Examination of the site preference of metals in $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ spinel-type oxides by X-ray Absorption Near-edge Spectroscopy

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Abstract

Materials adopting the spinel-type structure have received considerable attention owing to the compositional diversity and the large number of potential applications for these materials. Although many studies of ternary spinel-type oxides have been completed, few studies have investigated quaternary materials. The $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ spinel-type system was investigated in this study by X-ray absorption near-edge spectroscopy (XANES) and powder X-ray diffraction to study how the metal-site preference changed depending on composition. The Al $L_{2,3}$ -edge XANES spectra showed that Al occupied the tetrahedral and octahedral sites when x in the chemical formula was low, and preferentially occupied the octahedral site as x increased. The Ga K-edge XANES spectra confirmed that Ga^{3+} has a strong preference for residing in the tetrahedral site and that this ion only partially occupied the octahedral sites when the concentration of Ga^{3+} in the system was sufficiently large. The Ni K-edge XANES spectra showed that Ni^{2+} has a strong preference for residing in the octahedral site, and that more Ni^{2+} was present in the tetrahedral site in NiAl_2O_4 vs. NiGa_2O_4 . Rietveld refinement of powder X-ray diffraction patterns from the ternary end members were in general agreement with these results. This study has demonstrated the utility of using XANES to investigate the site preference of Al and Ga through the examination of Al $L_{2,3}$ - and Ga K-edge spectra, respectively.

Keywords: Spinel; metal oxides; XANES; coordination number

1. Introduction

The spinel structure-type can be substituted with a wide range of elements, which is ideal for tuning the properties of new and existing materials [1,2]. For example, spinels incorporating Ni or Fe can result in magnetic materials, while spinels incorporating Zn or Al often have high band gaps and a high enough conductivity to make them suitable for optoelectronic applications [3,4]. As such, spinels are technologically relevant in areas such as high temperature catalysis, magnetic recording media, or transparent conducting oxides, as well as many other applications [4-6]. The ideal AB_2O_4 structure-type, derived from the natural spinel $MgAl_2O_4$, crystallizes in the cubic $Fd\bar{3}m$ space group with one eighth of the tetrahedral holes filled by a divalent A cation, and one quarter of the octahedral holes filled by the trivalent B cation (Figure 1) [1,2,7,8]. These materials can also be described by the inversion parameter, x [1,9]. The inversion parameter describes the amount of anti-site disorder in the system based on the fraction of trivalent ions present at the tetrahedral site [1]. In this case, the system is better described using the general chemical formula $(A_{1-x}B_x)[A_xB_{2-x}]O_4$, where the round brackets indicate the tetrahedral site and the square brackets denote the octahedral site [1]. The ideal spinel-type structure is adopted when $x = 0$, while the inverse spinel-type structure is adopted when $x = 1$, although partially inverted structures (i.e., $0 < x < 1$) are possible as well. When the inverse spinel structure-type is adopted, the B-site cation occupies all of the tetrahedral sites and half of the octahedral sites in the unit cell, with the A-site cation occupying the remaining octahedral sites.

Figure 1. The cubic crystal structure of AB_2O_4 spinel-type oxides is shown. The AO_4 tetrahedra are shown in blue while the BO_6 octahedra are grey. Oxygen anions are shown as red spheres.

