Effects of Fe substitution on the electronic, transport, and magnetic properties of ZnGa$_2$O$_4$: A systematic *ab-initio* study

Leonardo Pisani, Tulika Maitra, Roser Valenti

*Institut für Theoretische Physik, Universität Frankfurt, D-6 Frankfurt, Germany (*Dated: August 31, 2018*)

We present a density functional study of Fe doped into the tetrahedral and octahedral cation sites of the wide band gap spinel ZnGa$_2$O$_4$. We calculate the electronic structure for different substitutions and discuss the magnetic and transport properties for each case considering different approximations for the exchange-correlation potential. We show that for certain doped cases, significant differences in the predicted behavior are obtained depending on the exchange correlation potential adopted. Possible applications of the doped systems as magnetic semiconductors are outlined.

PACS numbers: pacs

I. INTRODUCTION

In recent years, spintronics has emerged as one of the most studied fields of research in the semiconductor physics because of the possibility of exploiting both the carrier spin and charge degrees of freedom for the storage and transport of information in semiconductor devices. Because of the already existing fabrication technology for III-V semiconductors, the doping of these systems with magnetic ions (especially the cases of Ga(Mn)As and Ga(Mn)N) is being intensively investigated and a large amount of theoretical and experimental work has been done in order to understand the underlying mechanism for the ferromagnetism in these doped semiconductors.

Recently, an alternative approach for this phenomenon has been considered by taking a non-magnetic spinel semiconductor as host material and by doping it with Fe. The spinel structure (stochiometric formula AB$_2$O$_4$) with two types of cation sites (tetrahedral A and octahedral B) offers new possibilities of obtaining ferromagnetic order by doping one or both type of cation sites with magnetic ions. First experiments on the solid solution ZnGa$_2$O$_4$-[Fe$_3$O$_4$]$_x$ with x=0.05,0.10 and 0.15 showed that long-range magnetic order is induced with Curie temperatures up to 200K. Similar attempts by Krimmel et al. on Fe$_{0.76}$In$_{2.17}$S$_4$ revealed, on the contrary, a spin glass state at low temperatures.

Along these lines, we investigate the electronic structure of Fe doped ZnGa$_2$O$_4$ within density functional theory (DFT) with special emphasis on the magnetic and transport properties. Since the description of these properties may be affected by the choice of the exchange correlation (XC) potential considered within DFT, we perform a comparative study of the properties by considering two different XC approaches: the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA). We observe that though the electronic structure of the parent compound ZnGa$_2$O$_4$ remains almost unaffected by the change of the XC potential chosen, the kind of Fe substitution (e.g. whether in A-site or in B-site) shows quite different magnetic and transport properties depending on the chosen XC functional.

We will show that the various doping options allow for a variety of interesting behaviors which range from spin-polarized metal to the so-called ‘transport half-metal’. Though both properties are of potential interest for spintronic purposes, we will discuss that alternative choices of substituent or host compound may improve the quality of these properties.

We have organized the paper in the following way. In section II we present a study of the volume optimization of the parent compound within LDA and GGA, which sets the reference frame for the doped cases. In the subsequent three sections (III, IV and V) we analyse the electronic structure properties of Fe-doped ZnGa$_2$O$_4$ within both XC potentials in three different limits, namely, Fe doped in the Zn position, Fe doped in the Ga position and Fe doped into both Zn and Ga positions respectively. Finally in section VI we present the summary of our calculations with a comparison to the available experimental data and conclude with suggestions for some possible future experiments.

II. PARENT COMPOUND

A. Computational details

We have performed DFT calculations using the full-potential linearized augmented plane-wave code WIEN2k. In our calculations, we chose APW+lo as the basis set. The atomic sphere radii were chosen to be 1.8 a.u. for Zn, Ga and Fe and 1.6 a.u. for O. Expansion in spherical harmonics for the radial wave functions were taken up to $l=10$ and the charge densities and potentials were represented by spherical harmonics up to $L=6$.

For Brillouin-zone (BZ) integrations we considered a 60 $k$ points mesh in the irreducible wedge and the modified tetrahedron method was applied.
B. Volume optimization

ZnGa$_2$O$_4$ crystallizes in a normal spinel structure (space group $Fd\bar{3}m$ (227)) with the primitive (rhombohedral) unit cell containing two formula units with Zn, Ga and O at the positions (1/8,1/8,1/8), (1/2,1/2,1/2) and (u,u,u) respectively (where u=1/4 corresponds to a perfect spinel structure). Zn is sorrounded by a tetrahedral environment of oxygens while Ga sits on an octahedral position. In order to adopt a reliable approximation for the XC potential in the description of the parent compound, we performed a full volume optimization within two widely used parametrizations of the XC functional: namely, the LDA and the GGA approach. For each selected volume we also considered the relaxation of the internal coordinate of oxygen (u parameter) as allowed by the symmetry in the space group 227, by using the damped Newton dynamics method, until a force value smaller than 1 mRyd/a.u. was reached. The energy minimum of the various selected volumes defines then the optimal volume. Fig. 1 shows the total electronic energy as a function of the volume of the rhombohedral unit cell for LDA and GGA ($V=\frac{1}{4} a^3$ where a is the conventional cubic cell parameter).

