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OF CHEMICAL BONDING AND ELECTRONIC STRUCTURE
IN SPINEL COMPOUNDS

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Development of a Fundamental Understanding of Chemical Bonding and Electronic Structure in Spinel Compounds

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Abstract

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Hundreds of ceramic compounds possess the spinel crystal structure and exhibit a remarkable variety of properties, ranging from compounds that are electrical insulators to compounds that are superconducting, or from compounds with ferri- and antiferromagnetic behavior to materials with colossal magnetoresistive characteristics. The unique crystal structure of spinel compounds is in many ways responsible for the widely varying physical properties of spinels. The objective of this project is to investigate the nature of chemical bonding, point defects, and electronic structure in compounds with the spinel crystal structure. Our goal is to understand and predict the stability of the spinel structure as a function of chemical composition, stoichiometry, and cation disorder. The consequences of cation disorder in spinel materials can be profound. The ferromagnetic characteristics of magnetoferrite, for instance, are entirely attributable to disorder on the cation sublattices. Our studies provide insight into the mechanisms of point defect formation and cation disorder and their effects on the electronic band structure and crystal structure of spinel-structure materials. Our ultimate objective is to develop a more substantive knowledge of the spinel crystal structure and to promote new and novel uses for spinel compounds.

The technical approach to achieve our goals is to combine first-principles calculations with experimental measurements. The structural and electronic properties of spinel samples were experimentally determined primarily with X-ray and neutron scattering, optical and X-ray absorption, and electron energy-loss spectroscopy. Total energy electronic structure calculations were performed to determine structural stability, band structure, density of states, and electron distribution. We also used shell-model total-energy calculations to assess point-defect formation and migration energies in magnesio-aluminate spinel.

Background and Research Objectives

Spinel (AB_2O_4) is a name for a class of ionic compounds with a rather simple crystal structure. The oxygen anions form a nearly cubic-close-packed (CCP) framework with a half of the octahedral and one-eighth of the tetrahedral interstices filled with divalent cations A and trivalent cations B. In normal '2-3' spinels, divalent cations A and trivalent cations B occupy tetrahedral and octahedral sites, respectively.

One important structural characteristic in spinel compounds is the cation disorder that represents the lattice-site exchange between divalent and trivalent cations. The degree of cation disorder is normally described by an inversion parameter, i , which defines the fraction of trivalent cations in tetrahedral sites. Some spinel compounds such as $MgCr_2O_4$ and $ZnFe_2O_4$ are always normal ($i=0$) while some others such as $MgIn_2O_4$ and $NiAl_2O_4$ are always inverse ($i=1$). Interestingly, some spinel compounds, e.g. synthetic $MgAl_2O_4$, exhibit an impressive range of cation disorder ($0 < i < 2/3$), depending on thermal processing conditions. Certain properties of spinel-structure ferrites such as saturation magnetization are determined entirely by the arrangement of constituent cations.

A second important structural characteristic of spinel compounds is that the spinel structure can accommodate large deviations from stoichiometry. Ideally, spinel is a compound with composition $MgAl_2O_4$, i.e. an equimolar mixture of magnesia, MgO , and alumina, Al_2O_3 . However, alumina-rich, non-equimolar compositions, denoted $MgO \cdot xAl_2O_3$ ($x > 1$), are stable at high temperatures (metastable at room temperature) for all compositions $x > 1$. In fact in the limit of large x , pure γ - Al_2O_3 is obtained, which possesses the spinel crystal structure. Deviations in composition from stoichiometric (equimolar) spinel have important ramifications on properties, e.g. increased electrical conductivity, increased mechanical plasticity, decreased radiation resistance. The underlying reason for the property alterations is the presence of a high point defect concentration in non-stoichiometric spinels, specifically cation vacancies. These are charge compensating defects to counter the effect of substitution of divalent Mg^{2+} by trivalent Al^{3+} .

Both stoichiometry and cation disorder can have profound effects on properties. In addition these two structural characteristics can influence one another. As a result of cation disorder, the nature of cation vacancies in non-stoichiometric spinel has never been resolved unambiguously by experiment. In order to further explore and expand the use of spinel compounds, it is important to understand the nature of the point defects that accommodate non-stoichiometry in spinel, and the physical origin and tendencies for cation rearrangements

in spinel, as well as the effects of these characteristics on physical properties. Our experiments have also shown that electronic band structure in spinel is very sensitive to the specific arrangement of cations in the spinel lattice. We will likely also find that the electronic band structure is sensitive to stoichiometry. This presents a great opportunity to understand point defect chemistry and cation disorder phenomena through the correlation of the electronic properties and band structure of spinel compounds.

The goal of this program is to understand the effects of point defects and cation inversion phenomena on crystal structure and electronic properties in spinel compounds. Our studies of the materials response to changes in stoichiometry and cation disorder aim to improve our understanding and eventually to make it possible to predict stable atomic arrangements in spinel compounds with different cation constituents. Certain criteria relating to cations such as cation size, electronegativity, and site preference energy were developed from first principles calculations. These criteria can provide us a scientific basis to identify the physical aspects of spinel compounds for different applications. This knowledge will impact future uses of spinel compounds.

Our research may also have a direct impact on materials processing technology. Oxide ceramics with spinel structure represent a class of materials employed in many applications. The control of structural properties through materials synthesis or post processing is important for different applications. Based on the developed criteria, we will be able to design and choose processing conditions to produce spinel compounds with controlled structural and physical properties. In addition, our studies will provide an insight into the mechanisms of susceptibility of materials properties to different environments such as high temperatures and ionizing radiations. Spinel ceramic oxides are also known to bond readily to metals, unlike other simpler oxides. Our studies will contribute to a better understanding of this potentially important attribute of spinel oxides for application in metal-ceramic joining technologies.

Our objectives are (1) to understand structural stability, chemical bonding, and electronic band structure in spinel associated with point defects due to non-stoichiometry and cation disorder; and (2) to predict the materials properties of spinel compounds for different applications. The technical approach to achieve these goals is to combine first-principles calculations with experimental measurements of electronic band structure and the nature of point defects in selected spinel compounds.

The precise crystal structure, including point defect chemistry and cation disorder, of selected compounds was determined by X-ray, neutron, and electron diffraction techniques. The

conduction band structure was measured by X-ray absorption techniques including near-edge extended X-ray absorption fine-structure (NEXAFS) and extended X-ray absorption fine-structure (EXAFS), and parallel electron energy-loss spectroscopy (PEELS), specifically with electron energy-loss near-edge fine structure (ELNES).

The experimental results were compared to theoretical results from first principles calculations to understand point defect and cation disordering mechanisms. Our research utilizes advanced computing and modeling capabilities at LANL. Changes in structural stability and band structure in spinel compounds were examined using total-energy electronic structure calculations. As a first step, we developed calculation schemes for treating multicomponent oxide ceramics with rather simple structures. Additional calculation techniques that enable us to systematically introduce cation disorder or non-stoichiometry into spinel were developed to examine the effects of cation distribution and other point defects on electronic properties. These calculations help to establish reliable starting points for predicting the non-equilibrium properties of spinel.

Importance to LANL's Science and Technology Base and National R&D Needs

This program relates to two core competencies at Los Alamos: (1) theory, modeling, and high performance computing; and (2) nuclear and advanced materials. In the later case, we are especially addressing the issue of materials that will function under extreme conditions or unusual applications. Our group has demonstrated that magnesium aluminate spinel possesses very high tolerance to radiation damage and consequently, spinel represents a candidate material for application in hostile radiation environments (high neutron or energetic particle flux fields). Spinel's high radiation resistance and chemical stability also makes it an attractive host material for the disposal of surplus actinides and high level radioactive wastes. This concept is in concert with the LANL mission statement that calls for "improving the environmental and nuclear materials legacy of the cold war."

Scientific Approach and Accomplishments

To illustrate the experimental and theoretical methods that we used in this project, we provide below details of two experimental and two theoretical studies that we performed in the course of this project. These examples include: (I) an X-ray and neutron diffraction study of point defects in non-stoichiometric magnesium-aluminate spinel compounds; (II) a NEXAFS/EXAFS investigation of structure and bonding in magnesium aluminate spinel, before and after exposure to particle irradiation; (III) first principles calculations of electronic

structures in spinel compounds; (IV) total energy calculations of point defect formation and migration energies in magnesio aluminate spinel.

I. The Distribution Of Cations And Charge-Compensating Cation Vacancies In Hyper-Stoichiometric Mg-Al-Spinel

The goal of this experiment was to determine the crystallographic nature of charge-compensating cation vacancies and the extent of cation disorder in hyper-stoichiometric and stoichiometric Mg-Al-spinel single crystals and polycrystalline powders. Hyperstoichiometric refers to spinel compounds with formula given by $\text{MgO} \cdot x\text{Al}_2\text{O}_3$, where x is greater than one, specifically $3.55 \geq x \geq 1$. Experiments were carried out using single crystal X-ray diffraction, neutron diffraction, and high intensity neutron powder diffraction.

I.1 Background

As mentioned above, the objective of the experiments described here is to use neutron diffraction to obtain a comprehensive description for the atomic structure of magnesio-aluminate spinel compounds. Such compounds are represented by the formula $\text{MgO} \cdot x \text{Al}_2\text{O}_3$, where x is 1 for stoichiometric (equimolar) spinel and $x > 1$ for non-stoichiometric, alumina-rich spinel compositions. We specifically desire to compare and contrast the atomic structures of equimolar and non-equimolar, hyperstoichiometric ($x > 1$, i.e. alumina-rich) compounds. Using crystal structure refinement procedures, we intend to determine (1) the extent of cation inversion in the spinel crystals; (2) the nature of the point defects that accommodate deviations in stoichiometry from the equimolar ($x = 1$) composition; and (3) the oxygen parameter, which indicates the relative dilation of the oxygen sublattice. Neutron diffraction is superior to X-ray diffraction for the measurements described here because the neutron scattering length (and likewise, cross-section) for a Mg nucleus is sufficiently greater than that of Al, so that their site-occupancies in a crystal may be distinguished [1]. The X-ray scattering factors for Mg^{2+} and Al^{3+} are too similar to reveal crystal site-occupancy distinctions by X-ray diffraction. The experiments outlined in this proposal provide a nice complement to our earlier neutron scattering experiments on neutron irradiated spinel single crystals, which were performed at LANSCE [2].

The crystal structure of magnesium aluminate spinel was determined independently by Bragg [3] and Nishikawa [4]. The conventional, cubic unit cell is illustrated schematically in Figure I.1. The space group is $F\frac{4}{d}\bar{3}\frac{2}{m}$ ($Fd\bar{3}m$; O_h^7 ; number 227 in the International Tables) [5-9]. In spinel, the oxygen ions assume a nearly cubic close-packed (*ccp*) spatial arrangement.

