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Isostructural versus Equilibrium Equations of State

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Recent experimental and theoretical studies demonstrate that the state of cation order-disorder in minerals, including dense oxide and silicate phases may have a significant effect on their P-V-T equations of state (EOS). One must distinguish, therefore, between the isostructural EOS (the P-V-T relationship for a constant state of structural order) and the equilibrium EOS (the P-V-T relationship adjusted for the appropriate state of cation order at each T and P). In experiments at moderate temperatures (typically 600 °C to 1000 °C for oxides and silicates), under which cation ordering changes gradually during the course of most experiments, the observed P-V-T EOS may represent neither an isostructural nor an equilibrium situation. [**Keywords**: equations of state, order-disorder, bulk modulus, thermal expansion, spinel]

1. Introduction

P-V-T equations of state for dense oxides and silicates are critical to the development of mineralogical models of Earth's inaccessible mantle [1-3]. The majority of EOS investigations report the composition and structure type of the phase under study, but do not document the state of cation order-disorder [4-5]. Recent studies, both experimental [6] and theoretical [7], reveal that P-V-T EOS in mantle-type oxide and silicate phases may be significantly affected by the state of cation order.

The significance of order-dependent EOS lies in the fact that many oxide and silicate minerals are subject to a wide range of cation order-disorder, depending on the temperature and pressure of equilibration. The variability of cation order-disorder state in numerous crustal minerals, including orthopyroxenes, clinopyroxenes, amphiboles, and other biopyriboles, feldspars, feldspathoids, carbonates, and oxide spinels, is well documented [8]. Indeed, the quenched states of cation ordering in these minerals are commonly employed as petrological geothermometers. Presumed mantle phases have also been demonstrated to display significant variations in cation ordering, including pressure-induced ordering [9]. Recent reports document unanticipated degrees of octahedral Fe-Mg order in olivines [10,11], phase B-type structures [12], and wadsleyites [13, 14]; dodecahedral Mg-Ca ordering in garnet [15]; and differing degrees of Mg-Si order in garnets [16], pyroxenes [17], and silicate spinels [16].

The objective of this article is to review recent evidence regarding the effects of cation order-disorder on EOS, to introduce the concepts of equilibrium versus isostructural EOS, and to examine some of the experimental consequences of these ideas.

2. Experimental Evidence for Order-Dependent EOS

Several experimental studies have demonstrated (at times inadvertently) the consequences of variations of cation order-disorder on EOS. Notable in this regard are studies of the thermal expansion of magnesium aluminate spinel, $MgAl_2O_4$ (the mineral "spinel"), in which the phenomenon of cation disorder was first documented by Barth and Posnjak in 1931 [19]. As will be deomonstrated in the following section, different ordered states of Mg and Al in spinel will result in different molar volumes and other EOS parameters. Effects of changing Mg-Al cation order-disorder during heating must thus be factored into calculations of spinel thermal expansion, as demonstrated by Yamanaka and coworkers [20]. Similarly, changes in Mg-Ti ordering in pseudobrookite-type $MgTi_2O_5$ led Bush and Hummel [21] to describe "anomalous" thermal expansion of that compound.

A more detailed explanation of the effects of cation ordering on EOS was proposed by Hazen and Yang [6, 22], who synthesized a suite of pseudobrookite-type $MgTi_2O_5$ samples with different ordered states and determined their compressibilities and high-pressure crystal structures. Pseudobrookite features two symmetrically distinct octahedral sites [23, see Fig. 1 therein]. M2 octahedra, which are occupied by Ti in the fully ordered variant, form an edge-sharing layer perpendicular to the orthorhombic *b* axis. Compression and thermal expansion of the *a-c* plane, therefore, is determined primarily by the behavior of M2 octahedra. M1 octahedra, which are occupied by Mg in the ordered form, cross-link the layers parallel to *b*. The *b*-axis behavior is thus affected by both M1 and M2.

Titanium octahedra are signficantly more rigid (both under compression and heating) than Mg octahedra. Consequently, in fully ordered $MgTi_2O_5$ both *a* and *c*, which are constrained by the Ti-bearing octahedral layer, show much less change than the *b* axis, which displays changes intermediate between those of Ti and Mg octahedra. In disordered $MgTi_2O_5$, on the other hand, the M2 layer is much more compliant, so the *a* and *c* axes display greater compressibility or expansibility, while the *b* axis still has a behavior intermediate between Mg and Ti. Consequently, ordered $MgTi_2O_5$ is 6% less compressible than the disordered variant [6] – a difference due entirely to the distribution of Mg and Ti over M1 and M2 octahedral sites.

