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Electronic structure of spinel oxides: zinc aluminate and zinc gallate

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Abstract. The electronic structure of zinc aluminate (ZnAl_2O_4) and that of zinc gallate (ZnGa_2O_4) were studied by the self-consistent tight-binding linearized muffin-tin orbital method with the atomic sphere approximation. The calculated results predict these zinc-based spinel oxides to be direct-gap materials. The direct gap at Γ is found to be 4.11 eV for ZnAl_2O_4 and 2.79 eV for ZnGa_2O_4 . With reference to the calculated band gap of 5.36 eV for MgAl_2O_4 , the systematic decrease in the gap is attributed to the presence of 3d orbitals of Zn and Ga and the associated p–d hybridization in the upper valence band of zinc aluminate and gallate. Comparison of the contour maps of the electron localization function of ZnAl_2O_4 and ZnGa_2O_4 with that of MgAl_2O_4 clearly shows the bonding to be less ionic in the zinc-based spinel oxides. Finally, the calculations yield a smaller electron effective mass for zinc gallate as compared to that for zinc aluminate, suggesting a higher mobility of electrons in gallate.

1. Introduction

Zinc aluminate (ZnAl_2O_4) and zinc gallate (ZnGa_2O_4) are members of the class of inorganic materials called spinels. They have a close-packed face-centred-cubic structure [1] with $Fd3m$ space group symmetry. These spinel oxides are wide-band-gap semiconductors; the optical band gaps are reported [2] to be about 3.8 and 4.1 eV for ZnAl_2O_4 and ZnGa_2O_4 respectively. Furthermore, in the polycrystalline form, they are found to be highly reflective from 300 nm which is well within the ultraviolet regime of the spectrum. This has attracted considerable interest amongst researchers for a variety of applications. For example, they are being studied as candidate materials for reflective optical coatings in aerospace applications [3]. Additionally, zinc gallate is proposed as phosphor material [4] and ultraviolet-transport electroconductive oxide [5].

There has been considerable work involving both experimental and theoretical methods on spinel oxides like magnesium aluminate (MgAl_2O_4), but there are very few reported studies on zinc aluminate (ZnAl_2O_4) and zinc gallate (ZnGa_2O_4). In particular, the known properties of these materials are just the crystal structure [1] and the optical spectra [2, 4, 5], and the electronic properties are relatively unknown.

On the theoretical front, we are not aware of any studies except that leading to the prediction of the stability of the normal spinel structure over the inverse structure for ZnAl_2O_4 [6]. We have therefore embarked upon a detailed theoretical study of these zinc-based spinel oxides. In an earlier work, we have reported the results of an atomistic simulation study [7] that included derivation of interatomic potentials, and determination of the equation of state and

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compressibility behaviour at the octahedral and tetrahedral sites in the spinel lattice, and the energetics of point defects in ZnAl_2O_4 and ZnGa_2O_4 . In the present work, we focus our attention on their electronic properties and report the results of electronic structure calculations within the framework of the local density approximation (LDA) to the density functional theory.

This paper is organized as follows. Section 2 briefly describes the method and relevant computational parameters used in the calculations. In section 3, we discuss the calculated results for electronic properties of these oxides in terms of band structure, density of states and electron effective mass. Finally, we give summary of the work in section 4.

2. Method

We employ the tight-binding muffin-tin orbital (TB-LMTO) method in the atomic sphere approximation (ASA) for electronic structure calculations. Since the standard LMTO-ASA method [8] and its localized representation the TB-LMTO method [9, 10] have been well described in the literature, we confine our discussions here to the relevant computational details of the method.

In the ASA, the crystal is divided into space-filling and therefore slightly overlapping spheres centred on each of the atomic sites. A total of 18 empty spheres were used for filling the space of the unit cell and they were of three different types. In all of the cases, the Zn 3d and Ga 3d electrons were always treated as the band electrons. Calculations were performed using the von Barth–Hedin local exchange–correlation potential [11]. The method is scalar relativistic, and combined correction has been taken into account. The self-consistency was obtained using 256 k -points in the irreducible zone. The tetrahedron method of integration with corrections due to linear approximation for the bands inside each tetrahedron was used for the Brillouin integration.

