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Structural, electronic, magnetic and hyperfine properties of Fe₂AlO₄ and FeAl₂O₄. A DFT study.

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Abstract

In this work, the structural, electronic, magnetic, and hyperfine properties of two Fe-Al spinel oxides, namely FeAl₂O₄ (hercynite) and Fe₂AlO₄ (Al-ferrite) were studied by means of Density Functional Theory (DFT)-based first principles calculations. To determine the structural and magnetic equilibrium structures of both oxides, different cationic inversion degrees, magnetic configurations and distributions were considered for Fe and Al ions in the octahedral and tetrahedral sites of the spinel structures. Calculations confirmed the preference of the Al ions to occupy the octahedral cationic sites and predicted that both Fe-Al spinel oxides present a semiconductor nature. They also enabled the determination that the lowest energy structure of FeAl₂O₄ corresponds to an antiferromagnetic normal spinel, in which Fe^{2+} ions populate the tetrahedral sites and Al^{+3} ions occupy the octahedral B sites. Partial inversion cases are also discussed for this system. The lowest energy structure of Fe₂AlO₄ corresponds to a system with a net magnetic moment in which eight Fe^{+2} ions populate the A sites and eight Fe^{3+} and eight Al³⁺ ions populate the B sites. It was also shown that FeAl₂O₄ presents a lower formation energy than Fe₂AlO₄. By comparing the predictions for the hyperfine parameters at the Fe sites with the experimental results obtained in the Mössbauer experiments, the validity of the proposed structural and magnetic structure of FeAl₂O₄ was confirmed. Finally, a discussion is made to compare the results of this study with the Mössbauer results

reported in the literature for Fe₂AlO₄.

Keywords: FeAl₂O₄, Fe₂AlO₄, Ab-initio, DFT, Spinel, Magnetism.

1. Introduction.

In recent years, modelling different kinds of materials in the framework of the Density Functional Theory (DFT) has allowed a deeper understanding of structural, electronic, magnetic, optical and transport properties (among others). Moreover, the combination of DFT-experimental results raises the possibility to correlate fine details of the electronic structure of a given system with its physical properties [1-3] and the role of defects in the origin of these properties. For these reasons, computational modelling has become a powerful tool in material science [7].

Among the oxide universe, spinel oxides have received considerable attention from both experimental and theoretical sides due to their intriguing electronic and magnetic properties and technological importance [2, 5, 8-13]. Progress in synthesis techniques raises a new interest in these oxides to improve their physical properties and expand their applications. Spinel oxide compounds take their name from the mineral MgAl₂O₄ and have the general formula XY₂O₄, where X represents a divalent transition metal (Mg, Mn, Zn, Cu, Fe, among others) and Y is a trivalent element, for example, Al, Fe, V, Co, or Mn, among others [8]. The spinel structure is characterised by two inequivalent cationic sites, tetrahedral (A) and octahedral (B) organized in a close-packed structure with a ratio of A sites /B sites = 1/2. The distribution of X^{2+} and Y^{+3} ions in the A and B sites can be expressed by $(X_{1-\delta}Y_{\delta})_A[X_{\delta}Y_{2-\delta}]_BO_4$, where round and square brackets denote the A- and B-sites, respectively, and δ is the so-called inversion parameter. When Y or X (or Y and X) are magnetic ions, super-exchange interaction between the magnetic cations can occur via intermediate oxygen ions because of A-O-A, B-O-B and A-O-B couplings. The arrangements of X and Y ions at sites A and B promotes competition between the possible super-exchange interactions and gives rise to a wide spectrum of magnetic behaviours and structures [12-18]. For this reason, the study of thin films or nanoparticles of these systems is intensive, and much remains to be learned about their properties when forming low-dimensional arrays and their combination in heterostructures [5, 16-18].

Fe-Al spinel oxides are compounds of great interest in areas such as geology and mineralogy [19-21]. Also, due to their versatile properties, these materials have potential applications in emerging technologies such as catalysts and nano pigments [22-25] and

magnetic nanocatalysts [26], among others. Hercynite presents a semiconducting nature, with a band gap in the order of approximately 3.1 eV [25], which fits in the range for application in photo-catalysts systems and as stable pigment for Dye-sensitised solar cells (DSSCs).

Ternary Fe-Al oxides crystallise with two possible stoichiometries, FeAl₂O₄ (hercynite) and Fe₂AlO₄ (Al-ferrite), with hercynite being the more stable. Hercynite is formed under relatively high temperatures and pressures and its synthesis is often problematic by traditional solid-state reaction methods [21]. Fe₂AlO₄ is reported as a meta stable phase [26] and for this reason, the experimental and theoretical studies of Al-ferrite are scarce.

Different experimental works reported structural, electronic, and magnetic characterizations of FeAl₂O₄ [21-31]. Given that Al is a trivalent cation, Al exhibits a strong preference for the octahedral B site of the spinel structure. Fe can be a divalent or trivalent cation, so Fe can occupy both tetrahedral and octahedral sites, but it is well-known that Fe cations prefer the tetrahedral site [32]. Based on these simple considerations, it is expected that Fe²⁺ ions occupy A sites and Al³⁺ ions B sites, (normal structure, (Fe)_A[Al]_BO₄). But, experimental studies reported by Jastrzebska et. al. [21, 27], Tristan et al. [33], and Fukushima et al. [31] revealed that different occupations of the cationic sites (inversion degrees) can be obtained depending on the synthesis method, demostratring that the analysis of hercynite has multiple challenges, and the comparison theory-experiments must be performed carefully. Although FeAl₂O₄ has a normal spinel structure, it is important to explore the effect of cationic inversion on its different properties.

⁵⁷Fe-Mössbauer spectroscopy (MS, Ref. 34 and 35) was also applied in the study of FeAl₂O₄ [36, 37]. ⁵⁷Fe-MS enables the determination of magnetic and charge symmetry-related properties, making it possible to obtain a complete description of the electronic and magnetic configuration near and at the ⁵⁷Fe probe nucleus [35]. All the information contained in the experimental results can be extracted by comparing it with *ab initio* predictions performed assuming different structural, magnetic, and electronic models (see Ref. 1 and 38).