The optimized lattice constant whose experimental value is $a=8.334$ Å, is found to be underestimated in LDA by about 1% and it is overestimated in GGA by about 1.5%. In Table I we show a comparison of tetrahedral (Zn-O) and octahedral (Ga-O) distances between the optimized ones and the experimental ones. Note that the experimental values are underestimated by LDA and overestimated by GGA. This kind of behaviour is generally not unexpected when adopting the LDA or the GGA approximations in the description of semiconductors. For instance, in a recent ab-initio study of the spinel ZnAl$_2$O$_4$, the LDA lattice constant underestimation was found to be of 1.1%. The origin of the LDA and GGA shortcoming may be ascribed to the inability of both approximations to describe properly the binding due to long-range forces like the van der Waals interaction (apart from the inaccuracy concerning exchange and correlation). In contrast, optimization of the u parameter for ZnGa$_2$O$_4$ converges to 0.3861 within LDA and 0.3866 within GGA, both in good agreement with the experimental value of 0.3867.

We have also estimated the residual and less important discrepancies due to the neglect of the zero point and thermal motion of the atoms. Assuming the cubic spinel to be an isotropic three dimensional harmonic oscillator with a spring strength given by the curvature of the energy vs lattice constant function, we estimate the ground state length fluctuation to be 0.019 Å within LDA. This represents a deviation of about 0.2% with respect to the classical adiabatic value. The thermal expansion from zero to room temperature is expected to produce an effect on the lattice parameter less than 0.1%, as inferable from the data of Josties et al., therefore these corrections fall within the inaccuracy of the XC approximations used here.

From the fit of the energy-volume curves of Fig. 1 to the Murnaghan equation of state we extract a bulk modulus for ZnGa$_2$O$_4$ of 217 GPa within LDA and 146 GPa within GGA. Structure optimizations for the spinels ZnAl$_2$O$_4$ and ZnGa$_2$O$_4$ have been performed in the past within the framework of the shell model providing a bulk modulus of 273 and 237 GPa respectively. Recently Levy et al. have measured the bulk modulus of ZnAl$_2$O$_4$ to be 202 GPa well below the value obtained by the shell model (273 GPa). Therefore, assuming that the shell model bulk modulus is affected by the same amount of discrepancy for both ZnAl$_2$O$_4$ and ZnGa$_2$O$_4$ and since our calculated values for ZnGa$_2$O$_4$ are lower than that of the shell model, we expect our results to be in a better agreement to experiment than the shell model result.

We conclude from the previous comparison that the gradient correction to LDA as implemented in GGA doesn’t produce a significant improvement upon the LDA itself as far as the host compound is concerned. However, in the following sections we will see that upon Fe substitution the LDA and GGA outcomes may turn out to be quite different.

![FIG. 1: (Color online) Volume optimization curves for LDA and GGA XC-functionals. The energy scale has been made arbitrary for plotting reasons and the volume scale measures the relative value respect to the experimental one.](image)

| TABLE I: Optimized and experimental tetrahedral and octahedral distances. |
|--------------------------|--------------------------|--------------------------|
|                         | LDA  | GGA  | exp.  |
| Zn-O (Å)                | 1.943 | 1.997 | 1.974 |
| Ga-O (Å)                | 1.975 | 2.018 | 1.991 |
In this section we present the density of states and bandstructure of the parent compound within the LDA and GGA approximations. In Fig. 2 both properties are shown only for the LDA approach since no significant modification is observed within GGA. These results prove to be in good agreement with previous calculations. The spinel ZnGa$_2$O$_4$ is a direct gap semiconductor with a measured band gap of about 4.0 eV. At the Γ point the band gap is calculated here to be 2.7 eV which reminds us of the renown tendency of LDA to underestimate the electronic band gap. No significant improvement on the gap value is detected within GGA. The density of states (DOS) shows the valence band to be mainly $s$ states with a peaked Zn weight due to the full $d$ orbital shell. The Ga $d$ states are confined below -10 eV (not shown) and strongly atomic-like.

It is important here to point out the dispersive feature of the band structure at the Γ point above the Fermi level which has mainly Ga and O character. The associated effective mass is calculated to be 0.28 times the electron rest mass and is rather isotropic; therefore doping with a magnetic ion may open the possibility for a high mobility electronic current which simultaneously might be fully spin polarized, as we will discuss in the next paragraphs. Finally, recalling that the DOS weights are given within the atomic sphere radii in the APW+lo basis, the smallness of the weight of the dispersive $s$ band at Γ (Fig. 2 right panel) is due to the large extension of the $4s$ state outside the sphere (interstitial region).