3. Results and discussion

3.1. Structural properties

The normal spinel lattice is characterized by the lattice constant a and the internal parameter u (which specifies the position of the oxygen anion in the cell). In the total-energy calculations, the lattice constant a was minimized at the experimental value of u which is reported [1] to take the values 0.389 and 0.387 for ZnAl_2O_4 and ZnGa_2O_4 respectively. The potential energy surface generated was then fitted to the Vinet equation of state to obtain the equilibrium structural parameters (volume, bulk modulus and its pressure derivative) for zinc aluminate and gallate.

The optimized values of the lattice constant turn out to be 7.91 and 8.174 Å, as compared to the experimental values of 8.086 and 8.33 Å for ZnAl_2O_4 and ZnGa_2O_4 respectively. For both spinel oxides, our calculated values of a are within 2% of the corresponding experimental values. Given that the divalent cation is the same in both spinels, the ion-size difference between Ga^{3+} and Al^{3+} should be responsible for the larger a -parameter in ZnGa_2O_4 as compared to ZnAl_2O_4 .

The calculated values of the bulk modulus (B_0) and its pressure derivative (B'_0), evaluated at zero pressure, compare favourably with those obtained earlier in an atomistic simulation study. [7] Their values (B_0 and B'_0) are predicted to be (262 GPa, 4.43) and (243 GPa, 2.71) for ZnAl_2O_4 and ZnGa_2O_4 respectively. No experimental data on these oxides are available for comparison with the predicted values.

3.2. Electronic properties

Now we discuss our results pertaining to the electronic properties of ZnAl_2O_4 and ZnGa_2O_4 via the energy bands, density of states and effective mass. To provide a benchmark for the calculated electronic properties of ZnAl_2O_4 and ZnGa_2O_4 , we include the TB-LMTO results for MgAl_2O_4 which has been extensively studied [12, 13]. A comparison between the electronic properties of MgAl_2O_4 and ZnAl_2O_4 would facilitate assessing the role of d electrons in the composition of the valence and conduction bands of the spinel oxides. Furthermore, we can also study the ion-size effect (Al^{3+} versus Ga^{3+}) by comparing the electronic properties of ZnAl_2O_4 and ZnGa_2O_4 .

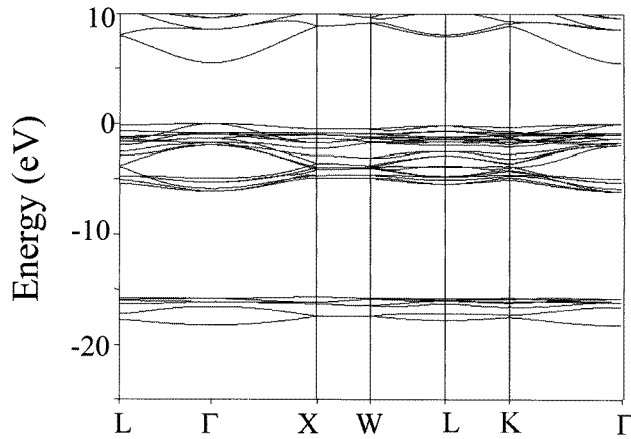


Figure 1. The band structure of MgAl_2O_4 .

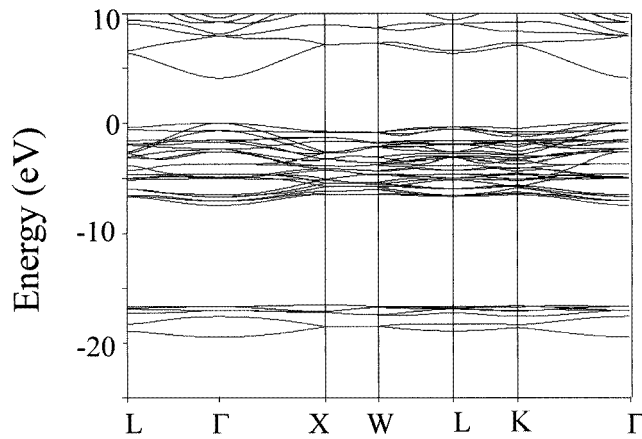


Figure 2. The band structure of ZnAl_2O_4 .