From the theoretical side, calculations at the DFT+U level predict that hercynite crystalize in the normal structure and behaves as an insulator (band gap of 2 eV) [39] and, in clear contradiction with the previously mentioned work, M. Yaseen *et al.* reported that FeAl₂O₄ is a half-metallic ferromagnet [30].

In the case of the Al-ferrite, Choi *et al.* [40] prepared Fe₂AlO₄ nanoparticles and investigated its structural, magnetic, and thermal properties. Also, Dong *et al.* [26, and ref 10-12 therein] reported the formation of Fe-Al-O systems. Magnetite-based spinel solutions were prepared by thermal treatments performed at temperatures below 1597 °C. Aluminum-spinel and its spinel solid solution may also be prepared by thermal treatments below 1780 °C. From the theoretical side, Walsh *et al.* reported a DFT-based study of the structural properties of normal and inverse Fe₂AlO₄ [39].

In this work, a DFT-based *ab initio* study of the structural, electronic, and magnetic properties of FeAl₂O₄ and Fe₂AlO₄ is presented considering three aspects that define the stability and formation of the Al-Fe spinel systems: the inversion degree, the spin configuration and, in the case of the inverted structures, the distribution of Fe and Al atoms at the cationic sites of the structures. Our predictions are compared with different experimental and theoretical results and ⁵⁷Fe-MS characterizations reported in the literature to give confidence to our predicted equilibrium structures and to discuss the origin of the properties under study. Therefore, our theoretical study provides structural, magnetic, and hyperfine information that can be useful for the assignment of crystallographic phases of Al-spinel compound observed in the experiments.

This paper is organised as follows. Section 2 details the calculation method used, Section 3 presents and discusses the results for each system under study, and finally, Section 4 summarizes the conclusions.

2. Theoretical and computational methods.

The crystal structure of XY₂O₄ spinel oxides belongs to the space group *Fd-3m* (Oh7) [8]. The structure is characterised by a face-centered cubic (F.C.C.) lattice with a close-packed arrangement of oxygen ions having two crystallographic sites for the cations, the A sites (tetrahedral oxygen coordination, Wyckoff position 8*a* (1/8, 1/8, 1/8)) and the B sites (octahedral oxygen coordination, 16*d* positions, (1/2, 1/2, 1/2)), see Figure 1. The oxygen atoms are located at 32*e* (*u*, *u*, *u*) positions of the FCC structure.

Three variables define the Al-Fe spinel oxides structure and must be considered in the calculations: the inversion degree, the spin configuration and, in the case of the inverted structures, the distribution of Fe and Al atoms in the cationic sites of the structures. For our study, a cubic cell that contains 56 atoms was used as a repetition unit for the calculations. This approach is computationally expensive but enables us to consider different occupations of the cationic sites by the Fe and Al atoms. Also, different magnetic

configurations with low symmetry can be explored to determine the structural and magnetic equilibrium structures for each Fe-Al spinel oxide.

The atomic arrangement of FeAl₂O₄ (hercynite) is composed of eight Fe, 16 Al, and 32 O atoms. The reported experimental lattice parameter of hercynite varies between 8.132 Å and 8.21 Å [17, 25, 31-33] depending on the sample preparation and growth conditions. As a starting point, *a* was set to 8.1572 Å and *u* to 0.2653 [33] for the normal structure. In the case of the Fe₂AlO₄, 16 Fe, 8 Al and 32 O atoms constitutes the Al-ferrite structure. The initial input data were the theoretical lattice parameters obtained by Walsh *et al.* (*a*=8.23 Å and *a*=8.43 Å for the normal and inverted structures, respectively [39]).

The calculations were performed using the DFT-based [41-43] ab initio Full-Potential Linearized Augmented Plane Waves plus the Local Orbital (FP-LAPW+lo) method as embodied in the WIEN2K code [44]. The exchange and correlation potential was described using the Wu-Cohen parameterization of the generalised gradient approximation (GGA) [45]. To better describe the highly correlated 3d orbitals of Fe, a Hubbard U term (GGA+U approach) was included in the framework self-interaction correction scheme [46]. In this work, U was set to 5.0 eV [1, 38]. This value is also supported by the linear-response approach, which enables the estimation of the parameters entering in the GGA+U calculations in a self-consistent approach [47, 48]. The muffin-tin radius (R_{MT}) of Fe, Al and O atoms were set to 2.0 Å, 1.8 Å and 1.5 Å, respectively. The parameter RK_{max} , which controls the size of the basis set, was set to 7 (here R is the smallest muffin-tin radius and K_{max} is the largest wave number of the basis set). The integration in the reciprocal space was performed using the tetrahedron method taking 25 k-points in the first Brillouin zone. In all cases, equilibrium cell volumes were determined, and the atomic positions were refined until forces on the ions were below the tolerance criteria of 2 meV/Å. From a careful study of the dependence of our results with the choice of the convergence parameters (basis set, k-points sampling, R_{MT}s, tolerance criteria for the structural refinement) the energy differences are converged in less than 5 meV/unit formula (u.f.). Finally, for some selected systems we performed calculations including spin-orbit coupling. We found that, in these systems with low symmetry, the inclusion of spin-orbit coupling does not affect the conclusions relative to the lower energy structural and magnetic phases, electronic structure, and hyperfine properties.

3. Results and discussions.

3.1. Structural and magnetic properties

In this section, the results of the structural and magnetic equilibrium configurations for FeAl₂O₄ and Fe₂AlO₄ are presented. The electronic and hyperfine properties of hercynite and the Al-ferrite equilibrium structures will be discussed in the next sections. First, we will discuss the FeAl₂O₄ system.