There are 56 atoms per cubic unit cell, 24 cations and 32 oxygen anions; thus, there are 8 MgAl_2O_4 molecular units per unit cell. The unit cell volume is eight times that of the 'ccp' oxygen sublattice cubic unit cell; consequently, the spinel lattice parameter is large ($a_0^{\text{MgAl}_2\text{O}_4} = 0.8083 \text{ nm}$ [10]). The Bravais lattice is face-centered cubic; the basis consists of two MgAl_2O_4 formula units. Of the 64 tetrahedral interstices between oxygen anions in the conventional unit cell, only 8 are occupied by cations in spinel, and they form a diamond cubic lattice. Similarly, of the 32 octahedral interstices, only 16 are occupied by cations. In ordered magnesio aluminate spinel, Mg cations occupy tetrahedral sites, while Al cations occupy the octahedral sites. Each oxygen anion is tetrahedrally coordinated by three Al (octahedral) cations and one Mg (tetrahedral) cation.

Barth and Posnjak [11-13] were the first to point out that many compounds exhibiting the spinel structure can accommodate significant amounts of cation disorder, at so-called *variate atom equipoints*. Verwey and Heilmann [14] introduced the designations "*normal spinel*" and "*inversed spinel*" for the limiting configurations of cations in spinel-structured compounds. In a 'normal' 2-3 spinel (where 2 and 3 refer to spinels composed of divalent and trivalent cations, as in magnesium aluminate), the larger divalent ions (Mg^{2+}) occupy tetrahedral (A) interstices between oxygen ions, while the smaller trivalent ions (Al^{3+}) lie in octahedral (B) interstices. Ionic radii for magnesium aluminate ions, obtained from Shannon and Prewitt [15], are shown in Table I.1. In an 'inverse' 2-3 spinel (e.g. ordered magnesioferrite, MgFe_2O_4), the A-sites accommodate the trivalent ions, while the B-sites are occupied by divalent and trivalent ions in equal proportions.*

Experiments show that cation order always falls somewhere between these two extremes. The general formula for the unit cell stoichiometry of a 2-3 spinel is given by:

$$\left(X_{1-i}^{2+} Y_i^{3+} \right)_8 \left[X_{\frac{i}{2}}^{2+} Y_{\frac{3-i}{2}}^{3+} \right]_{16}^{Bv} O_{32} \quad \left\{ \begin{array}{ll} i = 0 & \Rightarrow \text{normal spinel} \\ i = 2/3 & \Rightarrow \text{random cation arrangement} \\ i = 1 & \Rightarrow \text{inverse spinel} \end{array} \right.$$

* Cation occupancy in a normal 2-3 spinel obeys the Verwey-Heilmann principle of *maximal charge neutralization* [14], while in an inverse 2-3 spinel, this principle is defied. The Verwey-Heilmann principle states that if neutralization of charge is to be sharply localized around cations, then cations of high valence will have large coordination numbers, so as to be neutralized efficiently by numerous anions in the first coordination shell. But high valence cations generally possess small ionic radii and so, according to Pauling's first rule, they may be sufficiently small so as to "rattle" in their confining interstices within a close-packed arrangement of anions [16]. [Pauling's first rule is quantified in terms of a maximum radius ratio, R_A/R_X , between cation A and anion X, below which a cation would "rattle" in its site.]. The consequence of Pauling's first rule is that as cation valence increases, small interstices and small coordination numbers are preferable. The propensity for cation disordering observed in spinel may be a consequence of the struggle between these two counter purposes.

where X^{2+} and Y^{3+} are divalent and trivalent cations, respectively. The quantity in parentheses represents the average occupancy of A-sites (coordination IV), while the quantity in brackets represents the average occupancy of B-sites (coordination VI). The variable i is the so-called *inversion parameter*, which specifies the fraction of A-sites occupied by trivalent ions. Naturally-grown magnesium aluminate spinels exhibit approximately the normal spinel structure, so that $i \sim 0$; the same samples annealed at elevated temperature for a few minutes suffer cation inversion as high as $i = 0.3$ [17]. It has been demonstrated that synthetic magnesium aluminate is always partly inverse (e.g. [18]); inversion values from about 0.1 - 0.6 have been observed, the latter representing a nearly random cation arrangement [19, 20]. By comparison, in magnesioferrite, i is about 0.9 in the most highly ordered material (i.e. nearly inverse), but can deviate with thermal treatment to about 0.72, once again to a near random configuration (e.g. [21]). The degree of inversion i has been measured in magnesium aluminate using infrared absorption [22, 23], nuclear magnetic resonance (NMR) [24, 25], magic angle spinning NMR [26, 27], electron spin/paramagnetic resonance (ESR; EPR) [17, 20], and neutron diffraction [1, 19, 28]. In other spinel compounds such as the ferrites, a host of additional techniques are applicable to the determination of i , including electrical conductivity [29], thermopower (e.g., [30]), magnetometry (e.g., [31, 32]), X-ray diffraction (e.g., [21, 33]), and Mössbauer spectroscopy (e.g., [21]).

In the case of magnesio aluminate spinel, the crystal structure can accommodate large deviations in stoichiometry. Alumina addition to $MgAl_2O_4$ represents substitution of higher average valency on cation lattice sites. This additional positive charge can be compensated by creation of oxygen interstitials, valence reduction of matrix cations, or introduction of cation vacancies. Experiments indicate that the latter occurs in spinel [34]. In fact, a solid solution exists between two compounds: $MgAl_2O_4$ and $\gamma-Al_2O_3$, where gamma alumina is characterized as a cubic spinel with one-ninth of the cation sites vacant [35].

In principle, charge compensation in Al-excess spinel can be accomplished by the introduction of cation vacancies on tetrahedral sites (V_A''), on octahedral sites (V_B'''), or both. Relative to a normal spinel structure, vacancies in Al-excess spinel are created by one of the two following reactions:

Experiments indicate that vacancies in spinel are distributed on octahedral sites [36]. However, cation inversion complicates the interpretation of experimental measurements; so, uncertainty remains as to the vacancy distribution in non-stoichiometric spinel [37].

The oxygen sublattice also influences the ultimate atomic structure of spinel compounds. The oxygen sublattice arrangement provides additional, indirect evidence for the arrangement of cations in spinel crystals; this evidence is obtained from determination of the oxygen parameter, u . The following discussion refers to the schematic diagram in Figure I.2. Fig. I.2 shows two interpenetrating tetrahedra that make up the basic structural unit in the spinel crystal lattice. One tetrahedron consists of an A-site cation coordinated by four oxygen anions. The second tetrahedron consists of an oxygen anion, coordinated by one A-site and three B-site cations.

The oxygen parameter arises because, in real spinel crystals, the oxygen lattice is not 'perfect ccp.' This is partly attributable to the fact that each divalent cation (Mg^{2+}) in the lattice is too large to fit into one of the comparatively small tetrahedral A interstices; consequently the surrounding O^{2-} ions expand outwards by equal displacements along the body diagonals of the cube. If this dilatation did not take place, the bond length between an O^{2-} anion and an A-site cation would be precisely $1/8$ of the body-diagonal of the unit cell, i.e. $0.125 \cdot \sqrt{3} a_0$, where a_0 is the lattice parameter. In crystal structure refinements of MgAl_2O_4 , a significant oxygen dilatation is always observed [38]. This dilatation is usually reported in terms of the oxygen parameter, u : u is the fraction of the cubic unit cell edge defining the position of the oxygen ion at fractional coordinates u, u, u . For 'perfect ccp' oxygen packing, $u = 0.375$ for unit cell origin at $\bar{4}3m$; $u = 0.250$ for unit cell origin at $\bar{3}m$. Wyckoff [38] reports $u(\bar{4}3m) = 0.387$ or $u(\bar{3}m) = 0.262$ for natural MgAl_2O_4 . This represents an O-to-A-site bond length of $0.137 \cdot \sqrt{3} a_0$.

Now, consider the case in which a divalent Mg^{2+} ion exchanges places with a trivalent Al^{3+} ion. This positions a much smaller cation in the A interstice than before ($r_{\text{Al}^{3+}}^{\text{IV}} = 0.039$ nm; $r_{\text{Mg}^{2+}}^{\text{IV}} = 0.049$ nm; Table I.1). This, in turn, should relax the dilatation previously imposed on the surrounding oxygen ions. If, by irradiation for instance, one induces a significant number of $\text{Mg}^{2+}/\text{Al}^{3+}$ site exchanges within the crystal lattice, the O-to-A-site bond length should relax toward the 'perfect CCP' value of $0.125 \cdot \sqrt{3} a_0$. This is precisely what we found in a neutron diffraction study of neutron irradiated spinel single crystals [2]. Figure I.3 shows crystal structure refinement results for the O-to-A-site bond length and the oxygen parameter u for all of the spinel crystals measured in our previous study [2]. It is clear that the O-to-A-site bond length and u shift toward their 'perfect ccp' values after neutron

exposure. It should be noted that our structure refinements also indicated that the cations in the spinel crystals were nearly fully disordered following neutron irradiation. The data indicated that changes in the oxygen parameter apparently saturates with neutron fluence. For instance, both the 53 and 249 *dpa* (displacements per atom, a measure of dose) samples irradiated at ~670K show the same value for the O-to-A-site bond length ($0.1330 \cdot \sqrt{3} a_0$). These results indicate that Mg^{2+} ions increasingly occupy *B*-sites and Al^{3+} ions increasingly occupy *A*-sites as irradiation progresses.

The following treatment of spinel cation site occupancy in terms of cation inversion and non-stoichiometry and the associated diffraction effects follows roughly the procedures described by Dupree et al. [36] and Ibarra et al. [37].

It is a simple matter to show that for stoichiometric spinel and in the absence of short-range ordering effects, the normalized, average scattering powers for *A*- and *B*-sites are given by:

$$\begin{aligned} \hat{f}_A &= \frac{b_{\text{Mg}} - i(b_{\text{Mg}} - b_{\text{Al}})}{b_{\text{Mg}}} & \hat{f}_B &= \frac{b_{\text{Al}} + \frac{i}{2}(b_{\text{Mg}} - b_{\text{Al}})}{b_{\text{Al}}} \end{aligned} \quad \begin{matrix} \text{(a)} \\ \text{(b)} \end{matrix} \quad (\text{I.2})$$

In Eqn. (I.2), the *A*-site (8(a)) scattering power, $\hat{f}_A$, is normalized by the average coherent neutron scattering length for magnesium, $b_{\text{Mg}} = 5.375$ fm. Similarly, the scattering power $\hat{f}_B$ for the *B*-site (16(b)) is normalized by $b_{\text{Al}} = 3.449$ fm, the coherent neutron scattering length for aluminum, while $\hat{f}_O$ for the oxygen-site (32(e)) is normalized by $b_O = 5.805$ fm, the average coherent neutron scattering length for oxygen. Coherent neutron scattering lengths (which are analogous to the atomic form factors f in X-ray scattering) were obtained from Koester *et al.* [39].

Now consider a general spinel consisting of both cation inversion and non-stoichiometry. For Al-excess given by x , there will be n units of $\text{MgO} \cdot x \text{Al}_2\text{O}_3$ per unit cell. Based on a unit cell consisting of 32 oxygen ions in a *CCP* array, it is apparent that the relationship between n and x is:

$$n = \frac{32}{3x+1} \quad (\text{I.3})$$

where n is equivalent to the number of Mg atoms per unit cell. Now, the most general formula for the stoichiometry of a spinel unit cell is given by:

Here, the quantity in parentheses represents the occupancy of A-sites in the unit cell (the sum of these terms equals 8), while the quantity in brackets represents the occupancy of B-sites (the sum of these terms equals 16). Quantities Al_A and Al_A represent an imaginary distinction between the numbers of Al atoms on A-sites due to cation inversion and those on A-sites due to non-stoichiometry, respectively. Though this distinction is an artificial one, it serves a useful purpose in defining inversion in a non-stoichiometric spinel. Quantity Mg_B represents the number of Mg atoms in the unit cell on B-sites due to cation inversion.

