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Magnetic Ordering in Ilmenites and Corundum-Ordered Structures

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Abstract

In the last few years, the multiferroic materials have represented a very important research topic on the design of new technological devices. A better description for this kind of materials involves two or more forms of ferroic orders coupled in a single crystalline structure. The great number of studies in this field is focused on candidates that present the coupling between a magnetic order and ferroelectricity. However, these material classes are a challenging topic on first-principles calculations due to the strong correlation that arose from the unpaired electrons. Furthermore, the partial filling of d or f orbitals reduces a high localization and a strong interaction causing failures on the electronic structure prediction. The investigation of multiferroic materials aims at their application on the development of devices such as actuators, magnetic readers, sensors and data storage. Multiferroic materials are also alternatives to the production of technological applications based on spintronic. Our proposal is to show our experience in DFT simulations for magnetic states applied in oxides of ilmenites and corundum-ordered structures. Theoretical results reported for our group until now showed a good agreement with experimental results for half-metallicity, reduced band-gap, and/or ferromagnetic ordering.

Keywords: magnetism, DFT, co-linear ilmenites, oxides, semiconductor, spin, bulk, clusters, crystalline field theory degenerated

1. Introduction

Over the last few decades, the field of magnetism has assumed a remarkable importance in the field of science and technology due to the development of new technologies. Such kind of

technologies are based on the capability of control not only the electrical degree of freedom of electrons (charge) but also the magnetic nature associated with the intrinsic angular momentum of a given particle so-called spin [1].

For instance, in recent years, the scientific interest on the development of devices in the field of spintronic has been intensified. The performance of these devices depends on the spin polarization of the current used for information storage; i. e. the development of spintronic devices requires an effective way of control charge-based electronic properties by magnetic field, as well as of controlling the magnetic properties by electric currents [2–4].

In this context, multiferroic materials are essentially the best candidates due to the intrinsic multifunctional features associated with such class of compounds. In a general view, the most complete definition for these materials is based on two or more ferroic ordering (i.e. ferroelectricity, ferroelasticity, ferromagnetism, ferrotoroidicity) coupled in a single crystalline phase. Nowadays, the majority of studies are strictly focused on candidates that combine a magnetic order (ferromagnetism, antiferromagnetism) with ferroelectricity and are known as magnetoelectric multiferroics. The interest on multiferroic materials was rebirthed by theoretical reports about the scarcity of such compounds, which are also responsible for explain the unusual phenomena and successfully predict new candidates. The main advances addressed to such kind of materials are novel devices such as actuators, transducers and storage devices, as well as other potential applications including multiple state memories and novel memory media [5–9].

In order to clarify the unusual phenomena's commonly observed in such complex materials, as well as to design new candidates with feasible properties, the understanding of magnetism in solid state materials plays a fundamental role due to the complexity of the so-called itinerant electrons commonly founded in transition metals.

In this chapter, we propose a theoretical point of view about the magnetism of Ilmenite and Corundum-ordered structures—widespread candidates for multiferroic and spintronic applications—focusing on the relation between crystalline and electronic structure associated with the ground state magnetic ordering attributed to the materials. The following sections are dedicated to explain the (i) magnetism in solid state materials, (ii) the magnetic ordering of Ilmenite and Corundum-ordered materials, and (iii) theoretical approaches to investigate magnetic solid state materials.

1.1. Magnetism in solid state materials: a fundamental tool for new technologies

Magnetic materials are the ideal candidates for the consolidation of spintronic technology due to the high degree of freedom of the spin in these materials. Magnetism is one of the oldest and most fundamental scientific problems not completely clear until now. Numerous theories are proposed to explain the magnetic behavior of materials, as the well-known classical formalism where all substances have small magnets that align in certain directions depending on the chemical environment. Another theory is domain-based, where a magnetic domain represents a region with uniform magnetization, separated from other domains by

well-defined boundaries. This theory allowed the observation of the Curie temperature (T_C) above which the ferromagnetic domains become paramagnetic and the magnetism disappears [10, 11].

In the Quantum Theory of magnetism, the formalism is based on the quantum angular momentum of electron, so-called spin, associated with open-shell orbitals commonly founded in Transition Metals. In this way, the microscopic origin of the magnetism is the strong electron-electron interaction that arises from the chemical bond inside the crystalline structure. Moreover, the itinerant character associated with the magnetic moments can be localized or delocalized that originates dia- or paramagnetism in solid state materials. However, the collective magnetism in the perspective of ferromagnetism, antiferromagnetism and ferrimagnetism are the fundamental keys to overcome the main questions behind the solid state magnetic ordering [11]. A schematic overview about this kind of magnetic ordering is given in **Figure 1**.

A ferromagnetic (FM—**Figure 1a**) material is characterized by a spontaneous magnetization even in the absence of a magnetic field. At $T = 0$ K all magnetic moments are parallel ordered due to the stronger exchange interaction between them, differently of paramagnetic species that exhibit non-interacting magnetic moments. The conventional magnetic transition metal elements with ferromagnetic ordering are Mn, Fe, Ni and Co, where Mn and Fe can also show antiferromagnetic order depending upon the crystalline structure. In addition, the thermal energy eventually overcomes the exchange the electronic exchange in ferromagnets, producing a randomizing effect where the saturation magnetization goes to zero due to the disorder