While many of the ternary metal oxide spinels have been examined extensively (e.g., NiAl_2O_4), quaternary spinels involving three metals have been studied much less rigorously [1,2,7,8,10]. Given the large number of substitutions possible for the spinel structure, studying quaternary spinels provides a useful means of examining factors affecting site preference in metal oxides [10]. In particular, the competing effects of crystal field stabilization energy, cation radii, and covalency have been shown to play a significant role in determining the metal site preference in spinels [7,10,11]. This is found in the $\text{NiFe}_{2-x}\text{Cr}_x\text{O}_4$ system, where NiCr_2O_4 is a normal spinel (i.e., $(\text{Ni})[\text{Cr}_2]\text{O}_4$) while NiFe_2O_4 is an inverse spinel (i.e., $(\text{Fe})[\text{NiFe}]\text{O}_4$) [1,2,12]. While Ni^{2+} and Cr^{3+} should have the same octahedral crystal field stabilization energy, the spinel structure inverts as Cr^{3+} is exchanged for Fe^{3+} , with Ni^{2+} occupying half of the octahedral sites and Fe occupying the remaining octahedral and tetrahedral sites [11,12]. Interestingly, while the $\text{NiFe}_{2-x}\text{Cr}_x\text{O}_4$ system has been heavily studied as a corrosion product of high performance steels, no reports have been found regarding the $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ system when $0 < x < 2$ [3,12]. In the $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ system, the end members are largely inverse spinels and, as such, the substitution of Ga for Al is not expected to have a large impact on the site occupancy of Ni [1,13]. That being said, the changes in the site occupancy of Al and Ga are expected to be significant due to their very different site preferences [2,8,13,14]. While Ni^{2+} will largely stay in the octahedral sites, it should be noted that previous studies have suggested that NiAl_2O_4 should have slightly more tetrahedrally coordinated Ni^{2+} than NiGa_2O_4 [1,15].

X-ray absorption near-edge spectroscopy (XANES) has been used in this study to develop an understanding of how the coordination number (CN) of Al^{3+} , Ga^{3+} , and Ni^{2+} changes in $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ through the study of Al $L_{2,3}$ -, Ga K-, and Ni K-edge spectra. XANES is sensitive to the local electronic structure of atoms and can be used to provide information on the charge and CN of the absorbing atom. Al and Ga are peculiar in that Al^{3+} has been shown to prefer to reside in higher coordinate sites than Ga^{3+} even though the radius of Al^{3+} is significantly smaller [14,16]. The preference of Al^{3+} to adopt a 6-coordinate environment and Ga^{3+} to adopt a 4-coordinate environment in oxides is related to the covalency of the bonds that these ions form with oxygen [7]. Here, the strength of the site preference of Al^{3+} and Ga^{3+} , relative to the octahedral site preference of Ni^{2+} , has been studied in $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ by XANES. An examination of Ni K-edge XANES spectra from some members of the $\text{NiCr}_{2-x}\text{Fe}_x\text{O}_4$ system was completed to understand the changes observed in the Ni K-edge XANES spectra from

NiAl_{2-x}Ga_xO₄. Powder X-ray diffraction (XRD) was also performed to confirm the analysis of the XANES spectra. This study has not only identified how the Al³⁺ and Ga³⁺ CN changes depending on composition, but has also explicitly shown how sensitive the Al L_{2,3}-edge and Ga K-edge XANES spectra are to a change in the average CN of these ions.

2. Materials and Methods

2.1. Synthesis

NiAl_{2-x}Ga_xO₄ and NiFe_{2-x}Cr_xO₄ ($0 \leq x \leq 2$) were synthesized by the ceramic method. Stoichiometric mixtures of NiO (Alfa Aesar, 99%), α -Al₂O₃ (Sigma-Aldrich, 98%), Ga₂O₃ (Alfa Aesar, 99.99%), Fe₂O₃ (Alfa Aesar, 99.945%), and Cr₂O₃ (Alfa Aesar, 99.6%) were ground, pressed into pellets at 6 MPa, and placed into alumina crucibles. The samples were heated in air to 1200°C at 120-150°C per hour and held at this temperature for 3 days before being quench cooled in air. The samples were then ground and pelleted (as above) before being heated for another three days and then air quenched.

All samples studied were determined to be phase pure by powder X-ray diffraction using a PANalytical Empyrean system and either Co K $\alpha_{1,2}$ - or Cu K $\alpha_{1,2}$ -radiation. Lattice constants for NiAl_{2-x}Ga_xO₄ (Figure 2a) and NiFe_{2-x}Cr_xO₄ (Figure 2b) were determined using the X'Pert HighScore Plus software and are based on a cubic crystal system ($Fd\bar{3}m$) [17,18]. The lattice constants in the NiAl_{2-x}Ga_xO₄ system were found to increase linearly with increasing Ga concentration, in agreement with Vegard's law [19]. In the NiFe_{2-x}Cr_xO₄ system, the lattice constant decreases slightly up to $x = 1$, and then increases slightly when $x > 1$, which is consistent with other studies [20].