Based on the calculations performed considering different inversion degrees, distributions of Fe and Al cations at the B sites of FeAl₂O₄, and magnetic configurations, it was confirmed that the Al cation exhibits a strong preference for the octahedral B sites, while the Fe cations prefer the tetrahedral A sites, in agreement with previous results reported in the literature [39]. Employing Bader analysis [49], the charges in the Fe-, Al-, and O muffin-tin spheres were determined for the normal structure of FeAl₂O₄, (Fe)_A[Al₂]_BO₄. It was found that, irrespective of the magnetic configuration considered, the electronic charges inside the muffin-tin spheres of Fe atoms located at the A sites, and Al atoms at the B sites and O atoms were 23.94e, 10.63e, and 6.95e, respectively. To determine the valence of these ions calculations were performed to obtain the charges in the muffin-tin spheres of Fe, Al and O atoms in the reference systems which included FeO, Fe₂O₃, and Al₂O₃. The structural data used in these calculations are reported in refs. 50 (FeO), 51 (Fe₂O₃) and 52 (Al₂O₃). The charges at the Fe and O sites of $Fe^{2+}O^{2-}$ are 23.91e and 6.90e, respectively. In the case of $\text{Fe}_2^{3+}\text{O}_3^{2-}$, the charges at the Fe^{3+} and O^{2-} are 23.74e and 6.90e, respectively (see Table 1). Assuming nominal valence and comparing the charges in the Fe spheres of FeAl₂O₄ and the Fe-oxides references we can conclude that in normal FeAl₂O₄, Fe presents a 2+ oxidation state when located at the A sites in (see Table 1). In the case of $Al_2^{3+}O_3^{2-}$, the charges at the Al and O muffin-thin spheres are 10.65*e* and 6.95*e*, respectively, showing that Al is in a 3+ oxidation state in FeAl₂O₄. Fe²⁺ and Al³⁺ oxidation states are also obtained in the cases of the inverted or partially inverted FeAl₂O₄. Also, the Bader analysis reveals that the Al–O bonds presents a highly ionic character while the Fe-O bonds has a more covalent character, in agreement with previous results [26].

From the total energy of the different structures considered, we conclude that the lowest energy configuration of hercynite corresponds to a normal structure, $(Fe^{2+})_A[A1^{3+}_2]_BO_4$. The DFT-optimized lattice parameter of this lowest-energy structure is 8.18 Å and *u*=0.2655, in very good agreement with the experimental results (*a*^{exp} in the range 8.13-8.21 Å [17, 25, 31-33]). These results are summarised in Table 2. The energy difference between the energies of the normal (*E*_{norm}) and inverted (*E*_{inv}) structures of

FeAl₂O₄ is $\Delta E_I = E_{norm} - E_{inv} = -260$ meV/u.f. The negative value for ΔE_I indicates that the normal structure, (Fe²⁺)_A[Al³⁺ Al³⁺]_BO₄, δ =0, is more stable for FeAl₂O₄.

Concerning the magnetic properties of normal hercynite, the energy difference between the lowest energy antiferromagnetic state (E_{afm}) and the ferromagnetic one (E_{fm}) is $\Delta E_{afm} = E_{afm} - E_{fm} = -15$ meV/u.f. This energy difference is larger than our convergence error, indicating that the stable spin configuration of (Fe²⁺)_A[Al³⁺₂]_BO₄ is antiferromagnetic with the configuration shown in Figure 2 and Table 1 in supplementary information. This result is in clear contradiction with that obtained by M. Yaseen *et al.* [30], who reported that the ferromagnetic state is the stable configuration for FeAl₂O₄. The magnetic moments at the Fe sites (μ (Fe)) are $\pm 3.55 \ \mu_B$. These values are irrespective of the magnetic configuration considered (dispersion in μ (Fe) in the order of 0.1 μ_B). No spin-polarisation was found at the Al sites, while the magnetic moment at the oxygen atoms is smaller than $\pm 0.03 \ \mu_B$.

The calculations in this study (that correspond to 0 K) predict that FeAl₂O₄ crystallizes in the normal structure. Experimentally, different inversion degrees (δ in the range 0.08-0.23 [21, 27, 31, 33, 36]) were reported depending on the method and growth conditions of the FeAl₂O₄ samples. So, it was decided to explore cationic inversion (antisites). The attention was placed here on the case δ =0.125, (Fe_{1- δ}Al_{δ})_A[Fe_{δ}Al_{2- δ}]_BO₄, i.e. one Al and seven Fe atoms at A sites and 15 Al and one Fe atom at B sites. Our calculations show that the case in which one Fe atom is swapped with one of its Al nearest-neighbours is energetically most favourable. The energy necessary to exchange an Fe atom with one of its Al first neighbours is 50 meV/u.f. (580 K/u.f.). Considering that the synthesis processes of these systems are usually carried out at temperatures above 500 K and using methods that are far away from the equilibrium [21], the formation of antisites is then expected in FeAl₂O₄.

Experimentally it was reported that the lattice parameter increases with the inversion degree. The equilibrium lattice parameter *a* predicted for the partially inverted structure of FeAl₂O₄ with δ =0.125, was slightly larger than those obtained for the normal structure, but the difference is smaller than the convergence error. For larger δ values, the lattice parameter increases and for the inverted structure, (Al)_A[FeAl]_BO₄, *a*=8.21 Å is predicted, in agreement with the experimental trend. Cationic inversion also induces local geometrical distortions in the oxygen nearest-neighbours (ONN) coordination spheres of Fe at B site and Al at A site. Fe at B site induces enlargement of its four Fe-ONN bond-lengths. On the other hand, the Al atom at site A induces a contraction of the

Al-ONN bond lengths. As we mentioned before, the Fe atom at B site preserves the 2+ oxidation state and the Al located at A site maintains the 3+ oxidation state.