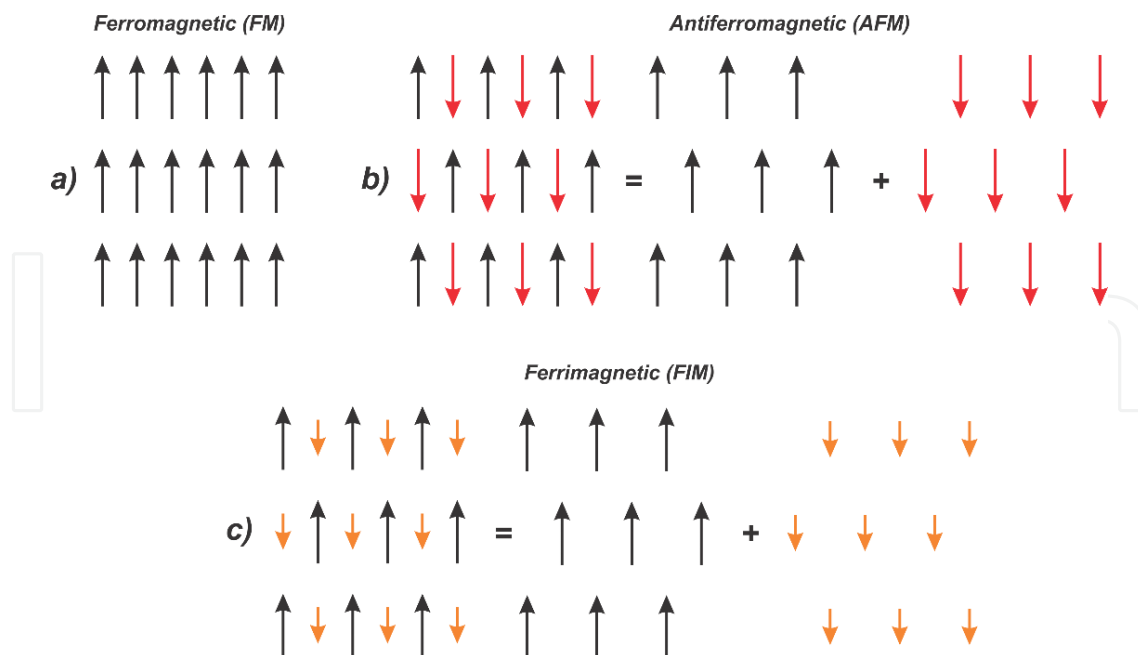


Figure 1. Different collective arrangements of magnetic moments for ordered magnetic systems: (a) ferromagnets, (b) antiferromagnets, (c) ferrimagnets.

associated with the magnetic moments. This occurs at a particular temperature called the Curie temperature (T_C) [1].

On the other hand, antiferromagnetic materials (AFM—**Figure 1b**) show an antiparallel arrangement between neighboring magnetic moments. In this case, this ordering can be attributed to the existence of negative exchange interaction between the nearest neighbors, as well as for some lattices that can be divided in two ferromagnetic sublattices, which exhibit an antiferromagnetic ordering between them. This class of compounds is the most common magnetic materials in the nature and shows good perspectives regarding the technological applications. In this class, both metals (Mn_2Au , Fe_xMn_y and others) and semiconductors/insulators (NiO , Cr_2O_3 , CoO , $BiFeO_3$, MnF_2 and others) are founded [12].

Ferrimagnetism represents an intermediate position between FM and AFM orderings. In this case, the simplest picture related to solid state materials can be understood by the assumption of two magnetic sublattices with antiparallel orientation but with different magnitude of each magnetization, resulting that the total magnetization does not vanish as for the antiferromagnetic case, as represented in **Figure 1c**. Magnetite (Fe_3O_4) is a well-known ferrimagnetic material, where the spins on the tetrahedral Fe A-sublattice are antiparallel to those on the octahedral Fe B-sublattice, resulting in a net magnetic moment for the B-site [11].

Let us now briefly introduce the concept of magnetic interactions, which are responsible for the collective ordering presented in **Figure 1**. In magnetic solid state materials different types of magnetic interaction can be observed, being responsible for intriguing properties associated to the fact that magnetic moments interact between them, enabling the long range magnetic ordering. In a general point of view, two main interactions are founded in solid state materials: direct and indirect. In the first case, the electrons of neighboring magnetic atoms directly interact through an overlap between atomic wave-functions called “direct exchange”. On the other hand, if the overlap of the involved wave functions is only small the direct exchange does not represent the dominating mechanism for magnetic properties because an additional atom act as a bridge between the magnetic centers, resulting in an indirect exchange interaction is responsible for magnetism. The representation of different kinds of magnetic interactions commonly founded in magnetic solid state materials is depicted in **Figure 2**.

1.1.1. Direct coupling

This type of coupling occurs when a direct overlap between the orbitals of adjacent magnetic sites is observed. The collective arrangement associated with the signal of direct coupling depends of the distance between species. At short distance the electrons tend to spend most of the time between the atoms giving rise to an antiparallel coupling due to the Pauli Exclusion Principle. However, at long distances the overlap between the orbital is reduced, inducing a minimization of potential energy for this interaction. This variation was named of Bethe-Slater curve, due to the elucidation of the behavior by these researchers. The representation of this curve is shown in **Figure 2a** [1, 11].