FIG. 2: (Color online) Bandstructure and decomposed density of states for ZnGa$_2$O$_4$ within LDA. The path chosen in the Brillouin zone is $L = (1/2,1/2,1/2)$, $\Gamma = (0,0,0)$, $X = (0,1,0)$ and $W = (1/2,1,0)$ in units of $2\pi/a$. The DOS is given in units of states per eV and per atom in all the figures.

C. Electronic structure

III. Fe DOPED INTO A POSITION

Substitution of Fe in one of the two Zn sites of the rhombohedral unit cell removes the inversion symmetry from the space group $Fd\bar{3}m$ and reduces it to the maximal subgroup $F\bar{4}3m$ (space group 216). In addition, the original 8 equivalent oxygen positions are now split in two non-equivalent sets (Wyckoff position 16$k$). Defining the doping concentration with respect to the total number of tetrahedral sites, this new structure corresponds to a 50% Fe doping. In a tetrahedral crystal field, the Fe $d$ levels are split into energetically lower $e_g$ states and upper $t_{2g}$ states.

We have calculated the electronic structure for this system within the spin polarized versions of the LDA and GGA approximations. Both approaches lead to very similar results, therefore we discuss here the LDA results and comment on quantitative differences with respect to GGA.

In Fig. 3 the density of states and bandstructure are shown for the spin-polarized LDA case (LSDA). Since no major modification with respect to the parent compound is observed as far as the Zn and Ga weights are concerned and the size of the band gap (2.7 eV) remains unchanged, we show in the DOS only the Fe and O weights (Fig. 3 right panels).

Note the full inclusion of the iron antibonding $3d$ majority (spin up) states within the band gap of the parent compound (Fig. 3 upper right panel), while the $3d$ minority (spin down) states hybridize with the highly dis-
persive s band at the Γ point (Fig. 3 lower right panel). In a previous work by Nonaka et al. the authors did a molecular orbital calculation of one Fe atom doped into the Zn position of a ZnGa₂O₄ cluster and found the Fe d-states to be located in the band gap of the host cluster.

Due to the absence of any d character at the Fermi level for the majority states, we may therefore argue that the conduction properties of this compound are strongly spin-dependent. In fact, the s conduction in the spin down channel may be hindered by the presence of the relatively localized d states which are instead absent in the spin up channel. The situation partially resembles the case of transition metal ferromagnets like Iron, Cobalt and Nickel, where the Fermi level lies in the d band but the effective spin polarization in transport is positive, due to the more mobile 4s(↑) electrons.

The exchange splitting is comparable in size with the band gap (2.7eV) and much larger than the crystal field splitting (0.8 eV). The oxygen hybridization is more pronounced in the majority spin bands than in the minority ones, as indicated by the larger weight of O in the majority states valence band. This is ascribed to the t₂g symmetry of the filled majority states which in a tetrahedral ligand field have a σ-bonding with oxygen, in contrast to the minority t₂g states which are here almost empty.

According to an ionic picture, iron in A position is expected to assume a 3d⁶ (Fe²⁺) configuration in a high spin state with a magnetic moment of 4 μB. The calculated total magnetic moment per unit cell is 4.01 μB and is distributed mainly among Fe, O₁ and interstitial contributions in a proportion 3.19, 0.08 and 0.47 μB, respectively. Recalling that the iron muffin tin radius considered in the calculation is 0.95 Å, we expect the interstitial magnetic moment to be mainly due to the d orbital tails leaking out of the atomic sphere.

Calculations within GGA give a total magnetic moment per unit cell of 4.03 μB, and the Fe, O₁ and interstitial moments are 3.28, 0.07 and 0.46 μB, respectively. Looking at the Fe moment one clearly sees a larger degree of localization within GGA with respect to LDA. To confirm this, we examine the total amount of charge in the atomic spheres and we find that it is increased in GGA respect to LDA. No other important differences have been detected.

Because of the highly localized nature of iron d states, one may argue about the importance of inclusion of orbital on-site correlations on top of a mere LSDA approach. We have performed a LDA+U calculation and considered two different versions of the double counting correction, namely AMF ("around mean field") by Cyzyk and Sawatzky and FLL (full localized limit) by Anisimov et al. (U=4.5 eV and J=1 eV). No relevant modification respect to the LSDA case has been noted in both cases. In fact, the LDA+U method aims at producing a fully orbitally polarized ground state by opening a gap between the occupied and non-occupied states. In the present case both versions result only in increasing the crystal field splitting c_{g-t_2g} of the minority states just above the Fermi level pushing the upper 3 t₂g bands further above.

It is also interesting to note that the ionic radii of Zn²⁺ and Fe²⁺ in a tetrahedral coordination are very similar, namely 0.6 and 0.63 Å. As a consequence, the global (lattice parameter) and local (tetrahedrally coordinating oxygen) readjustment of the structure due to the substitution is expected not to bring major modification to the electronic properties above discussed. This is in fact confirmed within both the GGA and LDA calculations where the force values acting on the O and Ga atoms are around 1 mRyd/a.u. and therefore negligible. This also confirms the minor importance of the differences between the two approaches when Fe is substituted in a tetrahedral site. In the next section we shall see that important differences appear when Fe is substituted in an octahedral site.