Based on the definition of cation inversion, it is apparent that:

$$Al_A = Mg_B \quad (I.4)$$

and the total number of Mg atoms per unit cell is given by:

$$Mg_A + Mg_B = n \quad (I.5)$$

and that:

$$n = Mg_A + Al_A \quad (I.6)$$

The remaining $8 - n$ A-sites are filled by excess Al atoms and their associated charge-compensating vacancies.

At this point, it is useful to redefine the inversion parameter, i . Let i represent not the fraction of *all* A-sites occupied by Al atoms, but the fraction of the n A-sites occupied by Al atoms that are not involved in non-stoichiometry. In other words,

$$i \equiv \frac{Al_A}{n} = \frac{Mg_B}{n} = \frac{Mg_B}{Mg_A + Mg_B} \quad (I.7)$$

By Eqn. (I.7), $Al_A = n i$ Al atoms in the unit cell occupy A-sites by consequence of cation inversion. The remaining $2 n x - n i$ Al atoms in the unit cell occupy A- and B-sites according to three possible schemes for the distribution of vacancies:

Vacancy Scheme (1): All vacancies reside on B-sites.

Vacancy Scheme (2): Vacancies are distributed at random over A- and B-sites.

Vacancy Scheme (3): All vacancies reside on A-sites.

It is straightforward to introduce non-stoichiometry into the calculation of scattering powers, to obtain $\hat{f}_A$ and $\hat{f}_B$ as a function of inversion i and the non-stoichiometry coefficient x . One finds:

$$\hat{f}_A = \frac{32(1-i)b_{Mg} + 64x\left(\frac{r}{1+r}\right)b_{Al}}{8(3x+1)b_{Mg}} \quad (a) \quad \hat{f}_B = \frac{32ib_{Mg} + 64x\left(\frac{1}{1+r}\right)b_{Al}}{16(3x+1)b_{Al}} \quad (b) \quad (I.8)$$

where r , the ratio of Al atoms on A-sites to Al atoms on B-sites is dependent on the vacancy distribution schemes defined above:

$$\begin{aligned} \text{Vacancy Scheme (1) : } r &= \frac{3(x-1) + 4i}{5x + 3 - 4i} \\ \text{Vacancy Scheme (2) : } r &= \frac{3x(x-1) + (3x+1)i - 2i^2}{2x(3x+1) - 7xi - i + 2i^2} \\ \text{Vacancy Scheme (3) : } r &= \frac{x-1+2i}{3x+1-2i} \end{aligned} \quad (I.9)$$

Substituting an expression for r from Eqn. (I.9) for a given vacancy scheme into Eqns. (I.8), two equations are obtained which can be solved for two unknowns x and i . The value of x is independent of the vacancy scheme (as it must be), and is given by:

$$x = \frac{(4 - \hat{f}_A)b_{Mg} - 2\hat{f}_B b_{Al}}{3\hat{f}_A b_{Mg} - 2(4 - 3\hat{f}_B)b_{Al}} \quad (I.10)$$

On the other hand, the cation disorder parameter, i , does depend on the vacancy scheme through the ratio r , so that in these calculations, three different values for i are obtained, depending on choice of vacancy scheme. In a fully-unconstrained crystal structure refinement, the procedure is: (1) determine $\hat{f}_A$ and $\hat{f}_B$ by refinement; (2) calculate x using Eqn. (I.10); (3) substitute for $\hat{f}_A$, $\hat{f}_B$, and x in Eqns. I.8 and I.9, to determine the inversion i for a specific vacancy distribution scheme.

The purpose of the experiments described here is to determine which, if any, of the vacancy schemes described in Eqn. (I.9) is operative in magnesium aluminate spinel-structured compounds. Our neutron diffraction experiments are intended to solve this long-standing puzzle, a subject of considerable debate in the literature for several decades.

1.2 Experimental

Equimolar spinel single crystals ($MgO \cdot xAl_2O_3$) with $x \cong 1$, were obtained from Union Carbide Corporation, San Diego, CA, USA. The crystals were cut into cylindrical pellets from transparent, 2 cm long boules, with [001] growth direction. Pellets were approximately 5 mm in diameter and 2-3 mm in height. Non-equimolar spinel single crystals with

$3.55 \geq x \geq 2.8$ were obtained from Dr. Angel Ibarra of Ciemat, Madrid, Spain. These pellets were approximately 10 mm in diameter and 1 mm thick.

The stoichiometries and the major impurities of most of the non-stoichiometric spinel samples (Table I.2) were determined either by electron-beam microprobe (EMP) or X-ray fluorescence (XRF) analyses. Single crystals which were found to be unsuitable for single crystal diffraction were pulverized and investigated by powder diffraction techniques. The single crystal volumes ranged from 7.8 to 30.5 mm³ and the amount of the powder samples ranged from 0.215 g to 2.05 g. A small piece from the Ibarra 7 crystal was cut out and analyzed by single crystal X-ray diffraction measurements. Since the X-ray atomic form factors of Mg⁺² and Al⁺³ are nearly equal, the measured octahedral and tetrahedral site occupancies tend to indicate the vacancy distribution regardless of the degree of cation disorder. Time-of-flight neutron diffraction data were collected at room temperature using the LANSCE single crystal diffractometer (SCD) and the LANSCE high intensity powder diffractometer (HIPD). At LANSCE, neutrons are produced by a spallation reaction when 250 nsec long pulses of 800 MeV protons hit a tungsten target at a repetition rate of 20 Hz. The SCD sample position was located 7.5 m from a 10°C chilled water moderator. The 2 θ angle was 90° to the center of the detector and the detector was rotated 45° out of the horizontal plane. The adjustable sample to detector distance was 26.5 cm. Neutron wavelengths were determined by their flight times from the moderator to the detector with a resolution of about 1%. A wavelength range of 0.5 Å to 8 Å was used. Two rotation axes allowed adjustment of the sample orientation and four to five settings were typically needed to collect a unique data set. Counting times were 4 to 8 hours at each crystal orientation. The HIPD chilled water moderator to sample distance was 9.1 m. From the eight detector banks available, only the four banks with the highest resolution ($\pm 90^\circ$ and $\pm 153^\circ$) were used. Their sample to detector distances were 1.02 m and 1.25 m, respectively. The d-spacing range and resolution for the $\pm 90^\circ$ banks are 0.4 Å to 6.65 Å and 0.5%, respectively; the d-spacing range and resolution for the $\pm 153^\circ$ detectors are 0.25 Å to 4.75 Å and 0.3%, respectively. The powder samples were encapsulated in thin walled vanadium cans.

Data reduction and structure refinements were performed using the General Structure Analysis System (GSAS) [40].

For the single crystal analysis, the integrated intensities were obtained to a minimum d -spacing of 0.38 Å, using the refined lattice constant and crystal orientation to calculate the position of all Bragg peaks. The integrated intensities were corrected for background,

incident spectrum, detector efficiency and the Lorentz factor. Absorption corrections were made but were less than 2%.

Two different Rietveld structure refinement strategies were applied:

strategy 1: refinement *without* constraints on stoichiometry and temperature factors

strategy 2: refinement *with* constrained stoichiometries and temperature factors

In strategy 1, experimental normalized scattering powers, $\hat{f}_A$ and $\hat{f}_B$ for A- and B-sites, respectively, are refined from the neutron diffraction data. Then, the stoichiometry x is determined from Eqn. (I.10), and finally, the cation inversion i is determined by substitution of $\hat{f}_A$, $\hat{f}_B$, and x into Eqns. I.8 and I.9 (following selection of a vacancy scheme in Eqn. I.9). The refined stoichiometry may then be compared to the analytically-measured x , based on EMP or XRF measurements, to evaluate the 'quality' of the refinement result. Likewise, the calculated i values can be compared between each vacancy scheme, to assess their physical relevance (for instance, negative values for i are not permissible).

In strategy 2, the stoichiometry x , based on an EMP or XRF measurement, is imposed as a refinement constraint. A vacancy scheme is selected (Eqn. I.9) and incorporated directly into the constraints of the refinement. The normalized occupancies of A-sites by Mg and Al (i.e., $\hat{Mg}_A$ and $\hat{Al}_A = \hat{Al}_A/8$), and of B-sites by Mg and Al ($\hat{Mg}_B$ and $\hat{Al}_B$), are individually refined until the calculated scattering powers, $\hat{f}_A$ and $\hat{f}_B$ of A- and B-sites, best-fit the experimentally measured values.** The cation inversion i is then calculated using Eqn. I.7, based on the refined value for $\hat{Mg}_B$ (n is determined from the experimentally obtained stoichiometry x , using Eqn. I.3). As was the case using strategy 1, the calculated i values can be compared between each vacancy scheme, to assess their physical relevance (again, negative values for i are not permissible). If stoichiometry values based on EMP and XRF measurements are reliable, then in principle, strategies 1 and 2 should yield identical results for a given vacancy scheme.

I.3 Results and Discussion

The refinement results from single crystal neutron diffraction experiments are listed in Table I.3 and include refinement residuals, lattice parameters, oxygen coordinate u in the unit cell, site occupancies as normalized scattering powers for A- and B-sites, isotropic temperature

** A-site occupancies are normalized by 8, the number of 8a sites in the unit cell (i.e. $\hat{Al}_A = Al_A/8$, $\hat{Al}_A = Al_A/8$, and $\hat{Mg}_A = Mg_A/8$). Likewise, B-site occupancies are normalized by 16, the number of 16d sites per unit cell (i.e. $\hat{Al}_B = Al_B/16$ and $\hat{Mg}_B = Mg_B/16$).

factors, as well as calculated values for the cation disordering and the stoichiometry, upon application of strategy 1. The unweighted refinement residual, R , and the weighted refinement residual, R_w , are defined in GSAS [40] as:

$$R = \frac{\sum |F_{obs}^2 - F_{calc}^2|}{\sum |F_{obs}^2|} \quad \text{and} \quad R_w = \frac{\sum w (F_{obs} - F_{calc})^2}{\sum w |F_{obs}|^2} \quad (\text{I.11})$$

The refinement residues define the agreement of the calculated intensities assumed by a structure model and the measured intensities. For the single crystal neutron diffraction data the refinement residues R_w and R were in the range between 4.7 to 7.7 % and 4.0 to 7.6 %, respectively.

With increasing hyper-stoichiometry, x , the lattice parameter decreases, due to an increase of the total vacancy concentration in the structure. Furthermore, the oxygen parameter, u , in the unit cell decreases. This relaxation of the oxygen sublattice by decreasing u from 0.263 to 0.258, produces an oxygen arrangement which is closer to the perfect cubic closed packing, compared to the pure stoichiometric case.