To study the magnetic properties of FeAl₂O₄ with δ =0.125, we considered the ferromagnetic case and different antiferromagnetic configurations. The lowest energy case corresponds to those in which the magnetic Fe moment at B site is $+3.55 \mu_B$, the same value that we obtained for Fe atoms at site A in the normal structure. The Fe atoms that remain at A sites present magnetic moments of $+3.55 \mu_B$ (three Fe atoms) and -3.55 μ_B (four Fe atoms). The Al atom at A site, the Al atoms located at B sites and the O atoms are not spin-polarized. In consequence, the total magnetic moment of the cell is zero and the system is still antiferromagnetic. A solution in which the magnetic moments of the Fe atom located at site B is -3.55 μ_B (1 atom) and +3.55 μ_B for Fe atoms at A site (7 atoms) i.e., the magnetic moments of Fe atoms at the A sites are aligned antiparallel to those of the Fe at site B. 22 of the 32 O atoms present a polarization of +0.03 μ B (the other 10 oxygen atoms present magnetic moments smaller than 0.009 μ_B). Then, the net magnetic moment of this configuration (including the polarization of the oxygen atoms and the interstitial region) is +24.0 μ_B per unit cell. The energy difference between this configuration and the antiferromagnetic one is $\Delta E = E_{afm} - E_{NMM} = -3$ meV/u.f. This energy difference is in the order of our convergence error, so both magnetic configurations can be considered as degenerate solutions and the lowest energy configuration of (Fe0.875Al0.125)A[Fe0.125Al1.875]BO4 could be antiferromagnetic or present a net magnetic moment in the order of 24.0 μ_B .

We can now turn our attention to the Al-Ferrite, Fe₂AlO₄. For this structure, the trivalent Al cation exhibits a strong preference for the octahedral B sites, while the Fe cations prefer the tetrahedral A site. For this oxide, our calculations predict that the lowest energy structure corresponds to $(Fe^{2+})_A[Fe^{3+}Al^{3+}]_BO_4$, i.e. eight Fe²⁺ atoms at A sites and eight Fe³⁺ and eight Al³⁺ populate the B-sites sublattice, a normal structure (see Figure 3 and Table 2 in supplementary information. The energy, difference between the normal and inverted ($(Al^{3+})_A[Fe^{2+}2]_BO_4$)) structure of FeAl₂O₄ is $\Delta E_I = E_{norm} - E_{inv} = -306 \text{ meV/u.f.}$ The lattice parameter obtained for this lowest energy structure is *a*=8.31 Å (see Table 3), smaller than the theoretical results reported by Walsh *et al.* (8.39 Å, Ref. 39) but in good agreement with the experimental values reported in Refs. [32, 40]. *u*=0.263 was obtained for the equilibrium structure (Table 3).

Concerning the magnetic properties of Fe₂AlO₄, the stable magnetic configuration corresponds to a case in which the magnetic moments of Fe at A site are

aligned antiparallel to those of Fe at B site (see Figure 3 and Table 2 in supplementary information). Magnetic moments of Fe atoms are +3.50 μ_B and -4.20 μ_B for Fe at A and B sites, respectively. No spin polarization was found at the Al atoms, while the magnetic moments at the oxygen atoms are smaller than ±0.10 μ_B . Consequently, the stable case corresponds to a system with a net magnetic moment of 8.00 μ_B per unit cell (the net magnetic moment includes the small polarization of the oxygen atoms and the interstitial region).

Once the lowest energy structures of FeAl₂O₄ and Fe₂AlO₄ were determined, we can discuss the relative stability of each spinel oxide. To this aim, we study the formation energy E_{γ} of hercynite and Al-ferrite can be written as:

$$E_{\gamma} = E - [N^{\text{Al}}\varepsilon(\text{Al}) + N^{\text{F}}\varepsilon(\text{Fe}) + N^{\text{O}}\varepsilon(\text{Fe})]$$
(1)1

In the above equation, *E* is the total energy of one formula unit of FeAl₂O₄/Fe₂AlO₄, N^{Al} , N^{Fe} , and N^{O} is the number of Fe, Al, and O atoms in the spinel oxide considered ($N^{\text{Al}} = 2$, $N^{\text{Fe}} = 1$, and $N^{\text{O}} = 4$ for FeAl₂O₄ and $N^{\text{Al}} = 1$, $N^{\text{Fe}} = 2$, and $N^{\text{O}} = 4$ for Fe₂AlO₄). ε (Al), ε (Fe) and ε (O) are the chemical potentials of Al, Fe, and O, respectively. To obtain the required chemical potentials, additional FP-LAPW+lo calculations were performed considering as a reference FeO, Al₂O₃ and we assume that ε (O) is the half of the total energy of an oxygen molecule. ε (Al), ε (Fe) and ε (O) must satisfy:

$$E(\text{FeO}) = \varepsilon(\text{Fe}) + \varepsilon(\text{O}) \tag{2}$$

$$E(Al_2O_3) = 2\varepsilon(Al) + 3\varepsilon(O)$$
(3)

To determine $\varepsilon(O_2)$ we performed calculations (with the same convergence criteria used to study the Fe-Al system) considering a cubic cell of dimension 20x20x20 Å with the two O atoms separated by a distance equal to the experimental O–O bond-length in the O2 molecule. From eq. (2) and (3) and the energies of FeO, Al₂O₃ and $\varepsilon(O_2)/2$ we determine $\varepsilon(Al)$, $\varepsilon(Fe)$ and E_y .

The E_{γ} values obtained for FeAl₂O₄ and Fe₂AlO₄ are -35 eV/f.u and -33 eV/f.u., respectively. Negative values indicate that both spinel oxides are formed. However, the lower E_{γ} value obtained for FeAl₂O₄ indicates that this stoichiometry is the stable one. This result would explain the difficulty to obtain Fe₂AlO₄ samples without precipitation of spurious phases.

3.2. Electronic structure.

The total density of states (DOS) obtained for the equilibrium structure of FeAl₂O₄ ((Fe)_A[Al₂]_BO₄) and partially inverted FeAl₂O₄ ((Fe_{1- δ}Al_{δ})_A[Fe_{δ}Al_{2- δ}]_BO₄), δ =0.125) are presented in Figures 4 and 5. The partial DOS of each of the constituent atoms of hercynite are also presented. As can be seen, a semiconducting nature is predicted for normal and partially inverted FeAl₂O₄ (inverted FeAl₂O₄, not shown here, also presents a semiconducting behaviour).

