Ordering in spinels—A Monte Carlo study

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ABSTRACT

We have extended a recently developed Monte Carlo technique which includes explicit exchange as well as movement of ions to systems involving heterovalent exchange. These Monte Carlo computer simulations, based on analytical inter-atomic potentials, are capable of providing detailed quantitative information concerning the thermodynamics of ordering of spinel (MgAl2O4), gahnite (ZnAl2O4), hercynite (FeAl2O4), NiAl2O4, and magnesioferrite (MgFe2O4) over a range of pressures and temperatures. At all temperatures and pressures ionic relaxation, lattice vibrations, and pressure are explicitly taken into account. Each compound has a larger expansion coefficient and smaller bulk modulus in the normal than in the inverse spinel structure. We predict only a small variation of order parameter with pressure, and that this will be more pronounced for inverse than normal spinels. We examine, briefly, the consequences of our results for the kinetics of cation ordering in these solids.

INTRODUCTION

The continuing growth in computer power has led to a tremendous increase in the contribution of computer simulation to the understanding of the physical and chemical properties of minerals. Atoms in simulation techniques and ab initio methods have proved extremely useful in providing detailed and accurate predictions of the structures and properties of silicate minerals. The principal objectives of these computations are to obtain insight into atomistic or microscopic processes that underlie macroscopic phenomena and to carry out simulations at pressures and temperatures beyond the accessible range of experimental techniques (e.g., Hazen and Downs 2000; Allan et al. 2001). For example, calculated seismic velocity profiles can be used to supplement models of density contrasts derived from seismic tomography and test proposed compositional models for the mantle.

Geological materials are often poorly characterized since many minerals occur deep within the Earth’s mantle and there are limitations in experimental techniques. This problem is acute since naturally occurring minerals contain a large number of elements, including minor and trace element impurities, which may be disordered over several crystallographic sites. Unfortunately, the present computational techniques available are largely restricted to idealized end-member systems (e.g., pure MgSiO3 perovskite) since kinetic barriers prevent classical Monte Carlo and molecular dynamics simulations being undertaken within a realistic timescale. Contact between experiment and theory is thus considerably restricted which is unfortunate considering the importance of solid solutions in mineral physics.

This paper seeks to address some of these problems and to describe and apply a Monte Carlo technique that can be readily employed to study the ordering mechanisms of solid (or liquid) mechanisms of solid (or liquid mixtures). As an example, we calculate the degree of ordering of the spinel AB2O4 (e.g., MgAl2O4, ZnAl2O4, FeAl2O4, NiAl2O4, and MgFe2O4) over a range of temperatures and pressures. We compare our results with experimental data (where available) and calculations in the static limit using a parameterized Hamiltonian (Warren et al. 2000).

The structure of spinel is shown in Figure 1 (e.g., Sickafus et al. 1999). The O ions form a cubic-close packed array and in each unit cell there are 32 tetrahedral and 64 tetrahedral holes available for occupation by cations. Of these, 16 tetrahedral and eight tetrahedral sites are occupied by cations or a regular manner so that tetrahedra share edges with one another and the tetrahedra share corners with the octahedra. In “normal” spinels all the A-cations are at the tetrahedral sites and the B-atoms are entirely at the octahedral sites. In the “inverse” structure half the B-cations occupy the tetrahedral sites while the remainder and all the A-cations occupy the octahedral sites. Thus, the normal structure is completely ordered, in the inverse structure, configurational disorder remains between A-and B-cations at the octahedral sites. However, this is an idealized picture. Spinels usually demonstrate some degree of disorder and in real systems the distribution of cations lies between the extremes represented by “normal” and “inverse” and is a function of temperature and pressure. Usually, the distribution of cations between tetrahedral and octahedral sites is described by the so-called inversion parameter, \( \chi \): \( (A_{1-x}B_x)_2(B_{2-x}A_x)O_4 \), where subscripts T and O refer to the cations at tetrahedral and octahedral sites, respectively (Navrotsky and Kleppa 1967; Navrotsky 1994). In this paper, we prefer to use an alternative description of spinels in terms of the order parameter, \( Q \) (Carpenter and Salje 1994; Harrison and Putnis 1999), which is defined as \( Q = 1-3\chi/2 \). \( Q \) varies from a value of one for completely normal spinels to −0.5 for completely inverse spinels. \( Q \) equals zero for a random arrangement of cations. Positive values of \( Q \) indicate thus a degree of normal ordering in spinels, while the negative values indicate some inverse ordering. Of the systems studied in this paper, MgAl2O4, ZnAl2O4, and FeAl2O4 are classified as normal spinels and NiAl2O4 and MgFe2O4 as inverse.

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