Based on these calculations using strategy 1, results in Table I.3 indicate that cation vacancies in hyperstoichiometric spinel most likely reside on octahedral B -sites. If a random or tetrahedral vacancy scheme is assumed, refinements yield physically impossible negative values for the inversion parameter i in the non-equimolar spinel samples (Ibarra 7 and Japan-95). But in the case of the octahedral vacancy scheme, the Ibarra 7 sample yielded a reasonable value for cation inversion, ~19%, as well as a stoichiometry of $x=3.1$, close to the experimentally measured value of $x=3.2$. On the other hand, calculation of the stoichiometry of the Japan-95 single crystal seems to have failed ($x=6.4$ by refinement versus the experimental $x=3.0$), while the calculated cation inversion in this sample is only 1%, rather unrealistic considering this is a synthetic crystal. It should be mentioned that the refinement of site occupancies result in quite large standard derivations, so that uncertainties in the calculated cation disorder values are likewise large.

The refinement results of the neutron powder diffraction experiments based on strategy 1 are listed in Tables I.4a and I.4b. The tables include the individual use of histograms, refinement residuals, lattice parameter, oxygen coordinate, site occupancies, isotropic temperature factors, as well as values for cation disordering and stoichiometry. The unweighted refinement residual, R_p , and the weighted refinement residual, R_{wp} , are used as defined in GSAS [40] as:

$$R_p = \frac{\sum |I_{obs} - I_{calc}|}{\sum I_{obs}} \quad \text{and} \quad R_{wp} = \frac{\sum w (I_{obs} - I_{calc})^2}{\sum w I_{obs}^2} \quad (I.12)$$

Although the unconstrained refinements of the hyper-stoichiometric spinel powder diffraction data result in good, as indicated by small refinement residuals (R_{wp} = 3.2 to 5.4 % and R_p = 2.2 to 4.0 %), interpretation of the results in terms of a cation vacancy model is not unambiguous. The results of these unconstrained refinements approximately confirm the single crystal result, i.e., in hyper-stoichiometric spinel, cation vacancies are most likely confined to octahedral *B*-sites, compared to a random *A-B*-distribution, and a vacancy distribution confined to tetrahedral *A*-sites is likely never realized. This is apparent mostly by observing that only in the case of a *B*-site only vacancy distribution, are positive inversion parameters (*i*) obtained in all refinements. But unfortunately, the quantitative results depend on the size the individual sample and on the number of measured histograms ($\pm 90^\circ$, $\pm 153^\circ$, or all four histograms) used in the refinements. Increasing both the sample size and the number of histograms included did not improve the 'quality' of the results. For example, if only histograms from the $\pm 153^\circ$ TOF detectors banks were used, the results were in all cases closer to expectation than when using all four detector bank histograms. Furthermore, in nearly all calculations of stoichiometry, the calculated Al_2O_3 content was usually excessive compared to analytical measurements.

Refinements were also performed using strategy 2, based on the same neutron powder diffraction data used to obtain Tables I.4a and I.4b. These refinements with constrained stoichiometries and temperature factors are shown in Tables I.5a and I.5b. This calculation strategy produced similar refinement residues (R_{wp} = 5.3 to 3.1 %, R_p = 3.9 to 2.2 %), compared to the unconstrained refinement. In these constrained refinements, a considerable increase in the standard derivations associated with site occupancy results was found, though the 'quality' of the results became more reasonable. Once again, the octahedral *B*-site cation vacancy model resulted in the best, i.e., most physically reasonable results.

In addition to the cation vacancy distribution in hyperstoichiometric spinel samples, it is also interesting to consider refinement results regarding variations in the lattice parameter, *a*, and the oxygen parameter, *u*, with change in stoichiometry (*x*). Figure I.4a shows the dependence of the lattice parameter *a* on hyper-stoichiometry, *x*, and Figure I.4b the dependence of the oxygen parameter *u* on *x*, for all the refinements presented here. A decrease in lattice parameter with increasing hyper-stoichiometry was confirmed, even though refinements were performed without use of an internal standard. To obtain small refinement residuals, it was necessary to make changes in diffractometer constants; this may have caused slight shifts in

refined lattice parameter values. All results produced here, using either single crystal or powder data, and using refinement strategy 1 or strategy 2, validate a similar relationship between the oxygen parameter and the lattice parameter as a function of non-stoichiometry (despite the uncertainties associated with a predominant vacancy model). In Figure I.4a, a significant decrease in the lattice parameter with increasing hyper-stoichiometry is shown. Progressing across the pseudo-binary solid solution system $\text{MgO} \cdot x\text{Al}_2\text{O}_3$ towards $\gamma\text{-Al}_2\text{O}_3$, from $x=1$ to $x=3.55$, this 3 % decrease in the occupancy of the structural site positions, results in a 5 % decrease in the unit cell volume.

In Figure I.4b, it is apparent that the oxygen coordinate is strongly effected by non-stoichiometry. With increasing hyper-stoichiometry, the oxygen parameter decreases significantly, from $u=0.262(1)$ for stoichiometric spinel to between $u=0.2576(1)$ to $u=0.2581(1)$ for $x=3.55$, depending on the refinement strategy and the use of histograms. In stoichiometric, normal, ordered spinel, the oxygen sub-lattice is forced to expand along the body diagonals of the cubic unit cell. With increasing hyper-stoichiometry, the oxygen sub-lattice relaxes toward the ideal cubic close-packing, as smaller Al^{3+} ions assume positions in tetrahedral intersites previously occupied by larger Mg^{2+} ions. Similarly, for equimolar spinel (as discussed earlier), an increase in cation disorder also leads to a decrease in oxygen parameter u . Indeed, the chromium-doped, natural single crystal (Cr-doped) exhibited the largest oxygen parameter in this study, $u=0.2635(1)$, compared to the other stoichiometric but disordered crystals. In this study, the oxygen parameter was found to decrease from $u=0.2626(1)$ for 15(5) % cation disordering to $u=0.2622(1)$ for 26(6) % cation disordering.

I.4 Summary

Cation disorder and the site distribution of charge-compensating vacancies in equimolar and hyper-stoichiometric Mg-Al-spinel structures were determined by neutron diffraction and least squares crystal structure refinement. For equimolar spinel, cation inversion (i) values obtained from synthetic spinel samples ranged from 15(5) % to 26(6) %. These values are typical for synthetic spinel. Natural chromium-doped spinel exhibited an ordered (normal) structure (standard deviation = $\pm 5\%$ _{abs}). In hyper-stoichiometric spinel samples, vacancies were found to be most likely distributed exclusively on octahedral B -sites. This conclusion is not without uncertainty, however, due to significant statistical fluctuations in the refinement results. One possible source of error is that during sample synthesis, microstructural domains with different stoichiometries develop. Also, use of unconstrained refinements resulted in significant systematic errors, and calculated stoichiometries were always shifted toward excessive Al_2O_3 contents, thus predicting structures whose densities are too low. In the

present study, we have clearly reached the limit of what Rietveld structure refinement is able to handle. Introducing non-stoichiometry and site vacancies in crystal structures should request the right setup of constraints. Despite the uncertainties, both unconstrained and constrained refinement strategies indicate that charge compensating vacancies in hyperstoichiometric Mg-Al-spinel most likely reside on octahedral *B*-sites.

II. NEXAFS and EXAFS Studies of Xe-Ion Irradiated Spinel (MgAl_2O_4) Single Crystals

X-ray absorption measurements (XAS) were performed on Xe-irradiated MgAl_2O_4 spinels at the Stanford Synchrotron Radiation Laboratory. The X-ray absorption spectra from both the Al and Mg K-edges (1566 and 1310 eV, respectively) were collected at BL 3-3. BL 3-3 utilizes a double crystal monochromator. This beam line supplies a flux of about 10^9 photons/s•100 mA, over an area of 1.5 x 2.5 mm and over an energy range 1150 – 2200 eV with resolution ~0.4 eV. In order to collect data from both absorption edges, we used YB₆₆(400) crystals in the monochromator. This allowed us to scan an energy range of 1150-2000 eV, covering both absorption edges with a resolution of approximately 0.6 eV. The analysis chamber used for these measurements consisted of a load-lock sample transfer system, a channeltron for partial-electron yield measurements, and an 15 x 22 mm AXUV-300M Photodiode (International Radiation Detectors) with a 1 μm Al shield for fluorescence yield measurements. The base pressure of the analysis chamber was 8×10^{-8} torr. A diamond window was utilized to protect the beam line vacuum from the high pressures in the experimental chamber. A removable Si mirror was available to cut off higher energy photons. XAS measurements were performed on many spinel samples that had undergone Xe irradiations over a range of fluences from 10^{-14} to 10^{-16} Xe/cm².

Near-Edge, X-ray Absorption Fine Structure (NEXAFS) spectra obtained from the Mg K-edge and the Al K-edge of spinel crystals, as a function of Xe ion implantation dose, are shown in Figures II.1a and II.1b, respectively. The NEXAFS results clearly indicate changes in absorption as a function of Xe dose. In the case of the Mg K-edge (Fig. II.1a), upon irradiation there is a loss of intensity in the peak at 1320 eV. This feature has essentially been removed by the time that the dose had reached 2.5×10^{15} Xe/cm². The feature at 1310 eV initially decreases as well, but then at a dose of 2.5×10^{15} Xe/cm² it begins to increase in intensity. Also, at this same dose a small peak at 1308 eV was observed.

The NEXAFS on the Al K-edge (Fig. II.1b) shows significant changes as a function of Xe dose. The sharp feature at 1592 eV broadens significantly and maybe more importantly shifts to lower energy. Another important changes occurs in the two peaks at 1570 and 1575 eV.

The ratio of I_{1570}/I_{1575} continuously increases as the dose is increased. Again at a dose of 2.5×10^{15} Xe/cm², a small shoulder appears at low photon energies, in this case at 1565 eV.

Theoretical electronic structure calculations are being performed to try to understand these changes. Calculations for unirradiated spinel crystals have been completed, and are shown in Figure II.2 along with unirradiated experimental NEXAFS spectra from Fig. II.1. The experimental NEXAFS measurements from the unirradiated spinel has been compared to the p-projected density of unoccupied states (DOS). The Mg K-edge NEXAFS spectrum (Fig. II.2a) is in excellent agreement with the calculated DOS. The Mg absorption shows three distinct peaks over the photon energy range of 1310 to 1320 eV. The calculated DOS has three clusters of states located at exactly the same energies where absorption features are observed experimentally. The excellent agreement with theory is repeated in the case of the Al K-edge (Fig. II.2b). In the Al K-edge NEXAFS spectrum, four peaks were observed over the photon energy range of 1565 to 1580 eV. The calculated DOS accurately predicts these features, including the small dip between the peaks at 1573 and 1575 eV. This agreement clearly validates the theoretical methods used in the calculation. We believe that we will be able to develop a model of disorder that accurately predicts the observed changes. The first calculations on the disordered surface predict the growth of the low energy component observed as the DOS increases at lower energies. These calculations are discussed in more detail in Section III of this report.