The valence band of $(Fe)_A[Al_2]_BO_4$ (located in the energy range -8.0 to 0 eV) is dominated by the O-2p contribution hybridized with Fe-3d states, evidencing the covalent nature of FeAl₂O₄. Above the Fermi Level, the conduction band has predominantly Fe-3d character with some admixture of O-2p states. For the normal structure, direct band gaps of 2.6 eV for both spin channels (see Table 4) are predicted. In the case of the partially inverted structure of FeAl₂O₄, and irrespective of the spin configuration considered the general features of the DOS are very similar to those presented for the normal case and only small changes in the band gap are observed (energy gaps of 2.8 and 2.5 eV for the positive and negative spin channels, respectively, see Table 4). These results are in relatively good agreement with the experimental findings that show FeAl₂O₄ as a wide gap semiconductor with a band gap in the order of 3.1-3.4 eV [25] and slightly depends on the inversion degree, the magnetic configuration and the distribution of Fe and Al atoms in the cationic sites of the structure. The results obtained here are also in good agreement with those reported by Walsh et al. [39], but here obtained considering a large unit cell, different inversion degrees, magnetic configurations, and cation distributions in the tetrahedral and octahedral sites. We note here that plane GGA calculations predict a metallic behaviour for FeAl₂O₄, irrespective of the inversion degree. This bad description of the electronic structure of FeAl₂O₄ obtained in the framework of GGA was expected due to the well-known underestimation of the band gap of oxide systems obtained in DFT calculations.

To avoid the use of the arbitrary external factor U introduced in the GGA+U formalism we performed calculations using the Tran-Blaha modified Becke-Johnson (TB-mBJ) [53, 54] approximation for the exchange and correlation potential, which yields band gaps with an accuracy comparable to state-of-the-art approaches. This formalism leads to band gaps in the order of 5 eV (see Table 4). This result is larger than

the experimental ones. To confirm the precise value of the band gap further experimental and theoretical studies are necessary. We mention here that M. Yaseen *et al.* reported (in the framework of TB-mBJ calculations) that FeAl₂O₄ is a half-metallic ferromagnet with 100% spin polarization [30], however the experimental findings and our calculations results refute it.

The DOS of the Al-ferrite (Fe₂AlO₄) presents similar features to those previously discussed for hercynite (see Fig. 6). The energy band gap is comparable to those obtained for FeAl₂O₄ (table 4), as it was expected due to the similar coordination and Fe-Al-O bond lengths. As far as we know, no experimental determinations of the band gap of Fe₂AlO₄ are reported in the literature.

3.3 Hyperfine properties at the Fe sites.

In the previous section, we present structural and magnetic models for normal and partially inverted FeAl₂O₄ and normal Fe₂AlO₄. To give confidence (or refute) these models we need to compare predictions derived from these structures with experimental information [1, 38, 55]. In this sense, as mentioned earlier, Mösbauer Spectroscopy (MS) is particularly adequate to study the chemical state and electronic and magnetic environment (at the sub-nanoscopic scale) of Fe sites because ⁵⁷Fe is one of the most adequate probes for MS [34, 35]. In this work, three hyperfine parameters that can be compared with the experimental ones were determined and discussed: the isomer shift (*IS*), the quadrupole splitting ($\Delta \varepsilon_Q$) and finally, the magnetic hyperfine field (*B*_{HF}). For details, see Refs. [34, 35].

First, we will discuss the normal FeAl₂O₄, $(Fe^{2+})_A[Al^{3+}_2]_BO_4$ case. In this structural arrangement, Fe²⁺ ions are located at the tetrahedral sites (A) of the spinel structure. In this case, the obtained hyperfine parameters at the Fe sites are *IS*(A)=0.95 mm/s $\Delta \varepsilon_Q(A)$ =3.25 mm/s and *B*_{HF}(A)= 39.1 T (see Table 5). An *IS* in the order of 1.0 mm/s is indicative of a 2+ oxidation state of the Fe ions, in perfect agreement with the results obtained in our previous analysis. The results obtained for the $\Delta \varepsilon_Q(A)$ deserve a discussion. In the normal structure, the cationic site A presents a cubic symmetry ($\overline{43m}$) and therefore $\Delta \varepsilon_Q(A)$ must be null. But, for the description of crystals with magnetic ordering, in which the positions of the atoms and the orientation of the magnetic moments must be also specified, symmetry becomes quite important factor. In the present case, the symmetry of the lowest energy magnetic structure of normal FeAl₂O₄ is smaller than the crystal space group. In consequence, the spin alignment breaks down the cubic symmetry

of the A-site, inducing a charge asymmetry and therefore a nonzero $\Delta \varepsilon_Q(A)$. Finally, the *B*_{HF} obtained is consistent with the results obtained for Fe at sites A in other ferrites [1, 38, 55].

At this point, we can make a first comparison with the experimental MS results. For a reliable comparison between theory and experiment, we will select experiments performed at low temperatures or those for which an accurate extrapolation to 0 K can be carried out, as in the case of the results reported by Öno [37]. In that experiment, the spectra were fitted with one interaction, i.e., one site for the Fe ions, that was attributed to Fe²⁺ located at cationic A sites. The reported values for *IS*, $\Delta \varepsilon_Q$ and *B*_{HF} were 1.10(4) mm/s, 3.25 mm/s (extrapolated value to 0 K) and 16.9 T, respectively (see Table 5). As can be seen, there is a good agreement between the DFT calculations and the MS experiment for the *IS* and the $\Delta \varepsilon_Q$ for Fe²⁺ at A sites. On the other hand, the DFT prediction for *B*_{HF} is twice as large as the experimental one. It is worth mentioning that the experimentally determined *B*_{HF} value is lower than those reported for other ferrites (usually in the order of 40 T). An inspection of the experimental data reveals that the MS spectra are characterised by broad lines, which could be a fingerprint of a magnetic relaxation process that cannot be described by the DFT calculations. This discrepancy deserves the deepest experimental investigation, as it was done in Ref. [55].