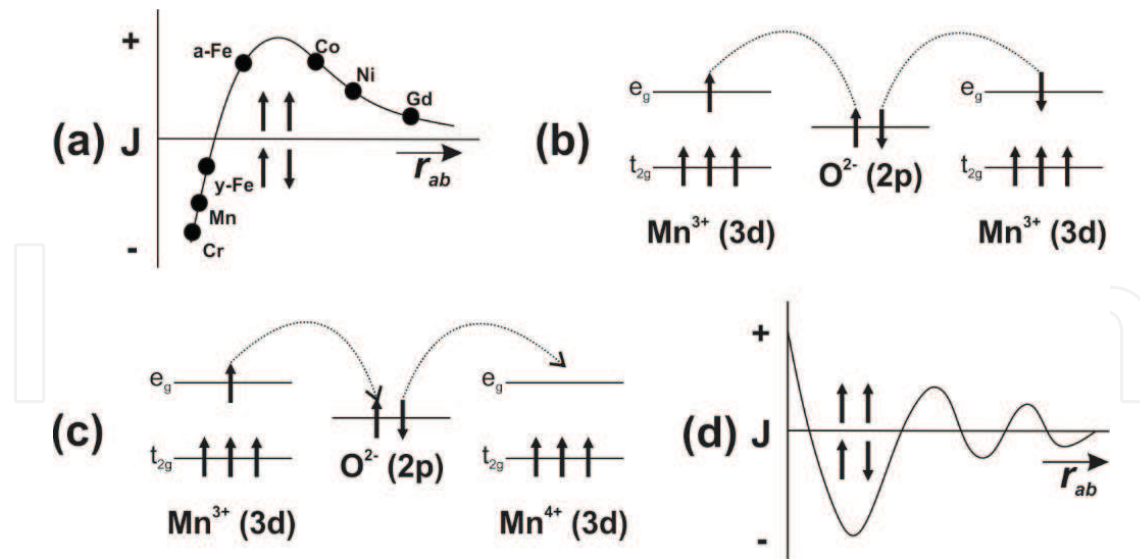


Figure 2. Representation of magnetic interactions in solid state materials. (a) Bethe-Slater curve for direct coupling. (b) Indirect coupling between Mn^{3+} mediated by oxygen atoms in MnO . (c) Oxygen-mediated indirect double-exchange coupling for cations with distinct orbital occupations. (d) RKKY coupling and its dependence with the distance between the magnetic centers.

1.1.2. Indirect coupling

In this case the electrons located in the partially occupied orbitals are separated from the neighboring electrons by an atom or non-magnetic ligand. The coupling force is dependent on the amount of energy transferred between the levels and the Coulomb repulsion between these particles. Another important feature of this model is that the oxidation numbers for the magnetic cations must be equal or have a difference equal to two, so that there is no movement between the levels. This model is present in several materials, such as the MnO shown in **Figure 2b** [1, 11].

1.1.3. Double-exchange indirect coupling

This coupling is quite similar to that previously mentioned; however the main difference lies in the movement of the electrons between the orbitals. As the oxidation numbers of the metals are different, in this case, the mismatched electrons of the A site can move to the B site, since it is possible to find unoccupied levels with the same spin orientation (**Figure 2c**) [1, 11].

1.1.4. RKKY coupling

The RKKY coupling was discovered by Ruderman, Kittel, Kasuya and Yosida (RKKY) and characterized as a long-range interaction. This type of coupling is very common in metals where the overlap between orbitals is minimal or zero, causing a polarized spin ion to induce a field on the conducting electrons of the neighboring atoms allowing a magnetic influence on a second polarized neighbor. As well as direct coupling, the orientation of neighbors is dependent on the distance between them as shown in **Figure 2d**. Another important feature

of this class of magnetic couplings is the existence of effects such as Giant Magnetoresistance and Spin Tunneling that can be explained by the use of RKKY Hamiltonian [1, 11, 13–15].

1.1.5. GKA rules

The Goodenough-Kanamori-Anderson (GKA) rule describe the interatomic spin-spin interactions between two atoms considering the existence of a virtual electron transfers between them (superexchange) and/or between a shared anion (so-called “bridge”) and the two atoms. As consequence, in this rule atoms with orthogonal orbitals do not overlap reducing the repulsion between the electrons, following the Hund’s rule. Therefore, the exchange interaction between spins is positive and a ferromagnetic ordering arises.

In addition, the GKA rule predicts some interactions that depend on the occupation of interacting orbitals. In the first case, an antiferromagnetic interaction occurs when the virtual electron transfer is between half-filled orbitals. In opposition, they are ferromagnetic once the virtual electron transfer is from a half-filled to an empty/filled orbital.

The GKA rules are important due to the introduction of bond character in the evaluation of the magnetic interactions. It is important to point out that the net spin does not change with the covalent component associated with the chemical bonds; however this component can extends the cation wave function out because the interaction between the orbitals is large, resulting in chemical dependent ferromagnetic/antiferromagnetic couplings associated the superexchange electron transfer [16].

1.1.6. Dzyaloshinskii-Moriya rule

The Dzyaloshinskii-Moriya [17–20] rule states that a low magnetic resultant is observed in antiferromagnetic material due to a long range interaction between magnetic atoms in disordered crystalline structures. This particular behavior is called weak-Ferromagnetism.

1.2. FeBO_3 ($\text{B} = \text{Ti, Zr, Hf, Si, Ge, Sn}$) materials: insights into interatomic distance and orbital overlap

Perovskites oxides, which have the general formula ABO_3 , are widely studied by theoretical or experimental efforts because of the large variety of intriguing properties, such as ferroelectricity, piezoelectricity, multiferroism and others [21–23]. The interest in this kind of structure arise from the possibility of to control the existence of different properties from chemical substitution or doping on A- and B-sites [24]. For instance, a very common mineral on earth surface (FeTiO_3) presents the ilmenite structure can shelter a high compositional diversity of A^{2+} and B^{4+} cations that occupy alternate basal-planes along the [001] hexagonal axis of a ordered corundum structure (R3) [25]. The most investigated ilmenite materials are based on Ti atoms in B sites with different atoms in A^{2+} ($\text{A} = \text{Mn, Fe, Ni, Co}$) cations; however, other materials were known in this structure [26–29].

Goodenough and Stickler proved that the magnetic ordering of ilmenite materials, mainly ATiO_3 ($\text{A} = \text{Mn, Fe, Ni, Co}$), are antiferromagnetic insulators and have two different magnetic

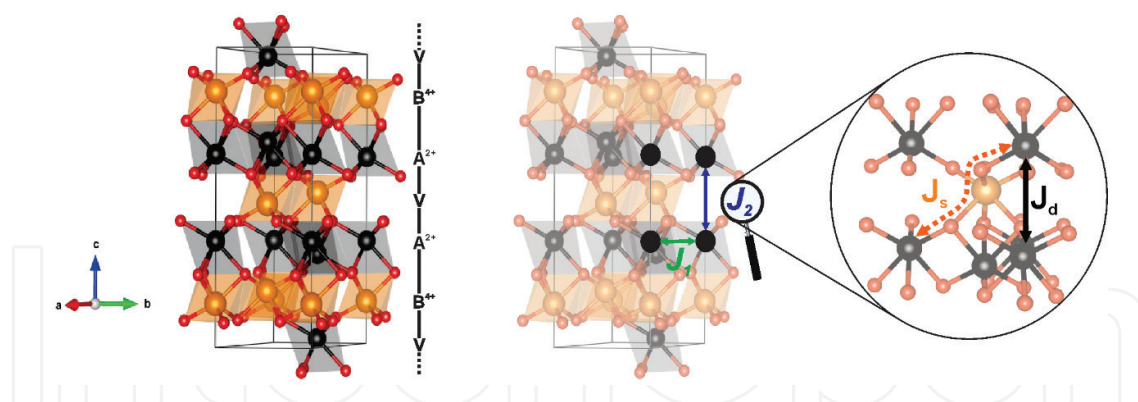


Figure 3. Ilmenite-type conventional unit cell and their exchange coupling constants. Black, orange and red balls represent A^{2+} , B^{4+} and O^{2-} ions, respectively.