III. First Principles Calculations Of Electronic Structures In Spinel Compounds

The spinel structure is found in materials displaying a wide variety of interesting behavior. This work is motivated by the resistance to radiation damage displayed by MgAl_2O_4 . Our premise is that low lying structural excitations to structures characterized by disorder on the cation sublattice are responsible for the stability of spinel. We want to study the energetics of disordering in the spinel structure, and our approach to this problem is to study trends between materials. Spinel containing transition metal ions (*e.g.* MgCr_2O_4) are likely to be dominated by hybridization between oxygen *p* states and metal *d* states and possible localization of the metal *d* -shell. These spinels will be the subject of another investigation. It seems likely that different, and simpler, considerations determine the stability of MgAl_2O_4 . We have therefore studied MgAl_2O_4 as a component of the set of spinels MgX_2O_4 , with X taken from the Al column. Specifically, we study the spinels MgAl_2O_4 , MgGa_2O_4 , and MgIn_2O_4 through *ab-initio* electronic structure calculations by calculating the energy of each of the materials for different internal geometry. Disorder in unit cell orientation may play a role in the properties of spinel-structure oxides but is not considered here. The energy is

minimized with respect to all internal coordinates using all electron force calculations. Our principle results are that 1) *the stability of disordered (inverse) structures increases with the size of octahedral ion*, 2) *the distortions that favor disorder are driven by electrostatic energy and charge transfer, rather than electronic energy*. Structures and structural distortions are described below, together with an analysis of structural stability. Band structure and a comparison with NEXAFS and PEELS data are also discussed.

III.1 Calculation

The electronic structure calculations in this investigation are based on Density Functional Theory (DFT) [41] using the Local Density Approximation (LDA) for exchange and correlation. The exchange-correlation function used was that of Hedin and Lundqvist [42] with parameters calculated in the Random Phase Approximation (RPA) [43]. The calculations were performed with an all-electron, full-potential electronic structure method developed at LANL [44] that uses Linear Muffin-Tin Orbitals (LMTO's) [45, 46] as basis functions. Valence basis functions in this method are numerical, atomic-like functions within non-overlapping spheres (muffin-tins) centered on atom positions, and Hankel or Neuman functions in the interstitial region between spheres. Different bases may use the same muffin-tin functions but different interstitial kinetic energies in order to obtain a good representation of the eigenfunctions in the interstitial. Also, in this method, different bases may use muffin-tin functions corresponding to different atomic principal quantum numbers but having the same orbital parameters. This is an important capability for all-electron oxide calculations, in which it is essential to include high level core states. All valence bases comprise a single, fully hybridizing basis set. This method does not use separate "energy panels" as other muffin-tin based methods do. Hence, basis functions may be labeled by *site:(nL)(multiplicity)* where *n* designates the atomic principle quantum number corresponding to muffin tin functions, *L* is the principle orbital parameter, and "multiplicity" denotes the number bases with the same *site:(nL)*, but different interstitial functions. The label *valence* may denote as many of the electronic states as desired. Usually, states identified as deep core states within the range of volumes considered are calculated as site-centered localized states. The valence base set used in the calculations reported here included

Mg: (2s2p)(2), (3s3p)(3), and (3d)(2),

O: (2s2p)(3) and O(3d)(2),

Al: (2s2p)(2), (3s3p)(3), and (2d)(2),

Ga: $(3s3p3d)(2)$, $(4s4p)(3)$, and $(4d)(2)$,

and In: $(4s4p4d)(2)$, $(5s5p)(3)$, and $(5d)(2)$.

In the polar semiconductor GaAs, inclusion of the Ga $3d$ state is necessary in an accurate calculation. Ionization of the Ga ion in MgAl_2O_4 necessitated the inclusion of the Ga($3s3p$) states in the present calculations. The analogous statement holds for In in MgIn_2O_4 . The composition of and parameters used for the basis set were chosen by experience and experimentation to produce converged energy differences for all structures. In the normal structure, there are fourteen atoms, two formula units, per primitive cell. This cell suffices for normal and inverse, and half inverse, fully ordered structures. It may be that the local randomness in orientation which produces the average cubic structure may influence structural properties. Here we make the assumption that it does not, and test the results against experiment.

Integration over the Brillouin zone was accomplished by Fourier quadrature. The k-point grid contained 108 points in the unit cell of the reciprocal lattice. The total energy was converged to less than 0.3 mRy with this choice. Atom positions in the unit cell were calculated by minimizing the total energy using all-electron force calculations. The force calculation with this method is very similar to that described in Reference [47], though the "incomplete basis set" contribution is substantially complicated by the site-centered nature of the basis functions. The normal spinel structure (as we calculate it) has three internal degrees of freedom; the inverse structure (as we calculate it) has fourteen internal degrees of freedom. Atom positions were varied until all force components were less than 1 mRy / bohr.

III.2 Results

III.2.a Structural parameters

The conventional cell of the spinel structure has eight (four atom) fcc-like oxygen sub-cells. Each of these sub-cells can support two tetrahedrally coordinated sites or four octahedrally coordinated sites. In the *normal* structure, each of these sub-cells has either two A ions in tetrahedral sites or four B ions in octahedral sites, and a sub-cell with tetrahedral occupation is surrounded by six sub-cells with occupied octahedral sites, and *vice versa*. There has been some discussion about whether the space group of the spinel MgAl_2O_4 is $Fd\bar{3}m$ (space group 227) or the (less restrictive) $F\bar{4}3m$ (space group 216) [48-50]. The first specifies the Al (octahedral) positions and allows a single distortion parameter while the second allows a [111] like distortion of the Al positions and a separate distortion parameter for O sites

surrounding Al (octahedral) positions and the O sites surrounding Mg (tetrahedral) positions. Our calculations have been performed using the $F\bar{4}3m$ space group. Our calculated symmetry is the higher symmetry $Fd\bar{3}m$. There is no breaking of this symmetry within the accuracy stated in Table III.1.

In the *inverse* structure, the A ions are interchanged with half the B ions so that all the A ions are in octahedral sites and half the B ions are in tetrahedral sites. There are three configurations that accomplish this exchange. These configurations are degenerate and have a non-cubic symmetry lower than normal spinel (see Table 2). In a real material, these configurations occur randomly and produce the average higher symmetry structure of normal spinel. Our calculations have been performed in a hypothetical low symmetry ordered structure. The calculation results may suffer from lack of randomness; if the dominant interactions are short-ranged, however, it is reasonable to expect that the random inverse structure will be well represented by the low-symmetry ordered structure, with which it shares the same local environment. The symmetry used in the calculations was C_{2v} . Calculated structural parameters and degeneracies are given in Table III.2.

The agreement between experiment and calculation in Table III.2 provides an experimental validation for the calculational basis and cell of the normal structure. Comparison between experiment and calculation in the inverse structure is complicated by the uncertainty in the degree of inversion present in $MgIn_2O_4$. The calculated total energy and derivatives of the energy as a function of volume provide further structural parameters (equilibrium volume, bulk modulus, etc.) for comparison with experiment. Using the space group $F\bar{4}3m$, there are three internal parameters in the normal spinel structure. A full calculation would minimize the total energy with respect to all internal (and lattice) parameters at each volume. In Figure III.1, we compare such a calculation for normal $MgAl_2O_4$ with a calculation performed by calculating the internal parameters once near equilibrium and fixing these parameters at these values for all volumes. It is evident that this scheme produces energy curves accurate compared with calculated structural energy differences.

The equilibrium volume and bulk modulus calculated for $MgAl_2O_4$ is presented in Table III.3. Experimental references in Table III.3 are from Wyckoff [38].

Because there is a discrepancy between experimental and theoretical equilibrium volumes, there is an ambiguity in assessing the agreement between theoretical and experimental bulk moduli. For this reason, calculated bulk moduli are given both at the theoretical and experimental volumes.

III.2.b Structural Stability

Experimentally, MgAl_2O_4 and MgGa_2O_4 have the normal spinel structure. This statement does not preclude a small amount of cation exchange, and in fact MgGa_2O_4 has a transition to the inverse structure at about 25°C . MgIn_2O_4 is stable in the inverse structure. Using structural parameters calculated near equilibrium for each material (see the discussion preceding Figure III.1), we have calculated the energy as a function of volume in both the

normal and inverse structures for all three materials. The result is shown in Figure III.2. The calculated structures are in agreement with experiment, and the near degeneracy between normal and inverse structures is evident. To make this precise, we show in Figure III.3 the calculated difference in energy between normal and inverse structures at the experimental volume for each material. It is evident from these calculations that if MgAl_2O_4 is radiation resistant because of accessibility of its disordered states, MgGa_2O_4 should possess this resistance in greater degree. This has not yet been tested experimentally.

The importance of structural relaxation in stabilizing the observed structures is evident in Figure III.4. This figure shows the normal-inverse energy difference for all three spinels as a function of lattice constant. The wrong sign and, except for MgIn_2O_4 , the wrong trend with volume are obtained if structural relaxation is not taken into account. The trend in the unrelaxed MgIn_2O_4 values is interesting and indicative of mechanism for stabilizing the inverse structure in this series. In normal MgAl_2O_4 , relaxation is such that O ions move toward Al ions in octahedral sites, and away from Mg ions in tetrahedral sites. The mechanism for lowering the energy is electronic: bonding states decrease in energy, at the expense of electrostatic energy, lowering the total energy. In the inverse structure, higher in energy, Al ions in tetrahedral sites repel O ions, which move, in part, toward Mg ions in octahedral sites; the relaxation is such that Mg maintains an approximately equal distance from both O and tetrahedral Al ions. In this structure, *lattice relaxation gains electrostatic energy at the expense of electronic energy*. This is an uncommon mechanism. As the size of the B-cation increases, the energy gained by relaxing the oxygen octahedra decreases simply because of the size mismatch; correspondingly, the electrostatic energy gained by relaxing the lattice in the inverse structure increases due to the looseness of Mg in the octahedral cage and the potential for charge transfer.

III.2.c Electronic structure

The band structure and density of states (DOS) for both normal and inverse MgAl_2O_4 is shown in Figure III.5. The electronic energy of the lattice, a sum of energies over occupied

states, is, apart from deep core states, the area under the DOS to the start of the band gap in Figure III.5. These states are predominantly O states, the bonding part of the Al-O octahedral states. Note that the Fermi energy, the highest occupied level increases from the normal to the inverse structure. This is an indication, confirmed numerically, that the electronic energy increases on going from the normal to the inverse structure. The difference is due to the energy gained by Al in the O octahedra in the normal structure. Figure III.6 shows the band structure and DOS for MgGa_2O_4 , and Figure III.7 that for MgIn_2O_4 . On comparing these figures, it is evident that the gain in electronic energy in the normal structure decreases from the Al spinel to the In spinel.

Evident also in Figure III.5 is a peak in the conduction band (the states above the gap in these figures) DOS of the inverse structure, just above the gap. This feature is not present in the normal structure and is seen in PEELS spectra when spinel samples are irradiated (Figure III.8). This feature persists in the Ga and In spinels, Figures III.6 and III.7. We analyze the nature of this peak by considering the nature of the bands giving rise to this feature. Figure III.9 shows the DOS of inverse MgAl_2O_4 . Shaded in this figure is the contribution to the inverse DOS from electron bases centered on O sites. It is evident from this figure that this peak in the inverse DOS arises from O bands. These bands drop in energy in the inverse structure, due to the decrease in bonding/anti-bonding splitting in the inverse structure and flatten due to the decrease in Al bonds, thereby forming a peak in the DOS.