A Rietveld refinement of powder XRD patterns from NiAl₂O₄ and NiGa₂O₄ was completed to confirm the interpretation of the XANES spectra. Patterns for Rietveld refinement were collected in the 2θ range of 10° to 120° using the instrument described above and Co K $\alpha_{1,2}$ radiation. Refinement was performed using the Rietveld refinement program found in the X'Pert HighScore Plus software package [17]. The model used to refine the data was based on a previously reported crystal structure [21]. The occupancy of Ni²⁺ and Al³⁺ or Ga³⁺ in the tetrahedral and octahedral sites was varied in 0.2 increments, and the refinement was determined to be the best when the weighted refinement profile value (weighted R_p) was the lowest.

Figure 2. a) Change in the a lattice constant for $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ depending on the Ga concentration (x). b) Change in the a lattice constant for $\text{NiFe}_{2-x}\text{Cr}_x\text{O}_4$ depending on the Cr concentration (x).

2.2. XANES

2.2.1. Al $L_{2,3}$ -edge XANES

The Al $L_{2,3}$ -edge XANES spectra were collected at the Canadian Light Source (CLS) using the Variable Line Spacing Plane Grating Monochromator beamline (VLS PGM, 11ID-2) [22]. Samples of $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ were ground to a fine powder and mounted on C tape before being inserted into the vacuum chamber. Fluorescence spectra were collected using a 0.025 eV

step through the absorption edge and an entrance slit of 50 μm . The spectra were calibrated by periodically collecting a spectrum from Al metal foil (Alfa Aesar, 99.99%) and setting the peak maximum of the first derivative of the spectrum to 72.55 eV [23].

2.2.2. Ni and Ga K-edge XANES

The Ni and Ga K-edge spectra were collected in transmission mode at the Pacific Northwest Consortium/X-ray Science Division Collaborative Access Team (PNC/XSD-CAT, Sector 20) bending magnet beamline (20-BM) located at the Advanced Photon Source (APS; Argonne National Laboratory) using ionization chambers filled with 100% $\text{N}_{2(\text{g})}$ and a Si (111) crystal monochromator [24]. Sample preparation consisted of spreading a thin layer of finely powdered material between two pieces of Kapton tape. Multiple sample layers were used to maximize absorption and sample uniformity.

Spectra from each sample were collected using a 0.2 eV step through the absorption edge for Ga, and a 0.15 eV step through the absorption edge for Ni. The spectra were calibrated by concurrently collecting spectra from a reference material and setting the peak maximum of the first derivative of the spectrum to a known value. Ga metal (sandwiched between two layers of Kapton tape) was used as a reference material for the Ga K-edge with the reference spectrum calibrated to 10367 eV [23]. Ni metal foil was used as a reference material for the Ni K-edge with the absorption edge energy set to 8333 eV [23]. All spectra collected were calibrated, normalized, and analyzed using the Athena software program [25].

3. Results

3.1. Structure refinement by powder XRD

A Rietveld refinement of the powder XRD patterns from NiAl_2O_4 and NiGa_2O_4 was performed to develop an understanding of how the occupancy of the tetrahedral and octahedral sites varied depending on composition. The results of the Rietveld refinements are presented in Figure 3 and Table 1. It was observed that Ni^{2+} partially occupies the tetrahedral site in NiAl_2O_4 , but that only a very small concentration of Ni^{2+} (if any) was present in the tetrahedral site in NiGa_2O_4 . This assessment was made by examining how the weighted refinement profile value (weighted R_p) changed depending on the occupancy of Ni^{2+} in the tetrahedral site (Figure 4). These results are in general agreement with what is known about the site preference of Al^{3+} , Ga^{3+} , and Ni^{2+} [1,11,15]. However, it is difficult to perform a similar analysis of the quaternary

materials because of the difficulty in determining the site occupancy of three different cations across multiple sites. XANES was used in this study to assess how the relative occupancy of Al^{3+} , Ga^{3+} , and Ni^{2+} in the tetrahedral and octahedral sites changed depending on the Ga^{3+} concentration in $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$.