To determine the ground state magnetic order of this systems we performed an antiferromagnetic calculation doubling the present unit cell. Comparing the total energies of antiferro- and ferromagnetic configurations we found that the ferromagnetic state is lower in energy by about 61 meV. This state was also predicted to be the ground state in this doping limit from a proposed phenomenological model in an earlier communication by two of us.

IV. Fe INTO B POSITION

Substituting iron into 1 of the 4 Ga sites of the primitive unit cell of ZnGa₂O₄ causes the lattice symmetry to lower from cubic (space group 227) to the rhombohedral space group R3m (166). In this group, the 8 equivalent oxygen positions of the parent group (Wyckoff position 32e) split into 2c and 6h positions, with the latter being the oxygen atoms octahedrally coordinating iron. In an octahedral environment, the 3d orbitals of Fe are split into energetically lower t₂g and higher e_g manifolds.

For the present case we find a significant difference between the LDA and GGA outcomes. In fact we performed volume optimizations for both approaches and we find that LDA produces as a ground state an intermediate spin state for Fe, i.e. the unit cell magnetic moment is calculated to be 1 μB. Therefore, within a simplifying ionic picture, only the t₂g manifold is populated with 3 electrons in the up sector and 2 in the down one, resulting in a Fe³⁺ oxidation state in the low-spin state 1/2.

On the contrary, GGA describes Fe in a high-spin state with a unit cell magnetic moment equal to 5 μB. The reason for this strong difference may be connected to the element Fe itself. According to LDA, Fe is predicted to be non-magnetic and with a fcc structure while within GGA the correct magnetic bcc structure is found. Therefore we may expect GGA to be more reliable than LDA for the B site doping.

Another reason in favour of GGA is the end compound zinc ferrite, ZnFe₂O₄, where Fe replaces all the Ga atoms.
Recent bandstructure calculations\(^2\) have shown that the zinc ferrite behaves as a metal within LDA and as an antiferromagnetic insulator with a small gap within GGA. The transport gap has been measured to be 0.2 eV\(^{26}\) in support of the GGA outcome.

We can understand the strong discrepancy between LDA and GGA with the help of the Table \(\text{II}\) and recalling the typical Fe-O distances for the high-spin state of Fe (2.2-2.3 Å) and for the low-spin state (1.8-1.9 Å). We see that the Ga-O LDA distance is a low-spin distance, therefore after substitution and after volume optimization the Fe-O distance, which increases only by 1-2%, will remain of the low-spin state type. On the contrary the GGA Ga-O distance is much closer to the high-spin region and thus after volume optimization Fe will be in a high-spin state.

In Fig. 4 we present the GGA bandstructure and DOS. As in the previous case, the band gap of the parent compound remains approximately unchanged (~ 2.7 eV). The majority spin \(d\) states of iron (Fig. 4 upper panel) are fully occupied, of which the \(t_{2g}\) subband completely hybridizes with the oxygen valence band and the \(e_g\) antibonding states set the Fermi level. Concerning the minority states (Fig. 4 lower panel), those antibonding with oxygen are completely empty implying that the Fe is in an oxidation state \(3^+\).

From Fig. 4 we find thus a zero-temperature insulator with a band gap of 0.4 eV. It is interesting to compare this band gap with that of the end compound \(\text{ZnFe}_2\text{O}_4\) where within GGA it is calculated to be one order of magnitude less.\(^2\) This can be ascribed to the direct cation-cation bonding in the case of \(\text{ZnFe}_2\text{O}_4\). Since the Fe atoms are at the center of edge sharing oxygen octahedra, the \(t_{2g}\) orbitals are able to directly overlap among each other producing a widening of the \(t_{2g}\) bands due to hybridization. This causes the minority \(t_{2g}\) bands just above the Fermi level to become closer to \(E_F\) with a consequent reduction of the band gap. The spin splitting for the present doped system is of about ~2.5 eV, similar to the previous case, but the crystal field splitting is around ~1.8 eV, more than the double as for the previous case.

The unit cell magnetic moment which is calculated to be 5.0 \(\mu_B\) within GGA, is distributed mostly among the Fe muffin tin sphere, interstitial region and oxygen muffin tin sphere in a proportion 3.93, 0.40 and 0.10 \(\mu_B\) respectively.

Note that in this case, at the \(\Gamma\) point the \(d\) band in the minority sector remains above the Fermi level due to the oxidation state of Fe (3+) which leaves the minority antibonding \(d\) states unpopulated. Moreover, due to the larger crystal field effect, only the \(e_g\) bands hybridize with the 4s band at \(\Gamma\) while the \(t_{2g}\) states are pushed down just above the Fermi level. Therefore, if we were to reproduce a situation similar to the A site case (see previous section) in which the 4s band should be at the Fermi level, we would need a transition metal in a 3+ oxidation state with 9 electrons in the \(d\) shell, namely \(\text{Zn}^{3+}\), which doesn’t exist.