couplings constants: Intralayer (J_1) and Interlayers (J_2), as shown in **Figure 1**. J_1 refers to the magnetic exchange that happens between A-O-A atoms and is dominated by the coupling of a t_{2g} orbital in one cation with an e_g orbital in other. Therefore, the signal for exchange parameter depends upon the occupancies of the interacting orbitals making $MnTiO_3$ antiferromagnetic and $FeTiO_3$, $CoTiO_3$, $NiTiO_3$ ferromagnetic for intralayer coupling (J_1). In turn, J_2 interactions are mediated by the BO_6 clusters in the intermetallic connection A-O-B-O-A, having less contribution of a direct overlap in [001] direction because of the vacancy in cationic sublattice (**Figure 3**) with opposite magnetization directions between adjacent A layers (antiferromagnetic) [25, 30].

In Fe-based ilmenite materials the long-range exchange coupling (J_2) stabilizes the antiferromagnetism; since J_2 depends of intermetallic connection Fe-O-B-O-Fe, the non-magnetic B-site replacement can control such magnetic ordering. As previously discussed, the ilmenite structure arrangement creates vacancies between adjacent Fe^{2+} layers that are separated each other by a B-site plane. So, the interlayer magnetic coupling integral can be visualized as a direct coupling between 3d orbitals of adjacent Fe^{2+} cations. Furthermore, other evidence that the non-magnetic B-site substitution affects the magnetic ordering is: the vacancy formation occurs in this cationic sublattice and the direct exchange coupling depends on the distance.

This behavior was confirmed investigating the magnetic ground-state of $FeBO_3$ ($B = Ti, Zr, Hf, Si, Ge, Sn$) materials by means of Density Functional Theory (DFT) calculations [31, 32]. **Figure 4** shows the relative Energy between AFM and FM structures as function of ionic radii of B^{4+} site cations.

From these results, it was observed that the FEM state is stabilized for ilmenite materials with large B-site metals (Sn, Hf, Zr); whereas, ilmenite cells contracted (Si, Ge, Ti) exhibit an AFM behavior. This result can be discussed as function of electronic repulsion between Fe^{2+} atoms 3d orbitals in different layers. In this case, we use the c-axis oriented to $3d_z^2$ orbital, once the cationic vacancy induces a coupling in such direction. Therefore, the B-cation volume control the distance among different Fe^{2+} layers from an angular distortion in O-B-O bonds in axial plane, which causes an increase/decrease in B-O bond distances allowing a higher/

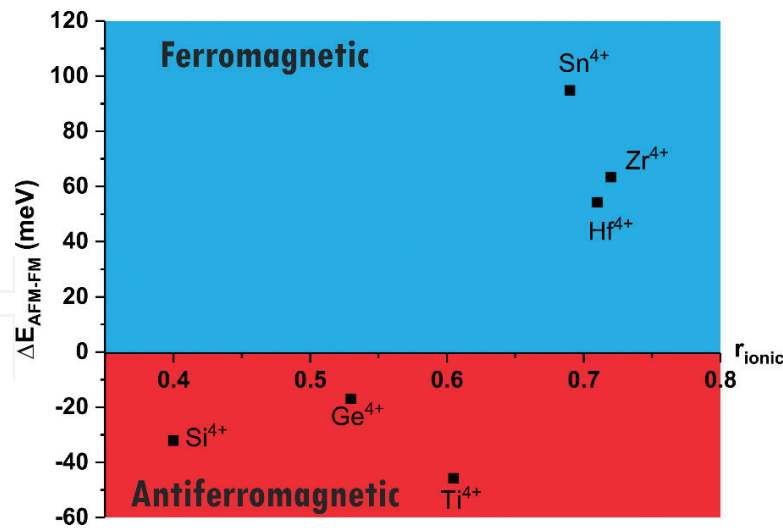


Figure 4. Energy difference (in meV) between AFM and FM configuration as function of B-site cation ionic radii (in Å).

lower interlayer distance between adjacent Fe^{2+} layers, affecting the signal of J , as represented in Figure 5.

In addition, the interlayer coupling has an additional degree of freedom associated with the Fe-O-B-O-Fe intermetallic connection, which is the responsible to originate a long-range coupling. This behavior can be related to the large overlap between valence orbitals from transition metals and 2p oxygen orbitals, which strengthen the intermetallic connection and, consequently, it induces a large electronic repulsion among unpaired electrons stabilizing the AFM configuration from Pauli Exclusion Principle. In case of the moving from Ti to Hf, it was noted that only FeTiO_3 shows a large contribution of 3d overlapped with O 2p orbital suggesting a higher overlap between these states providing strengthens in intermetallic connection that stabilizes AFM ground-state. In contrast, the smaller overlap between Zr(4d)/Hf(5d) and O(2p) orbitals allied to large Zr-O and Hf-O bond distances creates a smaller interlayer electronic repulsion responsible by FEM ordering.