Figure 3. Results of the Rietveld refinement of powder XRD data from a) NiAl_2O_4 and b) NiGa_2O_4 are presented. Vertical lines mark the positions of the expected peaks.

Table 1: Reitveld refinement parameters for NiAl₂O₄ and NiGa₂O₄

Parameters	NiAl ₂ O ₄	NiGa ₂ O ₄
<i>a</i> Lattice Constant (Å)	8.0487	8.2611
8a occupancy (tetrahedral site)	0.203(Ni) 0.797(Al)	0.0 (Ni) 1.0 (Ga)
16d occupancy (octahedral site)	0.3985(Ni) 0.6015(Al)	0.5 (Ni) 0.5 (Ga)
R _{expected}	3.4016	2.8296
R _{profile}	3.1811	2.5815
Weighted R _{profile} *	4.2628	3.4312

*Only parameters that gave the best fit to the data are provided.

Figure 4. The weighted refinement profile value (weighted R_p) is plotted versus the percent occupancy of the tetrahedral site by Ni²⁺. The lowest value (i.e., best fit) was determined when the tetrahedral site in NiAl₂O₄ contained 20% Ni²⁺ and when the tetrahedral site in NiGa₂O₄ was only occupied by Ga³⁺.

3.2. XANES

3.2.1. Al $L_{2,3}$ -edge XANES

Al $L_{2,3}$ -edge spectra are very sensitive to changes in the CN of Al [26-28]. The lowest-energy features present in the Al $L_{2,3}$ -edge spectra are primarily due to $2p \rightarrow 3s$ transitions while higher energy features may involve $2p \rightarrow 3d$ transitions [29,30]. The L_{3-} and L_{2-} edge features, which result from spin-orbit splitting, can be resolved in spectra from highly crystalline compounds containing Al with a single CN [26,28,30]. Further, the absorption edge energy from 6-coordinate Al is shifted by ~ 1.5 eV to higher energy relative to 4-coordinate Al, which is a result of a change in how the nuclear charge of the excited atom is screened depending on the number of nearest neighbor O atoms [26,28,29]. The octahedral L_{3-} and tetrahedral L_{2-} edges overlap in compounds containing Al in multiple coordinate environments, which limits the ability to observe these individual spin-orbit split features [26,28-30]. While the distinct L_3 and L_2 spin-orbit split peaks can no longer be individually observed in spectra from materials containing Al in multiple coordination environments, the transitions from 4- and 6- coordinate Al are represented by broad peaks occurring at different energies. The lowest energy peak corresponds to tetrahedrally coordinated Al while the higher energy peak corresponds to octahedrally coordinated Al [26,28-30].

The normalized Al $L_{2,3}$ -edge XANES spectra from the $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ system are shown in Figure 5. Two peaks are observed in the spectra with the lowest energy peak (T) representing tetrahedrally coordinated Al and the higher energy peak (O) mostly representing Al in an octahedral site. In these spectra, as Al is exchanged for Ga, peak T (tetrahedral feature) decreases in intensity and becomes broader to lower energy while peak O (octahedral feature) increases in intensity. That is, with increasing Ga content, Al increasingly occupies the octahedral site, and decreasingly occupies the tetrahedral site.

Figure 5. Normalized Al L_{2,3}-edge XANES spectra from NiAl_{2-x}Ga_xO₄. The tetrahedral feature is labeled as *T* and the octahedral feature is labeled as *O*. The intensity of peak *O* increased with increasing Ga concentration while peak *T* decreased in intensity and became broader to lower energy.

3.2.2. Ga K-edge XANES

The normalized Ga K-edge spectra from NiAl_{2-x}Ga_xO₄ are shown in Figure 6 and result from 1s → 4p transitions. The Ga K-edge spectra shift to higher energy with increasing coordination number for similar reasons described above for the Al L_{2,3}- edge XANES spectra [26,28,31]. In the spectra presented in Figure 6, peak *T* corresponds to tetrahedrally coordinated Ga while peak *O* corresponds to octahedrally coordinated Ga, as has been determined previously [26,28].