IV. Total Energy Calculations Of Point Defect Formation And Migration Energies In Magnesio Aluminate Spinel.

The energetics, structures and migration paths and energies of point defects in MgAl_2O_4 spinel were studied with shell model potentials. The properties of the hyper-stoichiometric (Al_2O_3 -rich) MgAl_2O_4 were also studied and compared with available experiments. The calculated results on vacancies, antisite defects, Frenkel defects, Schottky defects indicate that the disordering pairs of Mg^{2+} ion (replacing Al^{3+} ion) and Al^{3+} ion (replacing Mg^{2+} ion) antisites are the lowest-energy point defects (0.92 eV/defect) (Table IV.1). The disordering pairs energies are at least 1 eV more favorable than the other kinds of defects. The migration studies indicate that the Al and O ions are the easiest to migrate (Table IV.2). The studies of cell size with 8 MgAl_2O_4 formula unit indicate that the preferred defects are two Al^{3+} ions at Mg^{2+} sites and one vacancy at Mg^{2+} sites. These defects cause the system to exhibit the lowest relative energy and the smallest volume; this is consistent with available experiments [51, 52]. We have also tested other defects, but all of them produce larger volumes and less energy favorable structures. We also studied the strain fields of various kind of point defects

adjacent to an oxygen vacancy. The results indicate a 12% expansion in neighboring distance along $\sim[010]$ direction for an Al vacancy (from 1.8961Å to 2.1252Å), a 37% expansion along $[111]$ direction for a Mg vacancy (from 1.9486Å to 2.6696Å), while a 6.4% contraction along $\sim[110]$ direction for an O vacancy (from 2.4780Å to 2.3194Å). These results will help us to better understand the interaction of point defects with impurities and other structural defects.

Publications

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Table I.1. Ionic radii for tetrahedrally (IV) - coordinated Al^{3+} , Mg^{2+} , and O^{2-} ions and octahedrally (VI) - coordinated Al^{3+} and Mg^{2+} ions.

$r_{\text{Al}^{3+}}^{\text{IV}}$	$r_{\text{Mg}^{2+}}^{\text{IV}}$	$r_{\text{O}^{2-}}^{\text{IV}}$	$r_{\text{Al}^{3+}}^{\text{VI}}$	$r_{\text{Mg}^{2+}}^{\text{VI}}$
0.039 nm	0.049 nm	0.138 nm	0.053 nm	0.072 nm

Table I.2. Polycrystalline spinel samples for HIPD-measurements; spinel single crystals for SCD-measurements.

Sample description	Form	Composition x for $\text{MgO} \cdot x\text{Al}_2\text{O}_3$	Major Impurity
Ibarra 4, synthetic	Polycrystalline	3.55	50 ppm Mn
Japan 24, synthetic	Polycrystalline	3.2	not measured
Ibarra 5, synthetic	Polycrystalline	3.1	3500 ppm Mn
Ibarra 6, synthetic	Polycrystalline	2.8	2500 ppm Mn
Ibarra 7, synthetic	Single crystal	3.2	100 ppm Co
Japan_95, synthetic	Single crystal	3.0	not measured
Cr-doped, natural	Single crystal	1.0-1.1	≈ 1000 ppm Cr
MgAl_2O_4 _95, synthetic	Single crystal	1.0	not measured
MgAl_2O_4 , Clinard, synthetic	Single crystal	1.0	not measured
MgAl_2O_4 , Clinard, neutron-irradiated, synthetic	Single crystal	1.0	not measured

Table I.3. Refinement results of non-stoichiometric and stoichiometric spinel structures, $\text{MgO} \cdot x\text{Al}_2\text{O}_3$, for $3.2 \geq x \geq 1$, using single crystal neutron diffraction data (strategy 1).

Single crystal samples	Ibarra 7 $x = 3.2$	Japan-95 $x = 3.0$	Cr-doped, $x = 1-1.1$	MgAl_2O_4 , 95 $x = 1$	MgAl_2O_4 , Clinard $x = 1$	MgAl_2O_4 , Clinard n - irradiated $x = 1$
Refinement residual R_w [%], R [%]	5.7 7.6	4.7 6.7	7.7 6.4	4.9 4.0	6.5 4.7	5.7 4.5
Lattice parameter a [Å]	7.968(3)	7.970(6)	8.079(1)	8.070(1)	8.064(2)	8.077(1)
Oxygen coordinate u	0.2579(1)	0.2578(1)	0.2635(1)	0.2626(1)	0.2622(1)	0.2622(1)
Site occupancies $\langle f_A \rangle$, $\langle f_B \rangle$	0.755(16) 0.919(18)	0.712(13) 0.867(16)	1.015(14) 0.971(16)	0.947(14) 1.042(16)	0.867(16) 1.017(18)	0.898(15) 1.067(19)
Isotropic temperature factor U_{iso} for 8(a), 16(d), 32(e) [10^{-2}Å^2]	0.58(6) 0.68(6) 0.97(4)	0.65(5) 0.60(5) 1.04(4)	0.49(6) 0.34(5) 0.44(4)	0.37(5) 0.39(5) 0.57(4)	0.04(6) 0.10(7) 0.40(5)	0.23(6) 0.37(6) 0.57(5)
Inversion parameter i for B-site (B), random (R) and A-site (A) vacancy model [%]	19(14) B -3(15) R -75(20) A	1(24) B -65(28) R -240(42) A	-8(5) B -8(5) R -11(6) A	15(5) B 15(5) R 15(5) A	22(7) B 21(7) R 8(8) A	26(6) B 26(6) R 25(7) A
Calculated stoichiometry x for $\text{MgO} \cdot x\text{Al}_2\text{O}_3$	3.1(1)	6.4(4)	1.05(2)	1.00(2)	1.32(3)	1.04(3)

Table I.4a. Results of the fully unconstrained refinements of non-stoichiometric spinel structures ($\text{MgO} \cdot x\text{Al}_2\text{O}_3$, $x=2.8$) using powder neutron diffraction data (strategy 1).

Ibarra 6, $x = 2.8$	271 mg sample		412 mg sample		685 mg sample		histograms of all samples	
Used histograms	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$
Refinement residuals	4.5	3.3	4.3	3.2	4.7	3.4	4.6	3.4
R_{wp} [%], R_p [%]	3.4	2.2	3.3	2.2	4.2	2.4	3.4	2.3
Lattice parameter a [Å]	7.966(1)	7.966(2)	7.966(1)	7.966(1)	7.966(1)	7.966(1)	7.966(1)	7.966(1)
Oxygen coordinate u	0.2578(1)	0.2582(1)	0.2581(1)	0.2582(1)	0.2587(1)	0.2587(1)	0.2584(1)	0.2585(1)
Site occupancies	0.637(5)	0.681(9)	0.663(3)	0.693(5)	0.767(3)	0.806(5)	0.710(2)	0.750(4)
$\langle f_A \rangle$, $\langle f_B \rangle$	0.885(6)	0.897(9)	0.886(4)	0.895(5)	0.895(3)	0.895(5)	0.889(2)	0.896(3)
Isotropic temperature factor U_{iso} for 8(a), 16(d), 32(e) [10^{-2}Å^2]	0.19(4) 0.36(4) 0.92(1)	0.51(5) 0.49(5) 1.12(2)	0.39(3) 0.46(2) 0.92(1)	0.60(3) 0.57(3) 1.07(1)	0.53(2) 0.36(2) 0.63(1)	0.63(2) 0.39(2) 0.68(1)	0.42(2) 0.39(1) 0.76(1)	0.60(2) 0.46(2) 0.85(1)
Inversion parameter i for a B-Site (B) random (R) A-Site (A) vacancy model [%]	112(12) B 38(20) R -382(40) A	48(13) B -14(14) R -174(20) A	62(6) B -33(11) R -263(15) A	37(7) B -18(7) R -165(10) A	2(3) B -23(3) R -105(4) A	8(4) B -25(4) R -88(5) A	22(3) B -28(3) R -163(3) A	8(3) B -21(3) R -113(3) A
Calculated Stoichiometry x for $\text{MgO} \cdot x\text{Al}_2\text{O}_3$	12.0(5)	6.0(2)	8.3(2)	5.5(1)	3.40(2)	2.80(2)	5.12(2)	3.709(3)

Table I.4b. Results of the fully unconstrained refinement of non-stoichiometric spinel structures ($\text{MgO} \cdot x\text{Al}_2\text{O}_3$, $3.55 \geq x \geq 3.1$) using powder neutron diffraction data (strategy 1).

Ibarra 5, Japan-24, Ibarra 4	Ibarra 5, $x = 3.1$ 1984 mg sample		Japan-24, $x = 3.2$ 2049 mg sample		Ibarra 4, $x = 3.55$ 215 mg sample		Ibarra 4, $x = 3.55$ 1287 mg sample	
Used histograms	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$
Refinement residual R_{wp} [%], R_p [%]	3.6 2.6	3.3 2.3	5.4 4.0	4.6 3.0	4.8 3.5	3.6 2.4	4.7 3.5	3.9 2.7
Lattice parameter a [Å]	7.969(1)	7.969(1)	7.966(1)	7.966(1)	7.951(1)	7.951(1)	7.951(1)	7.951(1)
Oxygen coordinate u	0.2581(1)	0.2584(1)	0.2582(1)	0.2583(1)	0.2579(1)	0.2581(1)	0.2577(1)	0.2581(1)
Site occupancies $\langle f_A \rangle$, $\langle f_B \rangle$	0.656(4) 0.877(4)	0.710(9) 0.884(9)	0.755(3) 0.878(2)	0.784(5) 0.892(3)	0.711(7) 0.868(6)	0.751(11) 0.882(11)	0.638(4) 0.876(4)	0.658(6) 0.890(6)
Isotropic temperature factor U_{iso} for 8(a), 16(d), 32(e) [10^{-2}Å^2]	0.08(3) 0.12(3) 0.77(1)	0.54(5) 0.42(4) 0.99(2)	0.48(2) 0.35(1) 0.76(1)	0.64(3) 0.46(2) 0.84(1)	0.30(5) 0.31(4) 0.87(2)	0.57(6) 0.49(5) 1.07(2)	0.26(3) 0.28(2) 1.01(1)	0.49(4) 0.43(3) 1.21(1)
Inversion parameter i for a B-Site (B) random (R) A-Site (A) vacancy model [%]	68(10) B -59(12) R -358(12) A	18(12) B -35(13) R -179(18) A	-6(3) B -41(3) R -147(2) A	-4(3) B -27(3) R -102(3) A	3(10) B -63(11) R -238(12) A	2(12) B -36(13) R -141(16) A	112(12) B -75(24) R -496(28) A	71(11) B -24(13) R -253(19) A
Calculated stoichiometry x for $\text{MgO} \cdot x\text{Al}_2\text{O}_3$	10.5(2)	5.4(1)	4.14(2)	3.17(2)	6.37(4)	4.11(8)	14.6(4)	8.2(2)

Table I.5a. Results of the refinement of non-stoichiometric spinel structures ($\text{MgO} \cdot x\text{Al}_2\text{O}_3$, $x = 2.8$) using powder neutron diffraction data, and constraints of the stoichiometry and the temperature factors on both metal positions with a presumed vacancy model (strategy 2).