The energy bands of MgAl_2O_4 , ZnAl_2O_4 and ZnGa_2O_4 are given in figures 1–3. Accordingly, the spinel oxides are predicted to be direct-gap materials. Both the top of the valence band and the bottom of the conduction band are found to be at Γ . The minimum (direct) gaps turn out to be 5.36, 4.11 and 2.79 eV for MgAl_2O_4 , ZnAl_2O_4 and ZnGa_2O_4 respectively. Experimentally, the gap in MgAl_2O_4 is reported [14] to be about 7.8 eV, while those for

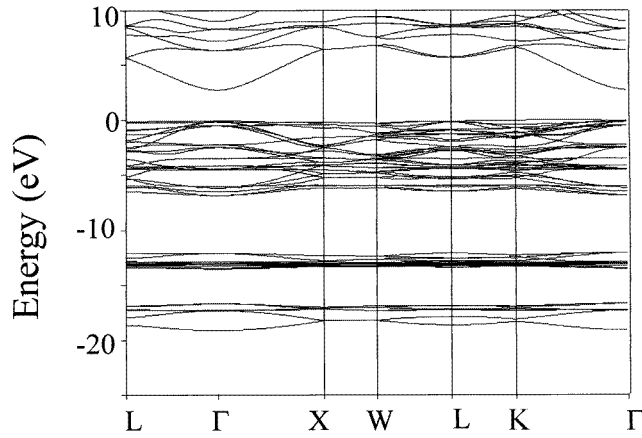


Figure 3. The band structure of ZnGa_2O_4 .

Table 1. Electronic properties of MgAl_2O_4 , ZnAl_2O_4 and ZnGa_2O_4 .

	MgAl_2O_4	ZnAl_2O_4	ZnGa_2O_4
Lattice parameter (\AA)	7.934	7.91	8.174
Direct gap, eV			
($\Gamma_{1c}-\Gamma_{15v}$)	5.36	4.11	2.79
($L_{1c}-L_{3v}$)	7.85	6.77	5.80
($K_{1c}-K_{2v}$)	8.84	7.64	6.62
($X_{1c}-X_{5v}$)	9.02	7.94	6.71
Indirect gap, eV			
($L_{1c}-\Gamma_{15v}$)	7.69	6.38	5.73
($K_{1c}-\Gamma_{15v}$)	8.54	7.12	6.60
($X_{1c}-\Gamma_{15v}$)	8.60	7.17	6.51
Upper valence bandwidth	6.28	7.59	6.81
Electron effective mass, eV			
$\Gamma-X$	0.36	0.36	0.22
$\Gamma-L$	0.38	0.32	0.21
$\Gamma-K$	0.39	0.38	0.23

ZnAl_2O_4 and ZnGa_2O_4 [2] are about 3.8–3.9 and 4.1–4.3 eV respectively. For ZnGa_2O_4 , another set of diffuse reflectance measurements lead to an estimate of the gap of about 5 eV [5]. Although the LDA calculations underestimate the band gap relative to experiments, we note here that the band gaps of ZnAl_2O_4 and ZnGa_2O_4 were derived from reflectance measurements of powder samples and may therefore require correction for the particle-size dependence of light scattering. Generally, lowering of the band gap is expected with the substitution of heavier cations (e.g. Zn for Mg or Ga for Al) in a series of compounds which are structurally isomorphous. The calculated results in fact show a lowering of the gap from MgAl_2O_4 to

ZnAl₂O₄ to ZnGa₂O₄ (table 1).