Now we can discuss the effect of the cationic inversion on the hyperfine interactions. In the case of $(Fe_{0.875}Al_{0.125})$ [Fe_{0.125}Al_{1.875}] BO4, the IS(A) at the 7 Fe-ions atoms that remain located at the A sites, is very similar to those of normal FeAl₂O₄ (0.97 mm/s, see Table 5), while the IS for the Fe ion located at B site (IS(B)) is in the order of 1.1 mm/s, also indicative of a Fe²⁺ oxidation state. $\Delta \varepsilon_0(A) = 3.21$ mm/s is obtained. This value is slightly smaller than those obtained for normal FeAl₂O₄, 3.25 mm/s. The main effect of inversion in $\Delta \varepsilon_Q(A)$ is the increment in the distribution (to 5%), which indicates environments slightly different for the Fe ions at A sites. This distribution in $\Delta \varepsilon_Q(A)$ is explained by the fact that the cationic inversion produces an asymmetric distribution of Fe and Al around Fe in the A sites. $\Delta \varepsilon_Q(B) = 3.15$ mm/s for the antiferromagnetic solution and 2.80 mm/s in the case of the structure with a net magnetic moment of 24.0 μ B was predicted. This difference in $\Delta \varepsilon_{Q}(B)$ for both magnetic configurations are related to the slightly different equilibrium structures predicted for each case. Finally, $B_{HF}(A)=43.2$ T (antiferromagnetic configuration) and 50.6 T (net magnetic moment of 24.0 μ B configuration), see Table 5. These theoretical predictions can be compared with the experimental results reported by Dormman et al. [36], who reported MS results for a sample of FeAl₂O₄ that presents an inversion degree of 0.22(3). The experimental spectra were fitted assuming a multiple interactions model. The hyperfine interactions associated with Fe²⁺ ions located at the cationic A sites are an average of three hyperfine interactions and are characterised by hyperfine parameters very similar to those previously discussed for the case of the normal FeAl₂O₄ structure. This experimental result (in combination with the theoretical ones) confirms that the cationic inversion produces a minor effect on the hyperfine interactions at the Fe nucleus at A sites (at least for these relatively lower inversion degrees). The interactions associated with Fe ions at B sites are characterised by *IS*=1.05 mm/s and ε_Q =2.80 mm/s, in excellent agreement with our theoretical results, particularly for the case of the solution with a net magnetic moment of 24.0 μ_B . Like the case of the normal structure, predictions for *B*_{HF} at A and B sites are twice as large as the experimental ones.

In the case of the metastable Al-ferrite (Fe₂AlO₄), the comparison theory-MS experiment is not clear and simple as in the case of hercynite because reports are scarce. As far as we know, only Choi *et al.* reported a hyperfine characterization of Al-ferrite [40]. In that work, the authors prepared Fe₂CoO₄, Fe₂AlO₄, and Fe₂CoO₄@Fe₂AlO₄ core/shell nanoparticles by using a high-temperature thermal decomposition method with seed-mediated growth and investigated the structural, magnetic, and thermal properties of the obtained nanoparticles by using X-ray diffraction (XRD), vibrating sample magnetometer, and MS. The crystal structure and crystallite size of the Fe₂AlO₄ nanoparticles (average particle size: 10.15 nm) were determined to be cubic with space group *Fd-3m* and *a*=8.2548 Å.

The measured Mössbauer spectrum of Fe₂AlO₄ obtained at 300 K was fitted with two hyperfine interactions. One interaction is a sextet characterised by IS(1)=0.26 mm/s, $\Delta \varepsilon_Q(1)=0.04$ mm/s and $B_{HF}(1)=45.58$ T. The second interaction is a doublet with IS(2)=0.20 mm/s and $\Delta \varepsilon_Q(2)=-0.83$ mm/s. The sextet was associated with Fe at A sites of the spinel structure of Fe₂AlO₄. The origin of the second interaction was not discussed. A critical analysis of this experimental result can be made before the theoretical modelling. Even when an *IS* in the order of 0.20-0.26 mm/s could be associated with a Fe³⁺ oxidation state, an interaction with an *IS* in the order of 1.0 mm/s, i.e. Fe ions in a 2+ oxidation state must be present in the Mössbauer spectrum of Fe₂AlO₄ because the only oxidation state of Al is 3+. Batista *et al* [56] and Da costa *et al*. [57] reported ⁵⁷Fe-Mossbauer results for 33% Al-doped maghemite. In this experiment, a doublet with hyperfine parameters that are very similar to those reported by Choi *et al*. [40] for Fe₂AlO₄ was observed. It is important to mention here that the lattice parameter estimated by Batista *et al* [56] for this 33% Al-doped maghemite coincides whit those reported by Choy *et al.* for Fe₂AlO₄ and that is difficult to distinguish between ferrites and maghemite nanoparticles by XRD. This discussion suggests that the phase observed by Choy *et al.* and associated with Al-ferrite probably corresponds to Al-doped maghemite nanoparticles.

Now we can address our predictions for the hyperfine interactions at the Fe sites of Fe₂AlO₄ with the experimental MS results. The predicted equilibrium structure of Fe₂AlO₄ is (Fe)_A[AlFe]_BO₄. According to this structure, DFT predicts two distinguishable interactions, one associated with Fe²⁺ at A sites and the second one associated with Fe³⁺ at B sites. The interaction associated with the Fe²⁺ ions at A sites is characterised by *IS*(A)=0.95 mm/s, $\Delta \varepsilon_Q$ (A)=3.20 mm/s and *B_{HF}*(B)=41.7 T with a very low distribution (smaller than 0.2%). These parameters are very similar to those obtained for the case of Fe at A sites of FeAl₂O₄. The interaction that corresponds to Fe³⁺ ions at B site of the spinel structure is characterized by $\Delta \varepsilon_Q$ (B)=0.63 mm/s, *B_{HF}*(B)=50.6 T, and *IS*(B)=0.45 mm/s. Note that $\Delta \varepsilon_Q$ (B) and *B_{HF}*(B) are different to those obtained for the case of Fe at B sites of FeAl₂O₄. These predictions are in poor agreement with the experimental ⁵⁷Fe-Mossbauer results reported by Choy *et al.* [40]. In our opinion, new experimental and theoretical studies (including the case of Al-doped maghemite) are necessary to unravel this complex case.