Likewise, for FeBO_3 ($B = \text{Ti, Zr, Hf, Si, Ge, Sn}$) ilmenite materials is expected a FM ordering due to the absence of d valence orbitals. Nevertheless, only Sn-based ilmenite has this configuration indicating a big effect of ionic radius and interlayer distance of the FeO_6 clusters. The

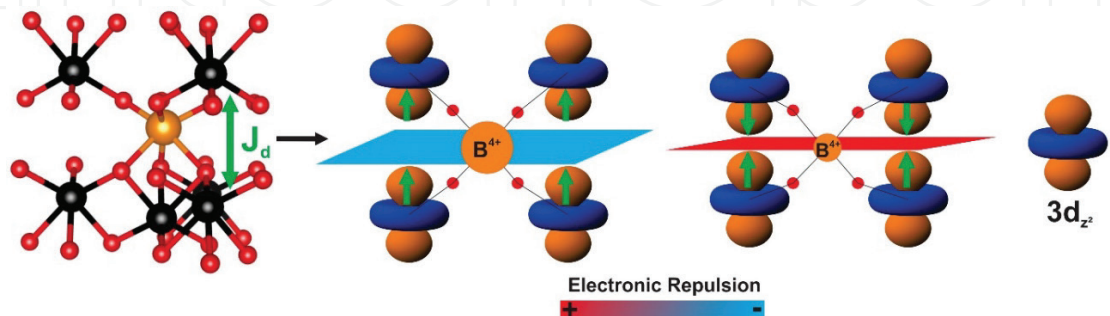


Figure 5. Representation of electronic repulsion between adjacent Fe^{2+} layer in FeBO_3 ($B = \text{Ti, Zr, Hf, Si, Ge, Sn}$) as function of ionic radius of B-site cation and its influence on magnetic ordering.

analysis of ionic radius and bond distance for FeBO_3 ($B = \text{Si, Ge, Sn}$) materials shows that the increase in ionic radius from Si^{4+} to Sn^{4+} results entails on a large distancing among Fe^{2+} layers in intermetallic connection that drastically reduce the electronic repulsion and stabilize the FM configuration. The information obtained by these theoretical results demonstrates that the control of magnetic ordering in ilmenite materials is based on a complex relation between ionic radius and valence orbitals of the B-site non-magnetic metals.

1.3. Magnetism in corundum-ordered structure (LiNbO_3 -type structure): magnetic properties in ferroelectric XNiO_3 and NiXO_3 ($X = \text{Ti, Ge, Zr, Sn, Hf and Pb}$) materials

The corundum ordered structure is most commonly called LiNbO_3 -type since this is the first material to present such crystalline phase. R3c materials are largely employed in development of memory devices, holographic data storage, electronic, electro-optical and optical devices, photo-induced devices and photocatalytic application due to a unique set of electronic, optical and ferroelectric properties usually observed for these materials. The first work on LiNbO_3 (LNO) structure were reported in 1949 and discuss this new structure as a ilmenite type; [33] however, in 1952 such information were refuted by Bailey [34, 35] that obtained results proving that, at room conditions, the LNO crystallizes in a R3c group instead of a R3 group characteristic of ilmenite. In particular, LNO structure has an ABO_3 general formula, lattice parameters $a = b \neq c$ and angles $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$; the A and B cations are both surrounded by six O atoms forming two distorted octahedra. Some features of LiNbO_3 -type structure are: (i) high distortion degree for octahedra within structure (**Figure 6a**); (ii) alternation between the cations A and B cation and vacancies along the c axis (**Figure 6b**); (iii) highly compacted layer composed by O atoms; (iv) the presence of intrinsic ordering vacancies [36–38]. These features are the responsible for the high ferroelectric properties characteristic of this type of structure.

The magnetism in this structure arises from unpaired electron from atoms occupying A or B sites within structure. In particular, the ground state spin ordering for materials in LiNbO_3 -type structure is determined by collinear interaction between layers in the structure and presents only one magnetic coupling constant (J) that refers to intralayer interaction (J) that occurs between M-O-M in the structure, where M is the magnetic cation in the structure (as observed in **Figure 6c**). At general, the magnetism in Solid State materials can be successfully described by Direct or Indirect interactions, Exchange interactions and Super Exchange interactions or Goodenough-Kanamori-Anderson (GKA) Rule; all of them, considers the unit cell magnetic resultant to determine the magnetism. However, the structural disorder makes such approaches not enough to predict the magnetism in R3c structures.

The magnetic properties for XNiO_3 and NiXO_3 ($X = \text{Ti, Ge, Zr, Sn, Hf and Pb}$) in R3c structures were evaluated by computational methodologies based on DFT [39, 40]. The obtained results for J for such materials were presented in **Figure 7**; as observed, TiNiO_3 , GeNiO_3 , ZrNiO_3 , PbNiO_3 , NiTiO_3 and NiHfO_3 are AFM and, as predicted by DMI interaction, are weak-ferromagnetic; whereas, the other materials are FM. The evaluation of structural properties for such materials evidences a connection between structural regularity and magnetic phase