The electronic structure of MgAl₂O₄ has been previously reported [12]; in deriving it, the orthogonalized linear combination of atomic orbitals (OLCAO) (within the LDA approximation) method was used. There is overall agreement between the TB-LMTO and the OLCAO calculations regarding the composition of valence and conduction bands. However, the OLCAO calculations reported the valence-band maximum to be along the Γ -K axis, predicting MgAl₂O₄ to be an indirect-gap material, in contrast to the prediction of a minimum direct gap in the present study. As pointed out in the OLCAO study, the difference between the direct and indirect gap was about 0.004 eV which is well within the accuracy of the OLCAO calculations. Note that the optical reflectivity measurements [14] reported the minimum band gap of MgAl₂O₄ to be direct at Γ .

Figures 4–6 give the total and partial (site-projected) densities of states (DOS) for the spinel oxides. In MgAl₂O₄, the upper valence band is composed mostly of O 2p orbitals with

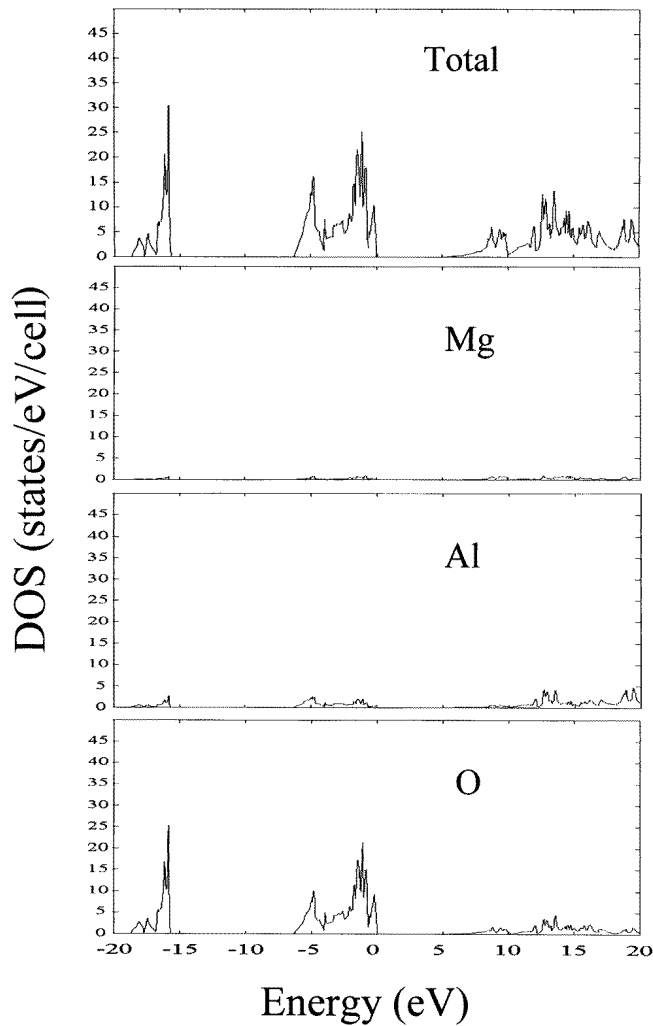


Figure 4. Total and partial densities of states of MgAl₂O₄.