Ibarra 6, $x = 2.8$	271 mg sample		412 mg sample		685 mg sample		all samples	
Used histograms	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$
Refinement residuals	3.7	3.4	3.4	3.1	3.8	3.4	4.5	3.3
R_{wp} [%], R_p [%]	2.6	2.3	2.5	2.2	2.9	2.5	3.3	2.3
Lattice parameter a [Å]	7.972(1)	7.971(1)	7.967(1)	7.967(1)	7.969(1)	7.969(1)	7.966(1)	7.966(1)
Oxygen coordinate u	0.2575(1)	0.2580(1)	0.2579(1)	0.2581(1)	0.2587(1)	0.2588(1)	0.2583(1)	0.2585(1)
Site occupancies for B-site vacancies	0.178(10) 0.822(10)	0.256(20) 0.744(20)	0.221(6) 0.779(6)	0.280(12) 0.720(12)	0.405(7) 0.595(7)	0.498(13) 0.501(13)	0.296(5) 0.704(5)	0.354(8) 0.646(8)
$\langle f_A \text{Mg} \rangle$, $\langle f_A \text{Al} \rangle$	0.780(5)	0.820(10)	0.802(3)	0.831(6)	0.894(3)	0.941(6)	0.839(3)	0.869(4)
$\langle f_B \text{Al} \rangle$, $\langle f_B \text{Mg} \rangle$	0.124(5)	0.085(10)	0.102(3)	0.073(6)	0.010(3)	-0.037(6)	0.065(3)	0.036(4)
Site occupancies for random vacancies	0.292(10) 0.644(10)	0.371(20) 0.565(20)	0.335(6) 0.601(6)	0.394(12) 0.542(12)	0.519(7) 0.417(7)	0.613(13) 0.324(13)	0.410(5) 0.526(3)	0.469(8) 0.468(8)
$\langle f_A \text{Mg} \rangle$, $\langle f_A \text{Al} \rangle$	0.870(5)	0.909(10)	0.891(3)	0.920(6)	0.983(3)	1.030(6)	0.928(3)	0.958(4)
$\langle f_B \text{Al} \rangle$, $\langle f_B \text{Mg} \rangle$	0.067(5)	0.027(10)	0.045(3)	0.016(6)	-0.047(3)	-0.094(6)	0.008(3)	-0.022(4)
Site occupancies for A-site vacancies	0.521(10) 0.288(10)	0.599(20) 0.209(20)	0.564(6) 0.245(6)	0.623(12) 0.186(12)	0.743(7) 0.066(7)	0.807(13) 0.001(13)	0.638(5) 0.170(5)	0.697(8) 0.111(8)
$\langle f_A \text{Mg} \rangle$, $\langle f_A \text{Al} \rangle$	1.048(5)	1.087(10)	1.069(3)	1.099(6)	1.159(3)	1.191(6)	1.106(3)	1.136(4)
$\langle f_B \text{Al} \rangle$, $\langle f_B \text{Mg} \rangle$	-0.048(5)	-0.087(10)	-0.069(3)	-0.099(6)	-0.159(3)	-0.191(6)	-0.106(3)	-0.136(4)
Isotropic temperature factor U_{iso} for 8(a), 16(d), 32(e) [10^{-3}Å^2]	0.33(4) 0.49(3) 0.66(2)	0.55(6) 0.48(4) 0.87(3)	0.47(2) 0.53(1) 0.66(1)	0.60(3) 0.53(2) 0.81(1)	0.56(2) 0.30(1) 0.54(1)	0.77(3) 0.34(2) 0.71(1)	0.70(2) 0.70(1) 0.87(1)	0.63(2) 0.54(1) 0.81(1)
calculated site occupancies $\langle f_A \text{Mg} \rangle$, $\langle f_B \text{Al} \rangle$	0.705(10) 0.973(5)	0.733(20) 0.952(10)	0.721(6) 0.961(3)	0.742(12) 0.945(6)	0.787(7) 0.910(3)	0.819(13) 0.886(6)	0.748(5) 0.940(3)	0.769(8) 0.925(4)
Inversion parameter i for B-Site (B) random (R) A-Site (A) Vacancy model [%]	58(2) B 31(2) R -23(2) A	40(5) B 13(5) R -40(5) A	48(1) B 21(1) R -32(1) A	34(3) B 7(3) R -47(3) A	5(2) B -22(2) R -75(2) A	-17(3) B -44(3) R -90(3) A	31(2) B 4(2) R -50(2) A	17(2) -10(2) -64(2)
Stoichiometry x for $\text{MgO} \cdot x\text{Al}_2\text{O}_3$	2.8(2)	2.8(3)	2.8(1)	2.8(2)	2.8(1)	2.8(2)	2.80(9)	2.8(1)

Table I.5b. Results of the refinement of non-stoichiometric spinel structures ($\text{MgO} \cdot x\text{Al}_2\text{O}_3$, $3.55 \geq x \geq 3.1$) using powder neutron diffraction data, and constraints of the stoichiometry and the temperature factors on both metal positions with a presumed vacancy model (strategy 2).

Ibarra 5, Japan-24, Ibarra 4	Ibarra 5, $x = 3.1$ 1984 mg sample		Japan-24, $x = 3.2$ 2049 mg sample		Ibarra 4, $x = 3.55$ 215 mg 1287 mg		Ibarra 4, $x = 3.55$ all samples	
Used histograms	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$ $\pm 90^\circ$	$\pm 153^\circ$
Refinement residuals R_{wp} [%], R_p [%]	3.6 2.7	3.3 2.3	5.3 3.9	4.6 3.0	4.7 3.5	4.8 3.4	4.8 3.5	3.8 2.6
Lattice parameter a [Å]	7.969(1)	7.969(1)	7.966(1)	7.966(1)	7.951(1)	7.951(1)	7.951(1)	7.951(1)
Oxygen coordinate u	0.2579(1)	0.2583(1)	0.2582(1)	0.2583(1)	0.2578(1)	0.2576(1)	0.2576(1)	0.2580(1)
Site occupancies for B-site vacancies $\langle f_A\text{Mg} \rangle$, $\langle f_A\text{Al} \rangle$ $\langle f_B\text{Al} \rangle$, $\langle f_B\text{Mg} \rangle$	0.193(10) 0.807(10) 0.800(5) 0.098(5)	0.281(21) 0.719(21) 0.844(11) 0.054(11)	0.354(8) 0.646(8) 0.885(4) 0.012(4)	0.397(13) 0.603(13) 0.907(7) -0.010(7)	0.274(16) 0.726(16) 0.856(8) 0.035(8)	0.125(9) 0.875(9) 0.781(4) 0.109(4)	0.143(7) 0.857(7) 0.790(4) 0.100(4)	0.174(11) 0.826(11) 0.806(6) 0.084(6)
Site occupancies for random vacancies $\langle f_A\text{Mg} \rangle$, $\langle f_A\text{Al} \rangle$ $\langle f_B\text{Al} \rangle$, $\langle f_B\text{Mg} \rangle$	0.315(10) 0.617(10) 0.895(5) 0.037(5)	0.403(21) 0.529(21) 0.939(11) -0.007(11)	0.478(8) 0.453(8) 0.981(4) -0.050(4)	0.521(13) 0.410(13) 1.003(7) -0.072(7)	0.405(16) 0.522(16) 0.958(8) -0.031(8)	0.255(9) 0.672(9) 0.883(4) 0.044(4)	0.274(7) 0.653(7) 0.892(4) 0.035(4)	0.305(11) 0.622(11) 0.908(6) 0.019(6)
Site occupancies for A-site vacancies $\langle f_A\text{Mg} \rangle$, $\langle f_A\text{Al} \rangle$ $\langle f_B\text{Al} \rangle$, $\langle f_B\text{Mg} \rangle$	0.558(10) 0.238(10) 1.085(5) -0.085(5)	0.646(21) 0.150(21) 1.129(11) -0.129(11)	0.724(8) 0.069(8) 1.174(4) -0.174(4)	0.767(13) 0.026(13) 1.195(7) -0.195(7)	0.666(16) 0.115(16) 1.161(8) -0.161(8)	0.517(9) 0.269(4) 1.087(4) -0.087(4)	0.535(7) 0.246(7) 1.096(4) -0.096(4)	0.566(11) 0.215(11) 1.111(6) -0.111(6)
Isotropic temperature factor U_{iso} for 8(a), 16(d), 32(e) [10^{-2}Å^2]	0.17(4) 0.29(2) 0.54(2)	0.56(5) 0.51(4) 0.86(3)	0.70(2) 0.59(2) 0.93(1)	0.67(3) 0.47(2) 0.87(2)	0.64(5) 0.68(4) 1.08(3)	0.47(3) 0.60(2) 0.98(1)	0.50(2) 0.61(2) 0.99(1)	0.50(3) 0.51(2) 1.013(1)
calculated site occupancies $\langle f_A\text{Mg} \rangle$, $\langle f_B\text{Al} \rangle$	0.711(10) 0.953(5)	0.742(21) 0.928(11)	0.769(8) 0.904(4)	0.784(13) 0.891(7)	0.740(16) 0.911(8)	0.686(9) 0.951(4)	0.693(7) 0.946(4)	0.704(11) 0.937(6)
Inversion Parameter i for B-Site (B) random (R) A-Site (A) vacancy model [%]	50(3) B 19(3) R -44(3) A	28(6) B -4(6) R 66(6) A	6(2) B -26(2) R -92(2) A	-5(4) B -38(4) R -103(4) A	20(5) B -18(5) R -94(5) A	64(3) B 26(3) R -51(3) A	58(2) B 20(2) R -56(2) A	49(4) B 11(4) R -65(4) A
Stoichiometry x for $\text{MgO} \cdot x\text{Al}_2\text{O}_3$	3.1(2)	3.1(4)	3.2(2)	3.2(3)	3.55(40)	3.55(20)	3.55(20)	3.55(30)

Table III.1 The structure of normal spinel as $F\bar{4}3m$ (space group 216) together with calculated internal parameters. The calculated parameters give a higher symmetry structure, $Fd\bar{3}m$ (space group 227). Mg Ga₂O₄ is close to a transition to the inverse structure; MgIn₂O₄ is inverse.

Tetrahedral:	(4c)	000			
	(4b)	$\frac{1}{4} \frac{1}{4} \frac{1}{4}$			
Octahedral:	(16e)	xxx	$\bar{x}\bar{x}x$	$x\bar{x}\bar{x}$	$\bar{x}x\bar{x}$
Oxygen:	(16e)	$u_1 u_1 u_1$	$\bar{u}_1 \bar{u}_1 u_1$	$u_1 \bar{u}_1 \bar{u}_1$	$\bar{u}_1 u_1 \bar{u}_1$
	(16e)	$\frac{1}{4}-u_2$	$\frac{1}{4}-u_2$	$\frac{1}{4}-u_2$	$\frac{1}{4}+u_2$
		$\frac{1}{4}+u_2$	$\frac{1}{4}+u_2$	$\frac{1}{4}+u_2$	$\frac{1}{4}-u_2$
		$\frac{1}{4}-u_2$	$\frac{1}{4}+u_2$	$\frac{1}{4}+u_2$	$\frac{1}{4}-u_2$
		$\frac{1}{4}+u_2$	$\frac{1}{4}-u_2$	$\frac{1}{4}-u_2$	$\frac{1}{4}+u_2$
		x	u_1	u_2	(exp)
MgAl ₂ O ₄		-.3750	.3887	.3887	(.387 ^a)
MgGa ₂ O ₄		-.3750	.3861	.3861	(.392 ^a)
MgIn ₂ O ₄		-.3750	.3861	.3831	(.372 ^a)

Table III.2 The structure of inverse spinel together with calculated internal parameters. The imposed symmetry is $Fmm2$; the calculation finds a higher symmetry. $MgAl_2O_4$ and $MgGa_2O_4$ are stable in the normal structure; $MgGa_2O_4$ is near an inverse normal transition. $MgIn_2O_4$ is inverse.