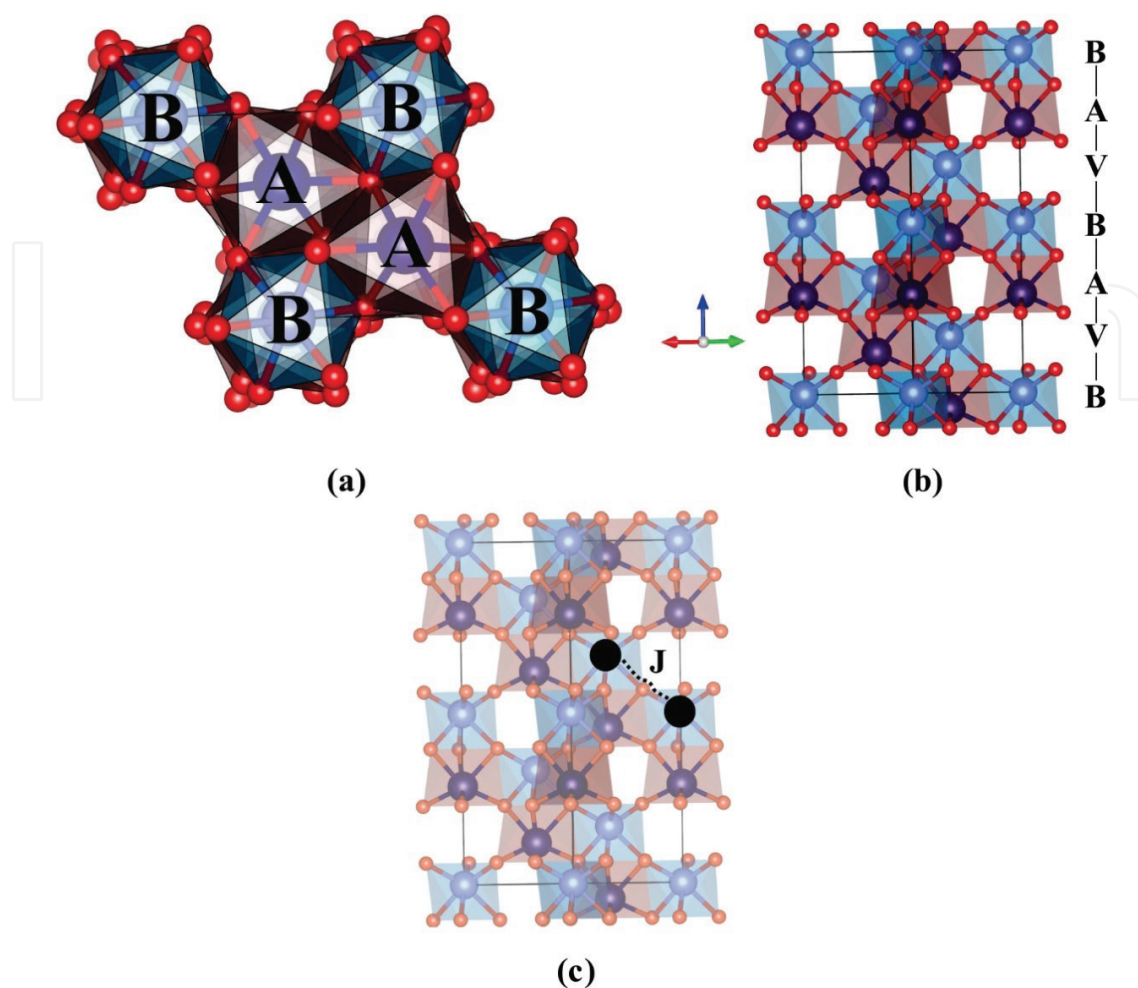


Figure 6. Crystalline structures of R3c structure showing the alternation between B, A and vacancies along z axis (a), $[AO_6]$ and $[BO_6]$ octahedra within structure (b) and magnetic coupling constant (J) for R3c structures (c).

stability, according to the relation between the distortion degree (δ) between $[AO_6]$ and $[BO_6]$, as expressed by $\delta_{[AO_6]}/\delta_{[BO_6]}$. Thus, for materials where the value of the equation is less than 1.5, the FM phase is more stable, whereas the AFM phase is more stable for materials with disorder ratio higher than 2.

Moreover, the theoretical investigation also provides information regarding to electronic levels of magnetic cations in $XNiO_3$ and $NiXO_3$. In these materials, FM and AFM ordering are originated from e_g and t_{2g} energy levels of Ni^{2+} cations localized on $[NiO_6]$ clusters. Furthermore, projected Density of States (DOS) clarifies why magnetic ordering is changed from chemical modifications. In particular, for AFM materials there are $[NiO_6]$ clusters magnetically ordered as α and β spins (**Figure 8**); structurally, these clusters are distributed by adjacent layers being each one oriented as one spin channel. Henceforth, α and β spins localized on e_g energy levels are responsible to stabilize the AFM state.

However, how to understand the origin of the FM ordering in these materials? The existence of the FM ordering in materials is dependent on the spin orientation being in the same direction on all magnetic clusters. Thus, it is necessary to discuss the electronic configuration

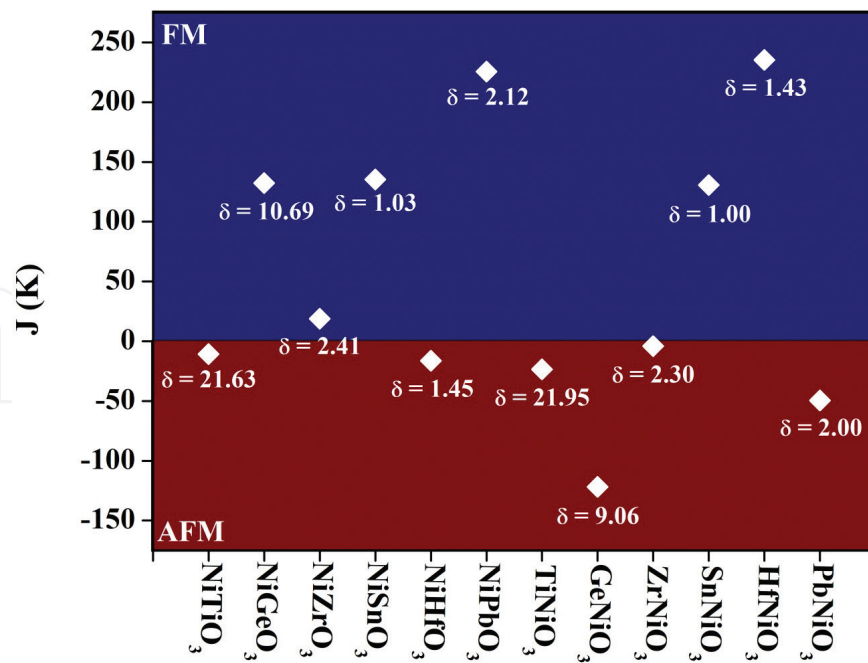


Figure 7. Magnetic coupling constant (J) for $XNiO_3$ and $NiXO_3$ ($X = Ti, Ge, Zr, Sn, Hf, Pb$) materials. The red region refers to the AFM materials, while the blue range represents the FM systems.

of the e_g and t_{2g} energy levels of Ni^{2+} . The projected DOS prove that in FM materials were observed a displacement on degenerated t_{2g} energy levels that creates two new groups of non-degenerated t_{2g} energy levels (**Figure 8**). In particular, the lowest t_{2g} energy levels and highest t_{2g} energy levels are occupied by α and β spins, respectively. For all $NiXO_3$ and $XNiO_3$ materials the $[NiO_6]$ clusters have the same electronic configuration, i.e., five α spins and three β spins giving rise to FM state, where all magnetic clusters are clearly at same orientation.