In conclusion, we find that doping Fe into Ga site in a concentration of 25% results in an antiferromagnetic semiconductor at zero temperature which could show conducting properties with increasing temperature. Namely, the \(t_{2g}\) minority states can be thermally populated and produce a spin-polarized current. But, due to flatness of the \(t_{2g}\) bands just above the Fermi level the mobility of the carriers would be very low. On the contrary, due to the strong difference in the hybridization of \(e_g\) and \(t_{2g}\) states with oxygen, the \(e_g\) bandwidth is much larger than the \(t_{2g}\) one, as clearly seen from the bandstructure shown in Fig. 4. Therefore, setting the
Fermi level into the majority $e_g$ manifold would induce a half-metallic behaviour with a fully spin-polarized current. This can be achieved by doping for instance with Mn instead of Fe.

V. Fe DOPED INTO A AND B POSITIONS

The third case that we considered in this study is the doping of iron in both sites A and B in a ratio 1:2 (Fe$_A$:Fe$_B$) and in a total concentration of 25 %. Accordingly, we double the rhombohedral primitive unit cell of the parent compound into a tetragonal unit cell containing 4 Zn, 8 Ga and 16 O. Defining the doping concentration with respect to the total number of occupied cation sites, 25 % doping of Fe (in both A and B sites) corresponds to substituting 1 Zn with 1 Fe and 2 Ga with 2 Fe in the tetragonal unit cell. Two inequivalent structures turn out to be consistent with this sort of doping (Figs. 5 (i) and (ii)), both belonging to the space group $Pm\overline{3}m$ (6). In the structure (i) the Fe$_A$ and Fe$_{B2}$ atoms form zigzag chains with O atoms in between them (e.g. Fe$_A$-O-Fe$_{B2}$-O-Fe$_A$) along the a direction and the Fe$_{B1}$ atoms are connected to the Fe$_A$ through O along the c direction. The angles Fe$_A$-O-Fe$_{B1}$ and Fe$_{B1}$-O-Fe$_{B2}$ are equal to 121° and there is no direct path between Fe$_{B1}$ and Fe$_{B2}$. In the structure (ii) the two Fe$_B$ are crystallographically equivalent and their distance is much shorter (2.92 \AA) than in the case (i) (5.83 \AA), therefore direct metal-metal bonding is realized in this situation.

To clarify the role of the on-site correlation typical of the transition metal ions for the present case we have performed calculations within the LDA+U potential, besides the GGA one. We will present here only the LDA+U results since no major differences have been detected from the GGA outcome. (The LDA calculation has not been taken in consideration because of the failure of LDA in describing Fe in the B case.) The values considered for the Hubbard and exchange parameters U and J are 4.5 and 1 eV, respectively.

In Fig. 6 we present the spin polarized density of states (DOS) and related bandstructure within L(S)DA+U for the structure of Fig. 5 (i). We have adopted a ferrimagnetic alignment of the Fe spins, specifically the Fe$_A$ spins are up and Fe$_B$ spins are down. Therefore the majority states of Fe$_A$ are spin up and the majority states of Fe$_B$ are spin down. The upper panel of the Fig. 6 which shows the bandstructure and DOS of the spin up species, will contain the Fe$_A$ majority states and the Fe$_B$ minority states, while the lower panel of Fig. 6 (spin down species) will contain the Fe$_A$ minority states as well as the Fe$_B$ majority states.

In Fig. 6 we present a simplified schematic energy level to show the approximate location of the $d$-bands of Fe$_A$ and Fe$_B$.

As the two Fe$_{B1}$ and Fe$_{B2}$ bands have rather similar features, we show in Fig. 6 (right panel) the sum of the two Fe$_B$ weights. In the energy range from -10 eV to about -3 eV the host compound valence band is found to have predominant oxygen character. In this range the Fe-O hybridization occurs mainly in the Fe$_B$ spin down bands (see lower panel of Fig. 6) and less importantly in the Fe$_A$ states. In the interval from -3 eV to -1 eV the impurity bands are clearly visible: the spin up bands (see upper panel) show the Fe$_A$ $e_g$ nonbonding and the $t_{2g}$ antibonding states in the order of increasing energy, and the spin down bands (lower panel) are mainly Fe$_B$ $e_g$ antibonding states spanning the same energy range. At the Fermi level (see also Fig. 6) the Fe$_A$ $e_g$ spin down band (lower panel), due to the lowering of the point symmetry at the A site, splits into an almost fully occupied band and an empty $e_g$ band at about 1.5 eV above the Fermi level. In the upper panel, the Fe$_B$ $t_{2g}$ spin up bands are found slightly occupied and above them we distinguish the empty Fe$_B$ $e_g$ states. In the same energy range we find in the lower panel the split $e_g$ spin down bands and the $t_{2g}$ bands of Fe$_A$. The effect of U will be discussed in the next paragraph.