Feature *T* was found to decrease in intensity while feature *O* was found to increase in intensity in the Ga K-edge spectra from NiAl_{2-x}Ga_xO₄ with increasing Ga concentration. It should be recognized that as the spectra have been normalized to each other, the apparent decrease in intensity of feature *T* with increasing Ga concentration does not imply that the concentration of tetrahedral Ga decreases. Instead, these spectra show that as Ga replaces Al, Ga is allocated primarily to the tetrahedral sites and then populates the octahedral sites when the Ga concentration increases and the Al concentration decreases.

Figure 6. Normalized Ga K-edge XANES spectra from $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$. The tetrahedral feature is labeled as *T* and the octahedral feature is labeled as *O*. The intensity of peak *O* increases with increasing Ga concentration while the intensity of peak *T* decreases, which is marked by arrows.

3.2.2. Ni K-edge XANES

The Ni K-edge is comprised of a pre-edge region, which can be described as resulting primarily from quadrupolar $1s \rightarrow 3d$ transitions, and a main-edge region resulting from dipolar $1s \rightarrow 4p$ transitions [32,33]. The $1s \rightarrow 3d$ transition is formally forbidden in octahedral symmetry; however, as the coordination around the metal centre decreases, inversion symmetry is lost, and the 4p- and 3d-states overlap, which results in an increase in the intensity of the pre-edge region because of an increase in the dipolar character of the transition [33]. As a result, this feature is very sensitive to changes in CN [32-35]. Changes in the main-edge region are often less well understood due to complicated electronic transitions into the conduction band as well as multi-scattering resonances [32,36,37]. Noting this, it has been observed previously that a decrease in the CN of a transition-metal in a series of isostructural materials because of substitution will result in the main-edge region of the transition-metal K-edge XANES spectrum decreasing in intensity and shifting to lower energy (e.g., $\text{Ca}_2B'\text{FeO}_5$ ($B' = \text{Al}, \text{Fe}, \text{Mn}$) and $\text{SrFe}_{1-x}\text{Zn}_x\text{O}_{3-\delta}$) [32,36,38].

The Ni K-edge spectra from $\text{NiFe}_{2-x}\text{Cr}_x\text{O}_4$ are presented in Figure 7 to show the sensitivity of transition-metal K-edge XANES spectra from spinels to changes in CN. As has

been determined previously, NiFe_2O_4 is an inverse spinel with Ni^{2+} primarily occupying half of the octahedral sites and Fe^{3+} occupying the tetrahedral sites and the remaining octahedral sites [1,2,12]. With increasing substitution of Fe^{3+} for Cr^{3+} , Ni^{2+} increasingly occupies the tetrahedral sites, as a result of the strong preference for Cr^{3+} to lie in octahedral sites [1,2,12]. This change in the average CN of Ni^{2+} is corroborated in the Ni K-edge XANES spectra presented here, as the pre-edge peak increases in intensity with greater Cr substitution while the main-edge features decrease in intensity and shift to lower energy.

Figure 7. Normalized Ni K-edge XANES spectra from $\text{NiFe}_{2-x}\text{Cr}_x\text{O}_4$. An increase in the Cr^{3+} concentration results in a decrease in the average CN of Ni^{2+} . This decrease in CN can be observed by an increase in intensity of the pre-edge peak (see inset), a decrease in intensity of the main edge, and a decrease in the energy of the main-edge with increasing x . The changes in the intensity and energy of the features observed with increasing Cr^{3+} concentration are marked with arrows.

Unlike the Ni K-edge spectra from $\text{NiFe}_{2-x}\text{Cr}_x\text{O}_4$, the Ni K-edge spectra from $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ presented in Figure 8 show relatively little change in the Ni^{2+} CN as Ga^{3+} replaces Al^{3+} . However, some changes in the spectra are observed, which will be discussed. For example, the pre-edge peak intensity decreases slightly with increasing Ga^{3+} concentration. This implies that, although Ni^{2+} has a fairly strong preference for residing in octahedral sites, some Ni^{2+} is present

in the tetrahedral site in NiAl_2O_4 . In comparison, much less Ni^{2+} is present in the tetrahedral site as Ga^{3+} is substituted for Al^{3+} , which is observed by the decrease in the pre-edge peak intensity. This observation is in agreement with previous comparisons of the ternary NiAl_2O_4 and NiGa_2O_4 oxides and the powder XRD results presented in Section 3.1 [15].