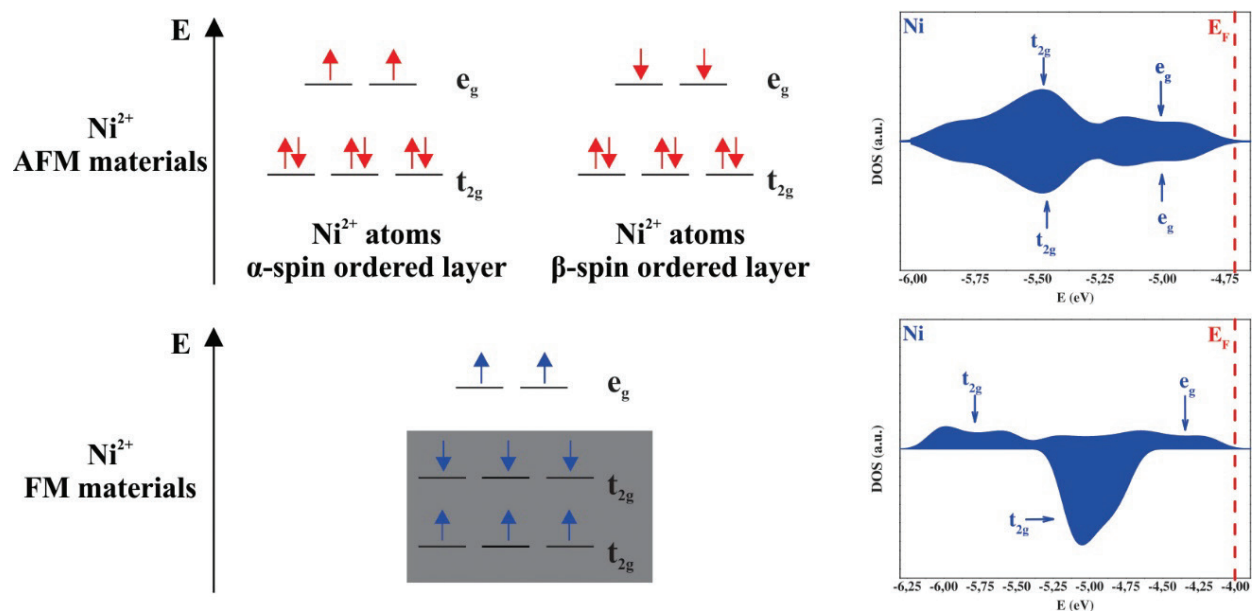


Figure 8. DOS projected results for e_g and t_{2g} energy levels localized on Ni^{2+} in AFM and FM materials. The gray region represents the broken on degeneration of t_{2g} energy levels.

Moreover, magnetic LNO-type materials have attracted the interest of materials scientist around the world in the last years as promising alternatives as smart and functional materials, mainly as multiferroic (MF) materials. The multiferroism consists on the coupling between magnetic ordering and some ferroic property in the same crystalline phase, but the main form of multiferroism is called of magnetoelectric (ME) coupling and are obtained by coupling between the magnetic ordering and ferroelectric properties. Consequently, electric polarization can be induced by a magnetic field or vice-versa.

The ME coupling was first reported in the first years of 1960s decade; thus, the study of this effect keep stable until that, in 2003, a strong coupling between ferroelectric and magnetic properties was observed for TbMnO_3 and TbMn_2O_5 materials as well as a high ferroelectricity for BiFeO_3 (BFO) films. Thenceforth, the study of MF materials increases drastically so that a fast search on *Web of Science* indicates at least 970 manuscripts focused in this class of material only in 2017. The investigation of multiferroic materials aims its application at development of several devices such as actuators, magnetic readers, sensors, tunneling and data storage devices. Moreover, MF materials are also potential alternatives for spintronics. The main representative of this class is the BFO; this material exhibits antiferromagnetic ordering as well as Magnetoelectric coupling at room conditions allied to a unique set of electronic, optical, magnetic and ferroelectric properties. In addition, other multiferroic materials were investigated by means of theoretical and experimental efforts, such as YMnO_3 , BiMnO_3 , PbNiO_3 (PNO), FeTiO_3 ; PbVO_3 , TbMnO_3 , TbMn_2O_5 , $\text{Ca}_3\text{CoMnO}_6$, LuFe_2O_4 , BaNiF_4 and others [41].

Even that many multiferroic materials are currently known, the development of MF material is this kind of material is delayed by crystalline structure and low Curie temperature (T_C); the first due to the fact that only 13 symmetry groups are able to exhibit multiferroic coupling, while the last makes its application impossible in technological purposes [42]. In a very restrict group of crystalline structures and, among then, are observed structures with lower and higher symmetry, such as $P2_1/c$, $P-1$, perovskite, ilmenite (R3) and LiNbO_3 -type structures (R3c). It is important to highlight that the R3c structure is the most common structure observed in known multiferroic materials, such as BFO, PNO, YMnO_3 , BiMnO_3 and TbMnO_3 .

2. Theoretical approaches to investigate magnetic solid state materials

Historically, the investigation of new materials aiming technological applications was a hard task that needed a long time of study. In this period, the theoretical-computational method was seen only as tool to study of materials already discovered. Front of the fact that the technological advance is extremely dependent on development of new materials, theoretical methods helped materials chemists and physicist on development materials at higher speed. Ever since, theoretical methods based on quantum mechanical simulations are an important tool to evaluate material properties, mainly at the molecular level [43].

Nowadays, innumerable theoretical methods are available; however, in the last 30 years the Density Functional Theory (DFT) changes the world offering the best relation between the

results precision and study time [44]. Another factor responsible for wide use of this theory is the high versatility, once presents good results to investigation of magnetic materials, semi-conductors, proteins, organic compounds and others [45].