4. Conclusions.

In this work, we have studied using of DFT-based calculations, two Fe-Al spinel oxides, namely FeAl₂O₄ (hercynite) and Fe₂AlO₄ (Al-ferrite). From our study, we obtain the structural and magnetic equilibrium structures of both oxides. FeAl₂O₄ presents the normal structure, in which eight Fe²⁺ occupy the tetrahedral A sites and the Al⁺³ ions are located at the octahedral B sites, (Fe)_A[Al₂]_BO₄. The predicted lattice parameter is 8.18 Å and *u*=0.2655. Our DFT calculations also predict that hercynite is an antiferromagnetic wide-gap semiconductor with μ (Fe)=±3.55 μ B. Besides, the effect of cationic inversion on the structural, electronic, and hyperfine properties of FeAl₂O₄ was discussed. We show here that the minimum energy necessary to generate an inversion degree δ =0.125 in otherwise normal hercynite is smaller than those provided by the thermal treatments usually applied for the growth of FeAl₂O₄ samples. This is an important point because the magnetic response of spinel oxides with magnetic cations (Fe in the present case)

depends on the Fe distribution on A and B sublattices. Here, we show that, for this inversion degree, a magnetic response of FeAl₂O₄ could appear. A successful comparison between calculated hyperfine parameters with those obtained in MS experiments gives confidence to our results. In the case of the Al-ferrite (Fe₂AlO₄), a metastable phase, our calculations predict that eight Fe²⁺ populates the A sites while eight Fe³⁺ and eight Al³⁺ are located at the B sites, (Fe²⁺)_A[Fe³⁺Al³⁺]_BO₄. For this system, we obtained *a*=8.31 Å and *u*=0.263. Our results show that Fe₂AlO₄ is a wide-gap semiconductor with μ (Fe, site A)=+3.50 μ B, μ (Fe, site B)=-4.20 μ B and then a net magnetic moment in the order of 8.00 μ B per unit cell.

CRediT authorship contribution statement

K. L. Salcedo Rodríguez: Conceptualization, Methodology, Data Curation, Formal analysis, Funding acquisition, Writing - Original Draft, Writing – review & editing. **J. J. Melo Quintero:** Data Curation, Formal analysis, Visualization, Writing-Review and Editing **C. E. Rodríguez Torres:** Formal analysis, Writing– review & editing, Funding acquisition **L. A. Errico**: Methodology, Data Curation, Formal analysis, Writing– review & editing– review & editing– review & editing and Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Tables

 $(Fe)_A[Al_2]_BO_4$

Oxide	Charge in the	Charge in the	Charge in the O	
	Fe sphere / oxidation	Al sphere / oxidation	sphere / oxidation state	
	state	state		
FeO	23.91 / 2+		6.90 / 2-	
Fe ₂ O ₃	23.74 / 3+		6.90 / 2-	
Al ₂ O ₃		10.65 / 3+	6.95 / 2-	
FeAl ₂ O ₄	23 94 / 2+	10.63 / 3+	695/2-	

Table 1. Electronic charge in the muffin-tin sphere of Fe, Al, and O atoms and nominal

FeAl ₂ O ₄	23.93 / 2+	10.65 / 3+	6.93 / 2-
$(Fe_{1-\delta}Al_{\delta})_{A}[Fe_{\delta}Al_{1-\delta}]_{B}O_{4}$	(site A)	(site A)	
δ =0.125. Antiferromagnetic	23.95 / 2+	10.63 / 3+	
solution	(site B)	(site B)	
FeAl ₂ O ₄	23.95 / 2+	10.65 / 3+	6.93 / 2-
$(Fe_{1-\delta}Al_{\delta})_{A}[Fe_{\delta}Al_{1-\delta}]_{B}O_{4},$	(site A)	(site A)	
δ =0.125. Solution with a	23.96 / 2+	10.63 / 3+	
net magnetic moment of	(site B)	(site B)	
24.0 μ <i>B</i> per unit cell			
Fe ₂ AlO ₄	23.95 / 2+	10.64 / 3+	6.92 / 2-
(Fe)A[FeAl]BO4	(site A)	(site B)	
	23.73 / 3+		
	(site B)		

Table 2. Calculated structural parameters (lattice parameter *a*, displacement parameter *u*) for the normal and inverse spinel lattices of FeAl₂O₄ along with the experimentally determined lattice parameter. Energies are referred to the energy of the (Al)_A[FeAl]_BO₄ structure. $\Delta E_I = E_{norm} - E_{inv}$ is the inversion energy per FeAl₂O₄ formula unit (u.f.). A negative ΔE_I indicates that the normal spinel structure ((Fe)_A[Al₂]_BO₄) is the stable one

System:	Structure	a^{exp} (Å)	a^{DFT}	u ^{DFT}	<i>E</i> (eV)	ΔE_I
			(Å)			(meV/u.f)
FeAl ₂ O ₄	Normal,	8.1572	8.18	0.2655(5)	-2.09	-260
	(Fe) _A [Al ₂] _B O ₄	[33]				
	Inverted,		8.21	0.255(1)	0	
	(Al) _A [FeAl] _B O ₄					

Table 3. Calculated structural parameters (lattice parameter *a*, displacement parameter *u*) for the normal and inverse spinel lattices along with the experimentally determined lattice parameter. Energies are referred to the energy of the $(Al)_A[Fe_2]_BO_4$ structure.

System	Structure	a^{exp}	a^{DFT}	<i>u</i> ^{DFT}	E	ΔE_I
		(Å)	(Å)		(eV)	(meV/u.f)
Fe ₂ AlO ₄	$(Al)_A[Fe_2]_BO_4$	8.23	8.28	0.251(1)	0	-384

	Journal Pre-proof						
	$(Fe)_A[FeA1]_BO_4$	[39]	8.31	0.263(1)	-3.07		

Table 4: Energy band gaps obtained for hercynite (FeAl₂O₄, normal and partially inverted structures) and Al-ferrite (Fe₂AlO₄) obtained in the framework of GGA, GGA+*U*, and TB-mBJ calculations.