According to an ionic picture, the oxidation states of Fe$_A$ and Fe$_B$ would be 2+ and 3+ respectively. However, due to the small overlap of opposite spin bands at the Fermi level, the ionic values are slightly changed (increased for Fe$_A$ and reduced for Fe$_B$). In fact the magnetic moment of the unit cell is found to be -5.97 $\mu_B$, while in the case of an ionic picture it would be -6 $\mu_B$, since the magnetic moment of Fe$_A$ and Fe$_B$’s are respectively 4 $\mu_B$ and -5 $\mu_B$ (4+2(-5)). A comparison with magnetite, which represents the end compound for Fe dopings in both A and B sites and it has a fully inverted spinel structure, i.e. (Fe$_{A^{3+}}$)(Fe$_{B^{2+}}$Fe$_{B^{3+}}$)O$_4$ tells us that in the compound (i) the Fe valence states are beginning to invert, namely the Fe$_A$ increases its oxidation state towards 3+ and Fe$_B$ decreases it to 2.5+.
An important point concerning the bandstructure shown in Fig. 6 is the role of the Hubbard U in the semimetal picture. Since the Hubbard U represents the on-site Coulomb correlations and no intersite Hubbard V has been included in our calculations, no effect on the electronic structure at the Fermi level of Fig. 6 is expected by varying U since it contains two sets of bands originating from two different sites. In fact, we performed a further calculation changing the U value of Fe$_A$ and Fe$_B$ and, as expected, only a relative shift respect to the Fermi level is found for occupied (downwards shift) and unoccupied (upwards shift) states leaving the relative position of the up and down bands at the Fermi level unchanged. The main effect of the Hubbard U is thus to open a gap between occupied and unoccupied states and to increase the crystal field splitting which is already taken into account by an only LDA description. Therefore in the case of Fe$_B$ sites, the Hubbard U just adds to the exchange interaction constant since the down states are fully occupied and the up states are almost completely empty, while in the case of Fe$_A$ site due to the presence of Fe$_B$ as second nearest neighbour, which further splits the degeneracy of the e$_g$ bands, the Hubbard U transforms this split into a sizeable gap. In a pure LSDA treatment the Fe$_A$ e$_g$ down bands wouldn’t show a relevant splitting, thus overlapping with Fe$_B$ t$_{2g}$ up bands and the conduction band wouldn’t have an almost pure spin polarization nature as in the present case.

Another important effect to take into account is the unit cell expansion or contraction due to the replacement of some of the Zn and Ga atoms with Fe. In this case we cannot describe Fe$_A$ and Fe$_B$ as in a 2+ and 3+ oxidation states, respectively, since the compound is partially inverted, and thus we cannot expect minor changes of the structure due to the similar ionic radii of Zn$^{2+}$ with Fe$^{2+}$ and Ga$^{3+}$ with Fe$^{3+}$, as seen in the previous cases. To have an idea of the structural modification, we recall that the ionic radius of Fe$^{3+}$ in A site is 0.49 Å and it is 0.78 Å for Fe$^{2+}$ in B site, while the Zn$^{2+}$ and Ga$^{3+}$ ionic radii are respectively 0.6 Å and 0.62 Å. We shall discuss the atomic forces for the present structure at the end of this section.

Finally, we can attempt a rough estimation of the ferromagnetic ordering temperature by exploiting the analogy with magnetite Fe$_3$O$_4$. The latter is known to have the highest ferrimagnetic temperature of 858 K. Considering the expression $k_B T_N \approx 4\sqrt{J_{AB}S_A S_B}$, where the coupling constant $J_{AB}$ between two B sites and between two A sites ($J_{AA}$) has been neglected with respect to the magnitude of $J_{AB}$, one obtains a good estimation of the Néel temperature for magnetite when $J_{AB} \approx 19 K$. In our case we assume a simple multiplicative rescaling effect of the magnetic ion concentration on the geometric factor $4\sqrt{J}$ and that the exchange constant doesn’t depend on the absolute spin value of the two Fe. Calculating the total energy differences between the ferromagnetic and ferrimagnetic alignment of the Fe spins we obtain an exchange constant $J_{AB}$ value of 25 K which by means of the above formula provides us with a transition temperature of 260 K.

We now discuss the case Fig. 6(ii). It is important to note that the driving mechanism here is due to the
Fe$_B$-Fe$_B$ bonding while in case (i) Fe$_B$ are connected to Fe$_A$ through oxygen and no direct Fe$_B$-Fe$_B$ bonding is realized.