Figure 8. Normalized Ni K-edge XANES spectra from $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$. The pre-edge peak intensity (see inset) decreases slightly with increasing Ga concentration, implying a minor increase in the average CN of Ni. The decrease in the energy of the most prominent main-edge feature with increasing Ga concentration (see arrow) is considered to be a result of an increase in the multiscattering path-length.

Along with subtle changes in the pre-edge peak of the Ni K-edge spectra from $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$, some changes in the main-edge region of the spectra are also observed; however, it is difficult to relate these changes only to a slight change in the Ni^{2+} CN because of substitution. With increasing Ga^{3+} concentration, the most significant feature in the Ni K-edge main-edge region shifted to lower energy, as is indicated by the arrow in Figure 8. As the pre-edge shows only a slight change, it is suggested that this shift of the main-edge is not a result of a change in the Ni^{2+} CN. Instead, it is suggested that this feature is strongly influenced by multi-scattering resonances [39]. With increasing Ga^{3+} concentration, the multi-scattering path-length would

increase because the ionic radius of Ga^{3+} is larger than that of Al^{3+} [16]. An increase in the multiscattering path-length would result in this feature shifting to lower energy [39].

4. Discussion

The Al $L_{2,3}$ -, Ga K- and Ni K-edge XANES spectra show that Al and Ni prefer to reside in the octahedral sites while Ga prefers to reside in the tetrahedral sites in $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$. As has been identified by analysis of the XANES spectra, and corroborated by Rietveld analysis of powder XRD data, Al^{3+} occupies the majority of the tetrahedral sites in NiAl_2O_4 as well as the octahedral sites not occupied by Ni^{2+} . As Ga^{3+} replaces Al^{3+} , Ga^{3+} substitutes primarily into the tetrahedral sites and increasingly occupies the octahedral sites as more Al^{3+} is replaced by Ga^{3+} . Further, the Ni CN was found to increase slightly in $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ with increasing x . The site preferences of Ni^{2+} , Ga^{3+} , and Al^{3+} in the $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ system are consistent with previous experimental and theoretical studies of the site preferences of these three metal cations [1,2,26,28]. It has been proposed previously that the ionic radius of the cation, the degree of interactions of the cation valence s- and p-states with the anion, and crystal field stabilization play a role in determining the site preference of cations [2,7,15]. In the case of Ga^{3+} , the complete electron d-shell poorly shields the nuclear charge, resulting in the s- and p-states experiencing a greater effective nuclear charge [7]. Thus, the 4s- and 4p-states of Ga^{3+} are found at lower energies relative to the 3s- and 3p-states of Al^{3+} [7]. The lower energy of the Ga^{3+} 4s- and 4p-states leads to greater overlap with the O 2p-states, favouring a covalent Ga-O bond [7]. As the Al^{3+} valence states are higher in energy than the Ga^{3+} valence states, the Al 3s- and 3p-states do not overlap as effectively with the O 2p- states, favouring a more ionic bond [7]. As greater orbital overlap is favoured in the smaller tetrahedral site, Ga^{3+} preferentially occupies tetrahedral sites over Al^{3+} [14].