3. The Case of Cubic Spinels

Hazen and Yang [7] presented a theoretical analysis of the effects of cation order-disorder on the EOS of cubic spinels. This analysis is possible because of the geometric simplicity of the cubic spinel structure, as well as crystal chemical systematics regarding expected bond distances, bond compressibilities, and bond thermal expansivities.

Cubic spinel oxides with the structural formula AB_2O_4 (space group $Fd3m$) 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

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on both tetrahedral and octahedral sites is obtained for the intermediate form, $^{[4]}(A_{0.33}B_{0.67})^{[6]}(A_{0.67}B_{1.33})O_4$.

Spinel has 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 $u \sim 1/4$. The cubic spinel structure thus has only two structural variables - unit-cell edge a and oxygen positional parameter u. The structure is completely determined, therefore, by its two independent cation-anion distances, designated d_T and d_O. For example, the unit-cell edge a is given exactly by:

$$a = \frac{40d_T + 8\sqrt{33d_O^2 - 8d_T^2}}{11\sqrt{3}} \qquad (1)$$

or,

$$a = \frac{8}{11\sqrt{3}}(5d_T + A), \qquad (2)$$

where

$$A = \sqrt{33d_O^2 - 8d_T^2}\,. \qquad (3)$$

Changes in cation-oxygen bond distances 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. Differentiating equation (1) with respect to P or T yields an exact expression for the dimensional change in unit-cell edge:

$$\frac{\partial a}{\partial P} \text{ or } \frac{\partial a}{\partial T} = \frac{8}{11\sqrt{3}}\left[5d_T' + \frac{33d_O d_O' - 8d_T d_T'}{A}\right]$$

Dividing this equation by the unit-cell edge a (eqn 2) yields an exact expression for the compressibility (or thermal expansion) of a in terms of bond distances, d_T and d_O, and bond compressibilities (or thermal expansivities):

$$-\beta = \frac{\partial a}{a\partial P} = \frac{5d_T'}{5d_T + A} + \frac{33d_O d_O' - 8d_T d_T'}{(5d_T + A)A}$$

$$\alpha = \frac{\partial a}{a\partial T}$$

Cation-anion bond distances, d_T and d_O, are known to within ±1% from spinel structure refinements and ionic radii tables [24,25]. Derivatives of d_T and d_O with respect to P and T, d_T' and d_O', are constrained by high-pressure or high-temperature structure studies or from comparative crystal chemical systematics [26]. Representative values for these parameters are listed in Table 1.

Table 1. Bond distances (Å) and their variations with pressure (x 10^4 Å/GPa) and temperature (x 10^6 Å/°C)

Bond	d_T	d_O	$\partial d_T/\partial P$	$\partial d_O/\partial P$	$\partial d_T/\partial T$	$\partial d_O/\partial T$
Mg-O	1.96	2.08	46	47	19	29
Fe^{2+}-O	2.01	2.13	49	47	19	28
Al^{3+}-O	1.77	1.91	27	25	2	17
Fe^{3+}-O	1.89	2.00	33	29	3	18
Si^{4+}-O	1.65	1.79	13	19	0	10
Ti^{4+}-O	1.80	1.98	14	25	0	14

These values are used to calculate unit-cell volumes, bulk moduli, and thermal expansivities for a variety of cubic spinels in both normal and inverse variants, as in Table 2.

Table 2. Calculated and observed [5] unit-cell volumes (Å^3), bulk moduli (GPa), and linear thermal expansivities (x 10^6 Å/°C) for normal (N) and inverse (I) cubic spinels.

Composition	Unit-cell Vol.		Bulk Modulus		Therm.Exp.Coeff.	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
$MgAl_2O_4$ (N)	530.0	528.1	199	194	9.2	9.1
$MgAl_2O_4$ (I)	528.9	-	196	-	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
Mg_2SiO_4 (N)	528.4	524.6	187	184	9.4	9.0
Mg_2SiO_4 (I)	546.9	-	174	-	9.8	-

Elastic properties of silicate spinel $(Mg,Fe)_2SiO_4$, presumed to be the dominant mineral phase in Earth's transition zone, are critical to mineralogical models of seismic discontinuities at 520- and 650-km. Bulk moduli and thermal expansivities for normal versus inverse variants of $A^{2+}B_2^{3+}O_4$ and $A^{4+}B_2^{2+}O_4$ spinels are predicted to differ significantly owing to the differential compressibilities or thermal expansivities of 2+, 3+, and 4+ cations in tetrahedral versus octahedral coordination. The calculations summarized in Table 2 demonstrate that the state of cation order-disorder in mantle minerals can have a dramatic effect on P-V-T equations of state. Note, for example, that the thermal expansivity of $MgAl_2O_4$ is 15% greater for the normal than for the inverse structure. In other calculations one finds that molar volume may differ by as much as 10% (as in the case of Na_2WO_4) and bulk modulus by as much as 17% (as in the case of Mg_2TiO_4). It is probable that other properties, including shear moduli and transport properties, will also be affected by differing states of cation order.