System	em Equilibrium Magnetic		Gap	Gap	Gap
	structure	configuration	(eV),	(eV),	(eV)
			GGA	GGA+U	TB-
					mBJ
FeAl ₂ O ₄ ,	$(Fe)_A[Al_2]_BO_4$	AF	metallic	2.6/2.6	5.4 /
					5.4
FeAl ₂ O ₄ ,	(Fe1- δ Al δ)A[Fe δ Al1-	AF	metallic	2.5 / 2.7	5.1 /
partially	δ]BO4, δ=0.125				4.9
inverted		+24.0 <i>μ</i> ^{<i>B</i>} per	metallic	2.8 / 2.5	4.8 /
		unit cell			5.3
Fe ₂ AlO ₄	$(Fe^{2+})_{A}[Fe^{3+}Al^{3+}]_{B}O_{4}$	8.0 μ per unit	metallic	2.2 / 3.2	3.6 /
		cell			5.4

Table 5: Experimental and theoretical hyperfine parameters at the Fe sites of FeAl₂O₄. Experimental values correspond to the extrapolation to 0 K from the experimental systematic. The interaction associated with Fe ions at the A sites reported by Dormman *et al.* [36] corresponds to an average of three hyperfine interactions, all associated with Fe^{2+} oxidation state.

		Fe at site A					Fe at site	B	
Syste m	Equilibrium structure	IS (mm/s)	Δε _Q (mm/s	<i>В_{НF}</i> (Т)	Dist. (%)	IS (mm/s	Δε _Q (mm/s	B _H F	Dist
		· · ·)))	(T)	(%)
4			Theo	ry					
$FeAl_2 O_4$	$(Fe)_A[Al_2]_BO_4$ $\delta=0$	0.95	3.25	39.1	<0.5 %	-	-	-	-
	Antiferromagnetic solution								
	$(\text{Fe}_{1-\delta}\text{Al}_{\delta})_{\text{A}}[\text{Fe}_{\delta}\text{Al}_{1-\delta}]_{\text{B}}\text{O}_{4}, \delta=0.125$	0.95	3.22	39.0	5%	1.06	3.15	39. 6	
	Antiferromagnetic solution								
	$(\text{Fe}_{1-\delta}\text{Al}_{\delta})_{\text{A}}[\text{Fe}_{\delta}\text{Al}_{1-}]_{\text{B}}\text{O}_4, \delta=0.125$	0.97	3.21	39.6	5%	1.08	2.80	43. 2	
	Solution with a								
	moment of 24.0								
	μ_B per unit cell								
			Experim	ental					



Figure 1: Crystal structure of the spinel oxides: gold balls represents the tetragonal sites (A-sites), light blue balls represent the octahedral sites (B- Sites), and red small balls represent the sites for the anions (oxygen atoms).



Figure 2: Predicted equilibrium structure of $FeAl_2O_4$ (hercynite), $(Fe^{2+})_A[Al_2^{3+}]_BO_4^{2-}$. Light blue balls denote the tetrahedral sites (A, populated by Fe^{2+} ions) and gold balls

represent the octahedral sites (B, populated by Al^{3+} ions). Arrows denote the relative spin orientation of the Fe atoms.



Figure 3: Predicted equilibrium structure of Fe_2AlO_4 (Aluminium ferrite), $(Fe^{2+})_A[Fe^{3+}Al^{3+}]_BO_4^{2-}$. Light and dark blue balls indicate the tetrahedral sites (A, populated by Fe^{2+} ions) and the octahedral B sites populated by Fe^{3+} ions, respectively. Relative spin orientations of the Fe atoms are also indicated. Al^{3+} ions at B sites are represented by golden balls.



Figure 4. Total and partial DOS of the dominant angular character of the constituent atoms of the lowest energy structure of normal FeAl₂O₄, (Fe)_A[Al₂]_BO₄, obtained in the framework of GGA+U (U = 5 eV) calculations. Energies are referred to the Fermi level.



Figure 5. Total and partial DOS of partially inverted FeAl₂O₄, (Fe_{1- δ}Al_{δ})_A[Fe_{δ}Al_{1- δ}]_BO₄, δ =0.125, obtained for the antiferromagnetic (left) and the configuration with a net magnetic moment (right) configurations. Results correspond to GGA+U (U = 5 eV) calculations. Energies are referred to the Fermi level.



Figure 6. Total and partial DOS of the dominant angular character of the constituent atoms of normal and ferrimagnetic Fe₂AlO₄, $(Fe^{2+})_A[Fe^{3+}Al^{3+}]_BO_4$, obtained in the framework of GGA+*U* (*U* = 5 eV) calculations. Energies are referred to the Fermi level.

CRediT authorship contribution statement

K. L. Salcedo Rodríguez: Conceptualization, Methodology, Data Curation, Formal analysis, Funding acquisition, Writing - Original Draft, Writing – review & editing. **J. J. Melo Quintero:** Data Curation, Formal analysis, Visualization, Writing-Review and Editing **C. E. Rodríguez Torres:** Formal analysis, Writing– review & editing, Funding acquisition **L. A. Errico**: Methodology, Data Curation, Formal analysis, Writing– review & editing– r

Declaration of Competing Interest

☑ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- -DFT study of structural, electronic, magnetic properties of FeAl₂O₄ (hercynite) and Fe₂AlO₄ (Al-ferrite).
- - Different inversion degrees, magnetic configurations and distributions of Fe and Al in the cationic sites were considered.
- - The structural and magnetic lower energy configurations of both oxides were determined.
- - FeAl₂O₄ present an antiferromagnetic semiconductor character with a normal structure.
- - Fe₂AlO₄ is a metaestable phase with a ferrimagnetic semiconductor nature.
- - Hyperfine parameters at the Fe sites were also obtained.