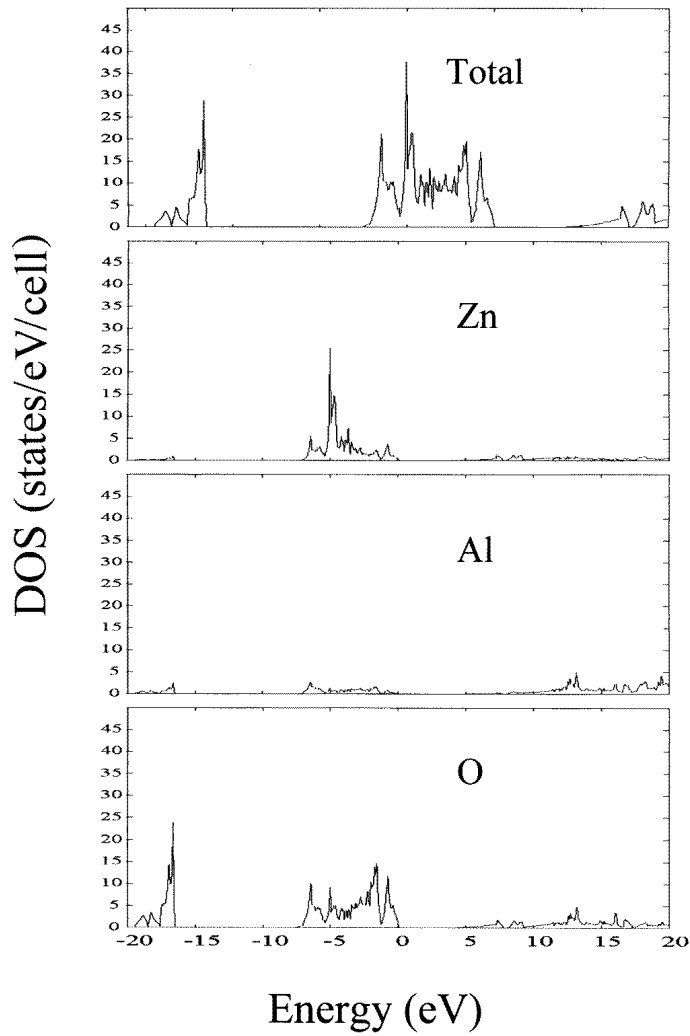


Figure 5. Total and partial densities of states of ZnAl_2O_4 .

the width of 6.3 eV. The replacement of Mg with Zn brings the contributions from Zn 3d electrons to the upper valence band in ZnAl_2O_4 . Instead of the O 2p-dominated band, the zinc 3d band appears inside the upper valence band and as a consequence the bandwidth broadens to 7.6 eV. In both cases, the bottom of the conduction band is composed of s and p states. It is therefore expected that changes in the electronic properties of ZnAl_2O_4 as compared to those of MgAl_2O_4 would solely be due to the mixing of Zn 3d and O 2p orbitals. We note here that the structural parameters of MgAl_2O_4 and ZnAl_2O_4 are nearly the same (e.g. $R_{\text{Mg-O}} = 1.896 \text{ \AA}$, $R_{\text{Zn-O}} = 1.904 \text{ \AA}$).

The role of d states in defining the electronic properties of the II–VI semiconductors has been extensively discussed by Wei and Zunger [15] who have concluded that the p–d hybridization at Γ repels the valence-band maximum upwards without affecting the conduction-band minimum in several II–VI semiconductors. In the present study, the hybridization of Zn 3d with the O 2p orbitals is clearly evident (figure 5). Hence the lowering