Predicted effects of order-disorder reactions on EOS are systematically different for $A^{2+}B_2^{3+}O_4$ (2-3) spinels, compared to $A^{4+}B_2^{2+}O_4$ (4-2) spinels, as enumerated by Hazen and Yang [7]. These unexpectedly large effects suggest that ordering behavior and elastic properties of silicate spinel must be reevaluated at appropriate mantle pressure and temperature.

4. Isostructural versus Equilibrium Equations of State

The observed and calculated effects of cation order-disorder on EOS have important implications for the design of experiments that purport to document EOS *in situ* at elevated temperature. In the simplest case, one must distinguish between two distinct end-member EOS.

The isostructural equation of state reports P-V-T data for a given state of cation order. In the case of fully ordered pseudobrookite-type $MgTi_2O_4$, for example, the unit-cell volume is 363.2 Å^3 and the isostructural bulk modulus (at room T) is 167 GPa. In the fully disordered variant, the unit-cell volume is 365.3 Å^3 and the isostructural bulk modulus is 158 GPa [6]. In experiments on dense oxides and silicates conducted at temperatures below about 500°C the state of cation order will probably not change significantly during experiments, which thus yield isostructural EOS data.

The equilibrium equation of state reports P-V-T for a compound at its equilibrium state of cation order. In general, this state of order will vary with temperature and pressure, and thus so will the inherent values of V_o, K_o, and thermal expansion coefficient. In the case of pseudobrookite, for example, V_o increases with disorder and K_o decreases with disorder. At higher temperatures, more disordered variants of $MgTi_2O_5$ will thus display systematically different bulk moduli. Most oxides and silicates achieve an equilibrium state of cation order rapidly at temperatures above 1200°C. Such high-temperature experiments, therefore, may be assumed to yield equilibrium EOS data.

In phases with significant variation in cation ordering, the concept of a P-V-T equation of state is not sufficient to define fully behavior under a range of P-T conditions. Care must be made to distinguish between isostructural and equilibrium EOS, and the state of cation order should be documented throughout an experiment. In effect, one must define a P-V-T-Q equation of state, where Q is one or more appropriate order parameters.

Complications will arise in experiments at elevated temperature, particularly in the range from 600° to 1000°C, over which range the state of cation order in many oxides and silicates may equilibrate relatively slowly compared to the duration of typical experimental EOS measurements. If the state of order changes gradually through the course of an experiment, but never reaches an equilibrium value, then the experiment will yield neither an equilibrium nor an isostructural EOS. The resulting P-V-T data will constitute an intermediate melange that are useful only if the variable state of order is recorded at each pressure and temperature.

Consider a situation, for example, in which the bulk modulus of ordered pseudobrookite-type $MgTi_2O_5$ is measured at 900°C – a temperature at which the sample will gradually approach an intermediate state of disorder during the course of the experiment. If unit-cell volume is measured at a regular series of increasing pressures, then the calculated bulk modulus based on P-V systematics will appear to be anomalously high, because V_o increases with increasing disorder. Similarly, if the sample is gradually heated at a given pressure then the measured thermal expansion coefficient may reflect neither an equilibrium nor an isostructural value.

An important check, therefore, is to determine the state of cation order throughout the experiment, preferably at every pressure and temperature. At a minimum, one should confirm that the sample's unit-cell volume has not changed during the course of the experiment. Fortunately, with the advent of high-resolution powder diffraction facilities at synchrotron x-ray sources, rapid, *in-situ* high-temperature, high-pressure structure analysis is possible, and the prospect of recording P-V-T-Q EOS is not beyond present capabilities.

5. Conclusions

Most of the minerals that are thought to form Earth's deep interior are subject to varying degrees of major element cation order-disorder. The presence of additional minor elements, including alkali metals, Al, and Fe^{3+}, will further complicate the ordering picture. Because of the potentially large magnitude of these effects, even a modest change in cation ordering can have a significant effect on the EOS parameters of mantle minerals. A 10% Mg-Si disorder in nominally ordered Mg_2SiO_4 silicate spinel, for example is predicted to decrease isothermal bulk modulus by >1% - a change comparable to a 5% decrease in Fe/(Fe+Mg). Consequently, as new *in situ* P-V-T-Q data on mantle minerals become available, mineralogical models of the earth may require revision.

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