Previous investigations of Al^{3+} and Ga^{3+} substituted oxides by analysis of Al $L_{2,3}$ -edge and Ga K-edge XANES spectra have also shown how these spectra change depending on the average CN of Al^{3+} and Ga^{3+} [26-28,31]. However, the magnitude of the changes in the T and O peak intensities in either the Al $L_{2,3}$ - or Ga K-edge spectra when Ga^{3+} substitutes for Al^{3+} in $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ is far greater than has been observed by analysis of these spectra from other quaternary oxide systems, especially those that contain Fe (e.g., $\text{Ca}_2\text{Al}_x\text{Fe}_{2-x}\text{O}_5$, $\text{Ca}_2\text{Ga}_{2-x}\text{Fe}_x\text{O}_4$, and $\text{Al}_{1-x}\text{Ga}_x\text{FeO}_3$) [26-28]. The reason for this difference can be ascribed to the difference in the octahedral site preference energies between Ni^{2+} and Fe^{3+} . Whereas the octahedral site

preference energy of Ni^{2+} is large and positive (9.0 kcal/g), and much higher than that of either Al^{3+} (-2.5 kcal/g) or Ga^{3+} (-15.4 kcal/g), the octahedral site preference energy of Fe^{3+} is negative (-13.3 kcal/g) and between that of Al^{3+} and Ga^{3+} [14]. An analysis of these octahedral site preference energies fits well with the observations reported here for the $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ system by analysis of Al $L_{2,3}$ -edge, Ga K-edge, and Ni K-edge XANES spectra as a positive energy implies an octahedral site preference.

5. Conclusion

This study has, for the first time, shown how the coordination numbers (CN) of Al^{3+} , Ga^{3+} , and Ni^{2+} change in the $\text{NiAl}_{2-x}\text{Ga}_x\text{O}_4$ spinel-type oxides because of the substitution of Al^{3+} for Ga^{3+} . Ga^{3+} prefers to occupy the tetrahedral sites and Ni^{2+} and Al^{3+} prefer to occupy the octahedral sites, as would be expected based on analysis of octahedral site preference energies [14]. The most significant result of this study is the report of the large changes observed in the Al $L_{2,3}$ - and Ga K-edge XANES spectra because of a change in the CN of Al^{3+} and Ga^{3+} . The significant changes observed in these spectra because of CN unambiguously shows the sensitivity of these spectra to changes in the CN of these ions. The sensitivity of these spectra to CN changes is useful for analysis of poorly crystalline materials and glasses that contain Al and/or Ga.