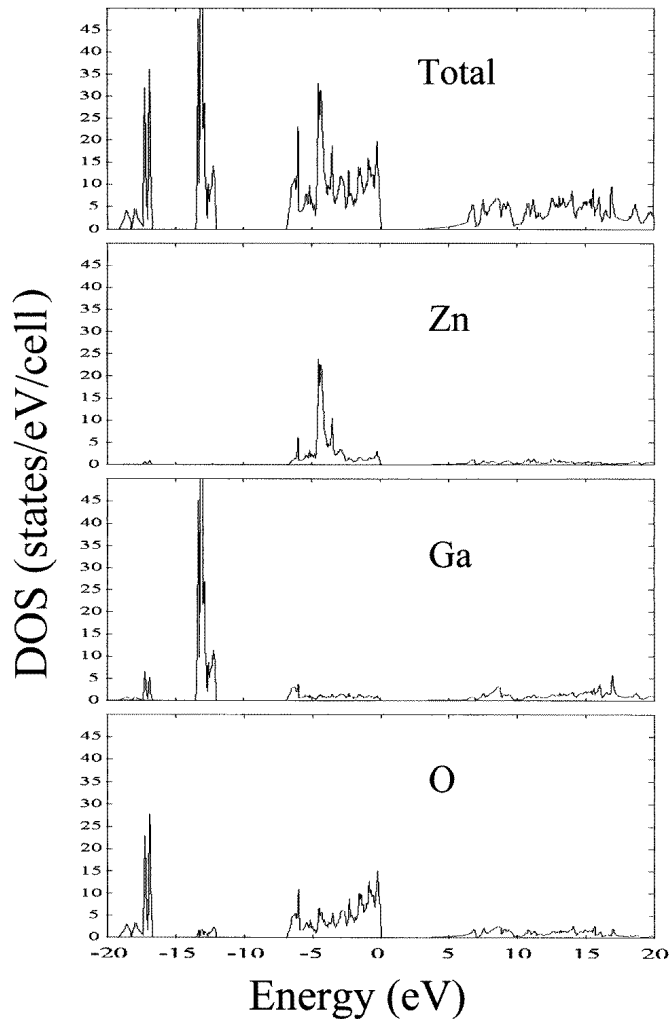


Figure 6. Total and partial densities of states of ZnGa_2O_4 .

of the calculated gap at Γ from 5.36 (MgAl_2O_4) to 4.11 eV (ZnAl_2O_4) can be attributed to the p–d mixing in the upper valence band of zinc aluminate. In ZnGa_2O_4 where Al is replaced by Ga, a narrow Ga 3d band appears between the upper valence band and the O 2s band (figure 6). This appearance of the Ga 3d band in addition to the Zn 3d band in the upper valence band further provides the p–d repulsion for the valence-band maximum at Γ , thereby reducing the gap to 2.79 eV.

In the spinels studied here, the valence-band maximum is flat, representing the rather large effective mass for the holes. On the other hand, calculations show that the electron effective mass is much smaller in ZnGa_2O_4 than that in ZnAl_2O_4 . However, the electron effective mass remains essentially the same in MgAl_2O_4 and ZnAl_2O_4 (table 1). Thus our calculations predict a higher mobility of electrons in ZnGa_2O_4 relative to both MgAl_2O_4 and ZnAl_2O_4 . Note that our calculated value of the electron effective mass is in agreement with the OLCAO-LDA results of 0.44.

A further insight into the bonding characteristics can be gained by examining the contour plots of the electron localization functions (ELF), defined as [16]

$$\text{ELF}(\vec{r}) = \left[1 + \left(\frac{D}{(C_F)\rho^{5/3}(\vec{r})} \right)^2 \right]^{-1} \quad (1)$$

where

$$D = T_0 - \frac{|\nabla\rho|^2}{8\rho} \quad (2)$$

$$C_F = \frac{3}{10}(3\pi^2)^{2/3} \quad (3)$$

$$T_0 = \frac{1}{2} \sum_i |\nabla\psi_i|^2. \quad (4)$$

It may be noted that the ELFs represent a measure of calibration of the degree of the electron localization with respect to the uniform density. The function can take values between 0 and 1 with the value of 1 representing complete localization. Thus, the ELFs are a useful interpretative tool for investigating the bonding characteristics of the system. Since we use the TB-LMTO method in the present study, we are well aware of its limitation of underestimating directionality in the electron distribution in solids. We will therefore restrict ourselves to making a comparative analysis of the variation in the bonding of these oxides.

The contour plots of the ELFs for MgAl_2O_4 , ZnAl_2O_4 and ZnGa_2O_4 are shown in figures 7–9. These contours which are projected on a plane parallel to the (110) plane show a strong localized region around the oxygens. They also show the differences in the nature of bonding among these spinels. In particular, the ELF is spherically symmetric in MgAl_2O_4 indicating that the bonding is dominated by the ionic component. Significant distortions in the ELF contours are observed when we replace Mg with Zn. Comparison of the Mg–O (figure 7) and Zn–O bond (figure 8) suggests reduced ionicity in the bonding for zinc aluminate. This effect is clearly due to the participation of the Zn 3d orbitals in the bonding. On the other hand, comparison between the Al–O bond (figure 8) and the Ga–O bond (figure 9) reveals a smaller effect on the bonding due to the localized Ga 3d orbitals in ZnGa_2O_4 . Furthermore, we notice that the contour plots show the presence of an empty channel with a relatively small charge

