	Mg-Fe^{2+}-Al-Fe^{3+}-Si	17
Magnesiowustite (Mg,Fe)O	Fe^{3+}, vacancies	Fe^{2+}-Fe^{3+}-vacancies	18

Notes:
1 = Aikawa et al. (1985);
2 = Akamatsu and Kumazawa (1993);
3 = Finger et al. (1993);
4 = Smyth et al. (1997);
5 = Hazen et al. (1993a);
6 = Gasparik (1990);
7 = O'Neill and Jeanloz (1993);
8 = Hazen et al. (1994);
9 = Angel et al. (1988);
10 = Woodland et al. (1997);
11 = Harlow (1997);
12 = Hazen et al. (1993b);
13 = Hugh-Jones and Angel (1997);
14 = McCammon et al. (1992);
15 = Fei et al. (1996);
16 = McCammon (1997);
17 = Hazen et al. (1992);
18 = Hazen and Jeanloz (1984).

substitutions or order-disorder couples that could affect EOS of potentially important mantle phases. Of special importance in understanding the equilibrium behavior of mantle phases are the as yet undocumented effects of trivalent cation substitution (Al^{3+} and Fe^{3+}) on EOS, as well as the possibility of changes in Mg-Si ordered states in dense oxide minerals at mantle conditions. In these cases, cation disordering will generally increase molar volume (Hazen and Navrotsky 1996).

EXPERIMENTAL CONSIDERATIONS

Appropriate modifications to mantle models must await new experimental measurements on equilibrium equations of state, particularly for possible high-pressure compositional and ordered variants of silicate spinels, perovskites, and majoritic garnets and their isomorphs. Comparative compressibility experiments are now under way on differently ordered variants of Mg_2TiO_4 spinel, which this study suggests is a suitable analog for ringwoodite. Similar efforts could be applied to suites of 2-3 aluminate and ferrite spinels, including magnesioferrite $MgFe_2O_4$ (O'Neill et al. 1992), $ZnAl_2O_4$ (O'Neill and Dollase 1994), $NiAl_2O_4$ (O'Neill et al. 1991), $ZnFe_2O_4$ (O'Neill 1992), and $CoAl_2O_4$ (O'Neill 1994).

Based on the unexpectedly large effects of cation order on molar volume, bulk modulus, and thermal expansion on spinels, it is important to recognize that different experimental conditions will yield inherently different *P-V-T* EOS and elastic constants, depending on the extent to which the crystals under study achieve equilibrium. At temperatures below 600 °C, most dense oxides and silicates undergo little cation redistribution over laboratory time scales and thus will yield an "isostructural" EOS (i.e., with a constant state of cation distribution) under any laboratory time scale. This is the EOS that is usually assumed in tabulations of mineral properties.

In contrast, at temperatures above 1200 °C, typical of some *in situ* laser-heated diamond-anvil cell experiments, most minerals will achieve an equilibrium state of cation order in seconds, and thus should yield an "equilibrium" EOS (i.e., with different cation distributions at different temperatures and pressures). If cation distribution varies with temperature and pressure, the resulting EOS and elastic constants will generally differ significantly from the isostructural values. Researchers should thus be alert to the possibility that, for measurements at high temperatures, structural variations will be superimposed on measured values of molar volume and elastic moduli, and EOS values may reflect a melange of structural states. Such an effect may provide an explanation for anomalous thermal expansivity observed in some studies (e.g., Bush and Hummel 1958; Yamanaka and Takeuchi 1983; Yamanaka 1986).

Even more pernicious is the likely situation that the degree of order will gradually approach equilibrium during the course of an experiment, thus superimposing effects of ΔV_{dis} and changes of EOS parameters with order-disorder on the measured unit-cell parameters and elastic constants. This situation is especially likely to occur for measurements of thermal expansion in the 700 to 1000 °C range, for which experiments are generally too lengthy to maintain an isostructural state, but too brief to attain an equilibrium state at every desired pressure and temperature (Wood et al. 1986; Yamanaka 1986; Peterson et al. 1991). Typical equilibration times of minutes to hours (e.g., O'Neill et al. 1991, 1992; O'Neill 1992, 1994; O'Neill and Dollase 1994) are comparable to times required to perform X-ray diffraction, Brillouin scattering, and ultrasonic EOS measurements. Each measurement of unit-cell volume or elastic constants, therefore, may be sampling a range of cation distributions.

The ultimate solution to this problem is to document *P-V-T-X* equations of state, where *X* is an appropriate order parameter. One possible intermediate experimental solution is first to determine a phase's equilibrium state of ordering as a function of temperature and pressure via a series of in situ and quench experiments. Then, as unit cell or elastic constant data are obtained at temperature and pressure, the structural state must be monitored in situ before and after every measurement. Finally, all elastic data should be tabulated with information on minor element composition and the state of ordering.

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