Imposed symmetry C_{2v} ($Fmm2$):						
Tetrahedral:	(1)	$x_1, 0, 0$				
	(2)	$\frac{1}{4}-x_2, \frac{1}{4}, \frac{1}{4}$				
Octahedral:	(1)	$x_3, y_3, y_3 \quad x_3, \bar{y}_3, \bar{y}_3$				
	(2)	$\bar{x}_4, y_4, \bar{y}_4 \quad \bar{x}_4, \bar{y}_4, y_4$				
Oxygen:	(1)	$v_5, u_5, u_5 \quad v_5, \bar{u}_5, \bar{u}_5$				
	(2)	$\bar{v}_6, u_6, \bar{u}_6 \quad \bar{v}_6, \bar{u}_6, u_6$				
	(3)	$\frac{1}{4}-v_7, \frac{1}{4}-u_7, \frac{1}{4}-u_7 \quad \frac{1}{4}-v_7, \frac{1}{4}+u_7, \frac{1}{4}+u_7$				
	(4)	$\frac{1}{4}+v_8, \frac{1}{4}-u_8, \frac{1}{4}+u_8 \quad \frac{1}{4}+v_8, \frac{1}{4}+u_8, \frac{1}{4}-u_8$				
Calculated symmetry:						
$x_2 = x_1, x_3 = y_3 = x_4 = y_4 = -\frac{3}{8}, v_7 = v_5, u_7 = u_5, v_8 = v_6, u_8 = u_6$						
Tetrahedral:		$x_1, 0, 0 \quad \frac{1}{4}-x_1, \frac{1}{4}, \frac{1}{4}$				
Octahedral:	(1)	$-\frac{3}{8}, -\frac{3}{8}, -\frac{3}{8} \quad -\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$				
	(2)	$\frac{3}{8}, -\frac{3}{8}, \frac{3}{8} \quad \frac{3}{8}, \frac{3}{8}, -\frac{3}{8}$				
Oxygen:	(1)	$v_5, u_5, u_5 \quad v_5, \bar{u}_5, \bar{u}_5$				
		$\frac{1}{4}-v_5, \frac{1}{4}-u_5, \frac{1}{4}-u_5 \quad \frac{1}{4}-v_5, \frac{1}{4}+u_5, \frac{1}{4}+u_5$				
	(2)	$\bar{v}_6, u_6, \bar{u}_6 \quad \bar{v}_6, \bar{u}_6, u_6$				
		$\frac{1}{4}+v_6, \frac{1}{4}-u_6, \frac{1}{4}+u_6 \quad \frac{1}{4}+v_6, \frac{1}{4}+u_6, \frac{1}{4}-u_6$				
		x_1	v_5	v_6	u_5	$u_6 \quad (u_{exp})$
$MgAl_2O_4$		.00956	.37195	.39063	.38288	.37612 (.3887 ^a)
$MgGa_2O_4$		.00784	.37767	.38629	.38303	.37963 (.392 ^a)
$MgIn_2O_4$		.00468	.39263	.38537	.38422	.39166 (.372 ^a)

Table III.3: Calculated structural parameters for MgAl_2O_4 . V_{eq} is the calculated ($T = 0$) equilibrium volume, V_{exp} is the room temperature experimental volume, B_{eq} is the alculated bulk modulus at V_{eq} , and B_{expv} is the bulk modulus at the V_{exp} . The quantities labeled *fixed* were obtained from energy-volume curves calculated with internal parameters calculated at V_{exp} ; the quantities labeled *relaxed* were obtained from energy-volume curves calculated with internal parameters re-calculated at each volume.

	<i>fixed</i>	<i>relaxed</i>
$V_{\text{eq}}/V_{\text{exp}}$	.9841	.9830
B_{eq} (GPa)	215.5	213.1
B_{expv} (Gpa)	202.0	196.8
B_{exp} (GPa)		196 ^a
$V_{\text{eq}} = 64.77 \text{ \AA}^3$ [38]	^a Reference [38]	

Table IV.1. Point Defect Formation Energies in MgAl_2O_4 .

defect energy (eV per atom)	V_{Mg}'' 27.25	Mg_i'' -17.62 (at 16c)	Frenkel Defect Pair $V_{\text{Mg}}'' + \text{Mg}_i''$ 4.815
defect energy (eV per atom)	V_{Al}''' 58.94	Al_i''' -45.12 (at 16c)	Frenkel Defect Pair $V_{\text{Al}}''' + \text{Al}_i'''$ 6.91
defect energy (eV per atom)	V_{O}'' 20.04	O_i'' -9.20.(at 48f)	Frenkel Defect Pair $V_{\text{O}}'' + \text{O}_i''$ 5.42
defect energy (eV per atom)	Mg_{Al} 30.40	Al_{Mg}' -28.56	Antisite Defect Pair $\text{Mg}_{\text{Al}}' + \text{Al}_{\text{Mg}}'$ 0.92
defect energy (eV per atom)			Schottky Defect Septet $V_{\text{Mg}}'' + V_{\text{Al}}''' + 4V_{\text{O}}''$ 3.54

Table IV.2 Point Defect Migration Energies in MgAl_2O_4 .

Mg^{2+} Vacancy	0.34 eV
Al^{3+} Vacancy	1.87 eV
Mg^{2+} Interstitial	0.91 eV
Al^{3+} Interstitial	2.83 eV
Mg_{Al}' Antisite	1.24 eV
$\text{Al}_{\text{Mg}}^\bullet$ Antisite	0.50 eV
O^{2-} Vacancy	1.19 eV

Figure Captions

Figure I.1. Unit cell of the spinel crystal lattice. All of the atoms in the primitive unit cell are shown in the diagram. The primitive unit cell consists of two adjacent octants (shown in bold) of the cubic, conventional unit cell. Only the tetrahedral, A-site cations are shown for the other octants of the cubic unit cell. These A-site cations form a diamond cubic lattice. The choice of origin for this diagram is $\bar{4}3m$. Assuming a normal spinel structure, the $\text{Mg}_2\text{Al}_4\text{O}_8$ basis for the cubic unit cell is recognized as the 8 oxygen and 4 Al ions plus the one Mg ion within the primitive unit cell, and the $4 \cdot (1/8) + 2 \cdot (1/4) = 1$ Mg ions on the corners and edges of the primitive unit cell. For clarity, all ions are drawn much smaller than their actual radii relative to the cubic cell edge a_0 ($a_0^{\text{MgAl}_2\text{O}_4} = 0.8083 \text{ nm}$). B-site cations are drawn slightly larger than their A-site counterparts, to indicate that both Al and Mg have larger ionic radii when they are octahedrally (VI) coordinated, compared to tetrahedral (IV) coordination (see Table 1). Also shown on the diagram is the definition of the oxygen parameter, u , for the $\bar{4}3m$ origin.

Figure I.2. Schematic diagram of the fundamental structural unit in spinel: two interpenetrating tetrahedra. One tetrahedron consists of an A-site cation coordinated by four oxygen anions. The second tetrahedron consists of an oxygen anion, coordinated by one A-site and three B-site cations. All ions are drawn smaller than their actual radii. B-site cations are drawn slightly larger than their A-site counterparts, as in Fig. 1. Also shown is the Oxygen - to - A-site bond length for a 'perfect cubic close-packed' anion sublattice.

Figure I.3. Histogram showing the Oxygen to A-site bond length and oxygen parameter u (for the $\bar{4}3m$ origin) for unirradiated and irradiated spinel single crystals from Reference [2]. Values were determined from the crystal structure refinement using GSAS. 'Unirradiated 1' is an control sample belonging to the high-dose neutron irradiated crystal pellets from Reference[2]. 'Unirradiated 2' is another control sample. Also shown is the Oxygen - to - A-site bond length and u for a 'perfect cubic close-packed' anion sublattice.

Figure I.4. (a) Evolution of the lattice parameter, a , as a function of hyper-stoichiometry;
(b) evolution of the oxygen parameter, u , as a function of hyper-stoichiometry.

Figure III.1. Energy versus volume for MgAl_2O_4 in the normal spinel structure. Circles, fitted with a solid line, are energies calculated using theoretical structural parameters calculated at the experimental volume; squares, fitted with a dotted line, are energies calculated with relaxation of all internal parameters at each volume.

Figure III.2. Energy vs volume for MgAl_2O_4 (a), MgGa_2O_4 (b), and MgIn_2O_4 (c) in the normal (open circles) and fully inverse (filled circles) structures.

Figure III.3. The difference in energy between normal and inverse structures at the experimental equilibrium volume in MgX_2O_4 where $X = \text{Al, Ga, and In}$.

Figure III.4. The difference in energy between normal and inverse structures as a function of lattice constant for the spinels MgAl_2O_4 , MgGa_2O_4 , and MgIn_2O_4 . The energy difference in ideal (open circles) and structurally relaxed (filled circles) is shown.

Figure III.5. The band structure and density of states for MgAl_2O_4 . The normal structure is shown by a dotted line, the inverse structure by a solid line.

Figure III.6. The band structure and density of states for MgGa_2O_4 . The normal structure is shown by a dotted line, the inverse structure by a solid line.

Figure III.7. The band structure and density of states for MgIn_2O_4 . The normal structure is shown by a dotted line, the inverse structure by a solid line.

Figure III.8. Parallel Electron Energy Loss Spectroscopy (PEELS) spectra from magnesium aluminate spinel single crystals, obtained using a dedicated scanning transmission electron microscope. In these spectra we examine the electron loss near edge structure (ELNES) in MgAl_2O_4 . The peak just below 80 eV is at the onset of the aluminum $L_{2,3}$ absorption edge and reflects the aluminum contribution to the density of states of the conduction-band from octahedrally coordinated aluminum ions. Following neutron irradiation to a high dose, a substantial fraction of aluminum atoms in the lattice relocate from octahedral to tetrahedral sites. This relocation is manifested in PEELS analyses by an enhancement of the ELNES peak at 78 eV. In a perfectly ordered, "normal" spinel crystal, this additional ELNES peak would not exist. Quantitatively, the occupation of tetrahedral sites by aluminum atoms increases from about 20% to greater than 50% following neutron irradiation.

Figure III.9. The density of states of MgAl_2O_4 . The normal structure is shown by a dotted line, the inverse structure by a solid line. Shaded is the contribution from orthogonal states centered on O sites.

Figure I.1

The Pauling Structural Unit for MgAl_2O_4

Figure I.2

Figure I.3

Figure I.4a

Figure I.4b

Figure II.1

Figure II.2

Figure II.3

Figure II.4

Figure III.1

Figure III.2

Figure III.3

Figure III.4

Figure III.5

Figure III.6

Figure III.7

Figure III.8

Figure III.9