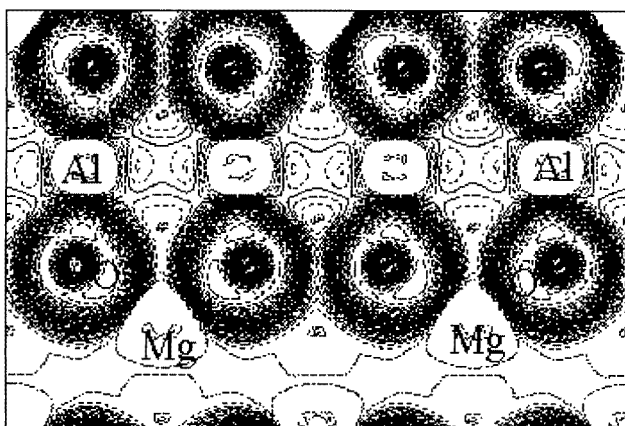


Figure 7. The ELF contour plot of MgAl_2O_4 along the (110) plane.

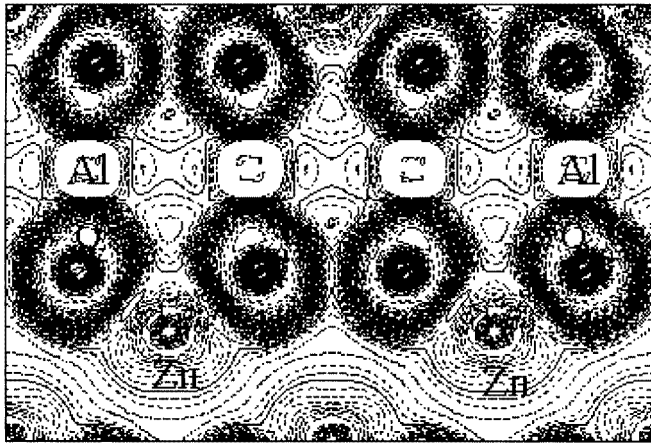


Figure 8. The ELF contour plot of ZnAl_2O_4 along the (110) plane.

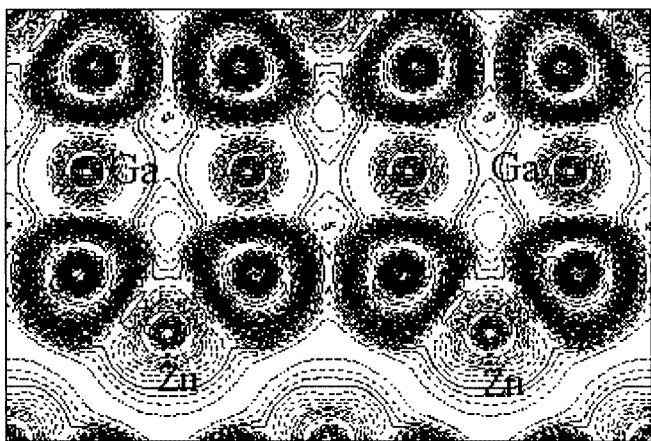


Figure 9. The ELF contour plot of ZnGa_2O_4 along the (110) plane.

localization for the spinels. It is suggested that such a channel would provide a diffusion path for ions in the spinel lattice [12].

4. Summary

We have studied the electronic structure of magnesium aluminate, zinc aluminate and zinc gallate spinels by means of the self-consistent tight-binding linearized muffin-tin orbital method with the atomic sphere approximation. The band structures along with the total and partial densities of states were used to analyse the details of the electronic properties.

Our study shows that the spinels, i.e. MgAl_2O_4 , ZnAl_2O_4 and ZnGa_2O_4 , are direct-band-gap materials with band gaps of 5.36 eV, 4.11 eV and 2.79 eV respectively. The systematic lowering of the gaps at Γ is due to the 3d orbitals present in ZnAl_2O_4 and ZnGa_2O_4 . The flat valence band indicates that the hole effective masses are rather large in these spinels. The electron effective masses are found to be similar for MgAl_2O_4 and ZnAl_2O_4 but considerably

less for ZnGa_2O_4 , suggesting a higher electron mobility in the gallate. The electron localization function contour plots clearly show that MgAl_2O_4 is more ionic than the zinc spinels.

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