Fig. 5 shows the total and decomposed densities of states within L(S)DA+U of both spin species. The magnetic ground state is found to have antiferromagnetic order between Fe$_A$ (majority spin $\uparrow$) and Fe$_B$ (majority spin $\downarrow$). The spin up bands (upper panel) of Fe$_A$ and Fe$_B$ are completely filled and confined in the valence band which has a charge gap of about 1eV with respect to the down spin manifold. The spin down bands (lower panel) are at the Fermi level for both Fe$_A$ and Fe$_B$, indicating a mixed valence oxidation state. Similar to case (i), the point symmetry at the Fe$_A$ site is reduced by the presence of next nearest neighbor Fe$_B$ which leads to the splitting of the Fe$_A$ eg band into two non-degenerate bands. One of them is completely empty (the peak just above $E_F$) and the other partially filled (the peak at $E_F$). The remaining charge partially occupies the antibonding spin up Fe$_B$ bands which have $t_{2g}$ symmetry. The system thus prefers to assume a partially inverted structure with respect to the fully inverse one of magnetite where only Fe$_B$ antibonding states are at the Fermi level. Due to the shorter Fe$_B$-Fe$_B$ distance of 2.92 Å the metal-metal bonding produces a larger bandwidth of Fe$_B$ states at $E_F$ as well as a higher electronic population of Fe$_B$ states in (ii) with respect to (i) as is clear by comparison of the DOS of the minority Fe$_B$ states between case (i) and (ii) (see Figs. 6 and 8 upper panel). We may therefore conclude that the degree of inversion in (ii) is larger than that in (i) and we may then argue that the driving mechanism in the inversion of magnetite is due to the direct cation(B)-cation(B) bonding.

Moreover, from the bandstructure (Fig. 8) it is clear that the spin down Fe$_A$ band at $E_F$ (lower panel) is much less dispersive than the spin up Fe$_B$ band (upper panel) resulting in a Mott-Hubbard like behavior of the A site. Therefore, we find here a particular kind of half-metallic behavior of the system with respect to the conventional full spin polarized half-metals. In fact, both spin species are here present at the Fermi level but only one of them ($\downarrow$ $t_{2g}$ Fe$_B$ states) is significantly conducting while the other ($\uparrow$ $e_g$ Fe$_A$ states) is strongly localized. This kind of system is called transport half-metal as opposed to a conventional half metal where the spin polarization (P) is 100%. We calculated the value of P for the present case according to the definition $P_n = \frac{N(v_n^{\uparrow}) - N(v_n^{\downarrow})}{N(v_n^{\uparrow}) + N(v_n^{\downarrow})}$, where $N$ is the density of states at the Fermi level for the two spin species and $v$ the respective Fermi velocity. From the calculated band structure and DOS we derive a value of $P_1$ equal to 35 % and of $P_2$ equal to 81 %. Since the bulk current is proportional to $N(E_F)v_2^2$, the $P_2$ value implies that 90.5 % of the current is carried by the spin $\uparrow$ electrons, (namely the minority spins of Fe$_B$) and a transport half-metal is clearly realized.

However, we should recall that the charge carrier concentration in this case is less than that in magnetite and therefore the metallicity of this system is poorer than the one of magnetite.

Finally, some considerations on the stability of the proposed structures should be done at this stage. Due to the lack of implementation of atomic forces calculation for an LDA+U potential in the WIEN2k code and aware of the fact that the inversion issue in spinels is not intrinsically due to on-site Hubbard effects, we have estimated the instability of structures (i) and (ii) respect to inversion by evaluating atomic forces within the GGA potential. The structures (i) and (ii) considered here are the GGA optimized ones and have not been relaxed after replacement of Zn and Ga with Fe. In Table II we show the moduli of the forces acting on Fe$_A$, Fe$_B$ and the oxygen connecting them, which are the most significant ones. Note the difference in magnitude between cases (i) and (ii) for Fe$_A$ and oxygen due to the larger degree of inversion of (ii) respect to (i). Comparing the force directions (not shown in the Table) we see that the distance between Fe$_A$ and oxygen has to become shorter, testifying the tendency of both structures to invert. Clearly the structure (ii) is significantly more unstable than the structure (i).
TABLE II: Comparison of forces on Fe and O atoms in structure (i) and (ii) (units mRy/a.u.)

|       | Fe\textsubscript{A} | Fe\textsubscript{B} | O    |
|-------|---------------------|---------------------|------|
| (i)   | 20.589 6.623 36.442 |                     |      |
| (ii)  | 40.395 9.240 60.324 |                     |      |

VI. CONCLUSIONS

In conclusion, we have performed a systematic \textit{ab-initio} study of Fe doped ZnGa\textsubscript{2}O\textsubscript{4} to investigate the effect of Fe substitution on the electronic structure of the parent spinel compound ZnGa\textsubscript{2}O\textsubscript{4}. For an accurate account of the magnetic and transport properties we considered various exchange correlation functionals and we observed that the electronic properties of the doped system depend significantly on the exchange-correlation functional used, especially when Fe is doped on the Bcation site or on both A and B cation sites of the spinel compound. Whereas in the case of Fe doped in the A site both LDA and GGA give qualitatively the same results (close to an ionic picture), B-site doping leads to different ground state spin of Fe within LDA and GGA. During the course of this study we also tried to explore the possibilities of obtaining a strongly polarized half-metallic groundstate which is a desirable property for spintronic applications. We observed that Fe doping in A-site could give rise to a spin polarized current due to the presence of highly dispersive s band in one spin channel. In B-site, Mn instead of Fe could lead to a half-metallic state by setting the Fermi level in a comparatively wider $e_g$ band in the spin up channel. Doping both A and B sites with Fe leads to a so called 'transport half metal' when there is a direct Fe-Fe bonding in the B-sites.