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References

- [1] R. J. Hill, J. R. Craig, G. V. Gibbs, *Phys. Chem. Miner.* 4 (1979) 317-339
- [2] G. D. Price, S. L. Price, J. K. Burdett, *Phys. Chem. Miner.* 8 (1982) 69-76
- [3] S. M. Patange, S. E. Shirsath, S. S. Jadhav, K. M. Jadhav, *Phys. Status Solidi A* 209 (2012) 347-352.
- [4] S. K. Sampath, D. G. Kanhere, R. Pandey, *J. Phys.: Condens. Matter* 11 (1999) 3635-3644
- [5] R. López-Fonseca, C. Jiménez-González, B. de Rivas, J. I. Gutiérrez-Ortiz, *Appl. Catal. A* 437-438 (2012) 53-62.
- [6] H. Dixit, N. Tandon, S. Cottenier, R. Saniz, D. Lamoén, B. Partoens, V. Van Speybroeck, M. Waroquier, *New J. Phys.* 13 (2011) 063002.
- [7] J. B. Goodenough, A. L. Loeb, *Phys. Rev.* 98 (1955) 391-408.
- [8] S. -H. Wei, S. B. Zhang, *Phys. Rev. B* 63 (2001) 045112.
- [9] K. N. Woods, A. M. Khasanov, J. G. Stevens, *Hyperfine Interact.* 188 (2009) 127-137
- [10] J. S. Díez Viñuela, C. Otero Areán, F. S. Stone, *J. Chem. Soc., Faraday Trans.* 79 (1983) 1191-1198
- [11] J. D. Dunitz, L. E. Orgel, *J. Phys. Chem. Solids* 3 (1957) 318-323.
- [12] G. C. Allen, S. J. Harris, J. A. Jutson, J. M. Dyke, *Appl. Surf. Sci.* 37 (1989) 111-134.
- [13] D. S. McClure, *J. Phys. Chem. Solids* 3 (1957) 311-317.
- [14] A. Miller, *J. Appl. Phys.* 30 (1959) 24S-25S
- [15] J. K. Burdett, G. D. Price, S. L. Price, *J. Am. Chem. Soc.* 104 (1982) 92-95.
- [16] R. D. Shannon, *Acta Crystallogr., Sect. A* 32 (1976) 751-767.
- [17] X'Pert Highscore Plus Program, Version 3.0e; PANalytical B.V.: Almelo, The Netherlands, 2012.
- [18] G. C. Allen, M. Paul, *Appl. Spec.* 49 (1995) 451-458
- [19] A. R. Denton, N. W. Ashcroft, *Phys. Rev. A* 43 (1991) 3161-3164.
- [20] S. Winell, Ö. Amcoff, T. Ericsson, *Phys. Status Solidi B* 245 (2008) 1635-1640.
- [21] J. N. Roelofsen, R. C. Peterson, M. Raudsepp, *Am. Mineral.* 77 (1992) 522-528.
- [22] Y. -F. Hu, L. Zuin, R. Reininger, T. K. Sham, *AIP Conf. Proc.* 879 (2007) 535-538.
- [23] A. Thompson, D. Attwood, E. Gullikson, M. Howells, K. -J. Kim, J. Kirz, J. Kortright, I. Lindau, P. Pianetta, A. Robinson, J. Scofield, J. Underwood, D. Vaughan, G. Williams, H. Winick, *X-ray Data Booklet*, 3rd ed.; Lawrence Berkeley National Laboratory: Berkeley, 2009.
- [24] S. M. Heald, D. L. Brewé, E. A. Stern, K. H. Kim, F. C. Brown, D. T. Jiang, E. D. Crozier, R. A. Gordon, *J. Synchrotron Radiat.* 6 (1999) 347-349.
- [25] B. Ravel, M. Newville, *J. Synchrotron Radiat.* 12 (2005) 537-541.
- [26] J. D. S. Walker, A. P. Grosvenor, *J. Solid State Chem.* 197 (2013) 147-153.
- [27] A. P. Grosvenor, F. Ramezanipour, S. Derakhshan, C. Maunders, G. A. Botton, J. E. Greedan, *J. Mater. Chem.* 19 (2009) 9213-9220.
- [28] J. D. S. Walker, A. P. Grosvenor, *Inorg. Chem.* 52 (2013) 8612 - 8620.
- [29] J. A. van Bokhoven, T. Nabi, H. Sambe, D. E. Ramaker, D. C. Koningsberger, *J. Phys.: Condens. Matter* 13 (2001) 10247-10260.
- [30] C. Weigel, G. Calas, L. Cormier, L. Galois, G. S. Henderson, *J. Phys.: Condens. Matter* 20 (2008) 135219.

- [31] K. Nishi, K. -I. Shimizu, M. Takamatsu, H. Yoshida, A. Satsuma, T. Tanaka, S. Yoshida, T. Hattori, *J. Phys. Chem. B* 102 (1998) 10190–10195.
- [32] A. P. Grosvenor, J. E. Greedan, *J. Phys. Chem. C* 113 (2009) 11366-11372.
- [33] T. E. Westre, P. Kennepohl, J. G. DeWitt, B. Hedman, K. O. Hodgson, E. I. Solomon, *J. Am. Chem. Soc.* 119 (1997) 6297–6314.
- [34] L. Galois, G. Calas, *Am. Mineral.* 76 (1991) 1777-1780.
- [35] F. Farges, M. Munoz, R. Siewert, V. Malavergne, G. E. Brown Jr., H. Behrens, M. Nowak, P. –E. Petit, *Geochim. Cosmochim. Acta*, 65 (2001) 1679-1693.
- [36] M. W. Gaultois, J. E. Greedan, A. P. Grosvenor, *J. Electron. Spectrosc. Relat. Phenom.* 184 (2011) 192-194.
- [37] J. R. Hayes, A. P. Grosvenor, *J. Alloys Compd.* 537 (2012) 323-331.
- [38] M. W. Gaultois, A. P. Grosvenor, *J. Phys. Chem. C* 114 (2010) 19822-19829.
- [39] J. J. Rehr, R. C. Albers, *Rev. Mod. Phys.* 72 (2000) 621-654.