Finally, recent work on [ZnGa\textsubscript{2}O\textsubscript{4}]\textsubscript{1-x}[Fe\textsubscript{3}O\textsubscript{4}]\textsubscript{x} for various large Fe doping concentrations, showed the existence of a ferromagnetic phase up to 200K. Mössbauer spectra were measured and provided a quadrupolar splitting of 0.52 mm/s. Assuming a nuclear quadrupole moment for $^{57}$Fe of 0.16 barn, as calculated in ref.\textsuperscript{28} within the LAPW method, the resulting electric field gradient (EFG) is 3.12 V/cm\textsuperscript{2}. Alternatively, assuming a nuclear quadrupole moment of 0.2 barn, as calculated in ref.\textsuperscript{28}, the EFG is 2.5 V/cm\textsuperscript{2}. When Fe is substituted into an A site no EFG develops due to the spherical local symmetry at the nucleus. Instead, in the case of Fe doped into B site the optimized structure provided us with an EFG at the Fe site of 2.11 V/cm\textsuperscript{2}, which compares fairly well with the experimental values. In the doping case of Fe into A and B sites we didn’t perform a structure optimization, and, since EFG is quite sensitive to structural changes, we obtain quite different values with respect to the experimental ones.

The Mössbauer experiment of Risbud \textit{et al.} detected the presence of only Fe\textsuperscript{3+}. This result would discard the option of Fe doped in the A site in favor of Fe doped on the B site since from our calculations Fe in the A site takes up an oxidation state close to 2+ and not to 3+. In fact, in ZnGa\textsubscript{2}O\textsubscript{4} the site preference of Zn\textsuperscript{2+} towards the tetrahedral sites is much stronger than the Fe one\textsuperscript{29} and this can explain why Risbud \textit{et al.} detected the presence of only Fe\textsuperscript{3+}, which probably occupies predominantly B sites. Alternatively, Mg\textsuperscript{2+} has a weaker preference for the A site than Ga and Fe, therefore replacing Zn\textsuperscript{2+} with Mg\textsuperscript{2+} can provide a practically easier way to populate A sites with Fe, and MgGa\textsubscript{2}O\textsubscript{4} would be a better host candidate for the properties presented here concerning Fe doping on the A site.

Acknowledgements We would like to thank R. Seshadri for useful discussions and the German Science Foundation for financial support. We would also like to thank P. Blaha for helpful discussion regarding the code WIEN2k.
15 D. Levy, A. Pavese, A. Sani and V. Pischedda, Phys. Chem. Miner. 28, 612 (2001).
16 S. K. Sampath and J. F. Cordaro, J. Am. Ceram. Soc., 81, 649 (1998).
17 S. K. Sampath, D. G. Kanhere and R. Pandey, J. Phys.: Condens. Matter 11, 3635 (1999).
18 International Tables for Crystallography; Ed. by Th. Hahn, Kluwer Academic Publishers (2002).
19 M. Nonaka, S. Matsushima, M. Mizuno and C. Zu, Key Engineering Materials 228-229, 303 (2002).
20 M.T. Czyzyk and G.A. Sawatzky, Phys. Rev. B 49, 14211 (1994).
21 V.I. Anisimov, I.V. Solovyev, M.A. Korotin, M.T. Czyzyk and G.A. Sawatzky, Phys. Rev. B 48, 16929 (1991).
22 T. Maitra and R. Valenti, J. Phys.: Condens. Matter 17, 7417 (2005).
23 P. Bagno, O. Jepsen and O. Gunnarsson, Phys. Rev. B 40, 1997(R) (1989).
24 D. J. Singh, M. Gupta and R. Gupta, Phys. Rev. B 63, 205102 (2001).
25 J. S. Kouvel, Phys. Rev. 102, 1490 (1956).
26 M. El-shabasy, J. Magn. Magn. Mater. 172, 188 (1997).
27 B. Nadgorny et al., Phys. Rev. B 63, 184433 (2001).
28 Philipp Dufek, Peter Blaha, and Karlheinz Schwarz, Phys. Rev. Lett. 75, 3545 (1995).
29 D. W. Mitchell et. al., Phys. Rev. B 53, 7684 (1996).
30 A. Navrostky and O. J. Kleppa, J. Inorg. nucl. Chem 29, 2701 (1967).