2.1. Density Functional Theory

Several computational approaches can be applied to evaluation of materials properties; for instance: Molecular Dynamics (MD), *ab initio* methods and Semi-Empirical Methods. The MD analyzes the system properties based on the behavior of ball-and-springs models under application of an Force external field to atoms representation, while *ab initio* and Semi-empirical methodologies uses different approaches to solve the Schrödinger Equation and to obtain the system Wave-function (Ψ). In turn, DFT assumes that the system Total Energy is a unique functional of electronic density; this methodology can be simplified in two postulates: [46].

- i. The ground state properties for a system can be exactly and completely determined by the Density Functional (ρ), which is only dependent of three variables that determines the position (x , y and z).
- ii. Any try function for electronic density will have energy greater or equal than the ground state energy for a real system.

However, the analytical function for electronic density is not known; thus, the electronic density is obtained by Hartree-Fock Equations (HF) for achievement of ρ by a Self Consistent Field (SCF) Method. Although this similarity was observed, the DFT shows a highest precision and computational cost in relation to HF simulations due to smaller number of variable. The HF and Semi-Empirical methods employ a number of variables in the $4n$ order, where n refers to the number of electrons in the system; whereas, the DFT is dependent on three variables [43, 44].

The DFT formulism was proposed by Kohn and Shan (KS) in 1965 and consists in two equations applied on two different systems; such systems consider that there are no or there are interactions between electrons, respectively. The results for both systems show a significant difference of energy between then, and, aiming to correct this difference, the Exchange-correlation Term (E_{xc}) was inserted in DFT proposed. The E_{xc} is the sum of kinetic and potential energy difference between both systems. The physical meaning of E_{xc} is the interaction between electrons in the investigated system and refers to 1% of system Total Energy; due to this, DFT describes 100% of system Total Energy.

The description of E_{xc} terms changes according to employed exchange-correlation functional and, hence, the choice of a functional has a giant effect on materials properties evaluation, as offering better results as offering a reduction in computational cost. Among the E_{xc} functional stands out local (LDA and LSDA), non-local (pure GGA, PBE) and hybrid (PBE0, B3PW91, B3LYP, HSE06) types; the last represents the most powerful alternative to predict materials project.

2.2. Magnetic materials modeling based on DFT

The DFT is widely used on materials modeling since offers an excellent relation time \times efficiency, as denoted by results precision on prevision of materials properties in a short time. For instance, a DFT methodology provides thermodynamic properties for bulk or surfaces of

materials directly or using some additional approach as Berry Phase [47, 48] or Bulk Modulus [49, 50]. In turn, in Solid State materials the magnetic interactions are usually described by the Heisenberg Hamiltonian; however, in computer simulations this approach cannot be used because later determinant is not an eigenstate of such Hamiltonian. Thus, it is necessary the application of the Ising model which possibilities the evaluation of J magnetic coupling constant and ground-state magnetic ordering for simple and complex magnetic structure since using the energy difference between AFM and FM magnetic states since the unpaired electrons are well defined in the model Eq. (1). The Ising Model is described by Eq. (2), where N refers to number of magnetic cations in unit cell, Z is the number of magnetic neighbors and S_x represents the spin charge for each magnetic atom in unit cell. Both Eqs. (1) and (2) are combined in Eq. (3). The application of Ising Model was performed after the structural optimization of magnetic materials and requires that the spin orientation of unpaired electrons is well defined in the model. The Ising Model is described by Eqs. (1) and (2), where N refers to number of magnetic cations in unit cell, Z is the number of magnetic neighbors and S_x represents the spin charge for each magnetic atom in unit cell. The application of Ising Model was performed after the structural optimization of magnetic materials and requires that the spin orientation of unpaired electrons is well defined in the model. Plus, in materials with more than one magnetic and not reproductive site, the Ising model should be applied to each magnetic ordering and thus, applied to ground-state model.

$$\Delta E_T = E_{T_{AFM}} - E_{T_{FM}} \quad (1)$$

$$\hat{H}_{Ising} = -N.Z.S_1.S_2.J \quad (2)$$

$$E_{T_{AFM}} - E_{T_{FM}} = -N.Z.S_1.S_2.J \quad (3)$$

The Ising Model methodology to prevision of magnetic properties of Solid State materials was employed by Ribeiro and coauthors [51], Chartier and coauthors [52], Feng and Harrison [53] and Lacerda and de Lazaro [39] to investigate materials and different crystalline structures proving the efficiency of this approach. The high efficiency and almost direct measurement offered by Ising Model indicates it as the best theoretical approach to investigation of magnetic solid state materials.

3. Conclusion

In this chapter, the role of Density Functional Theory calculations for strongly correlated materials was summarized, focusing in the description of the ground-state magnetic ordering for solid state materials, in particular $ATiO_3$ ($A = Ti, Zr, Hf, Si, Ge, Sn$) ilmenite derivatives and corundum ordered $XNiO_3$ and $NiXO_3$ ($X = Ti, Ge, Zr, Sn, Hf$ and Pb) materials. A review about the theories behind the magnetism in solid state materials was presented in order to clarify the contribution of collective magnetic ordering, local structure and exchange interactions.

In case of ilmenite ATiO_3 derivatives, the local structure associated with the magnetic ordering of Fe^{2+} layers was systematic investigated from theoretical calculations, resulting in chemical dependent interactions depending upon the interlayer distance (B-site cation volume) and orbital-resolved electron transfer. The summation between this analysis was helpful to predict new ferromagnetic materials such as FeSnO_3 , FeZrO_3 and FeHfO_3 .

Additionally, for corundum ordered XNiO_3 and NiXO_3 ($\text{X} = \text{Ti, Ge, Zr, Sn, Hf and Pb}$) materials the theoretical results indicates that the magnetic ordering is: (i) dependent on structural distortion in $[\text{XO}_6]$ and $[\text{NiO}_6]$ clusters; (ii) arise from $\text{Ni } t_{2g}$ and e_g not conventional energy degeneration and (iii) even antiferromagnetic materials presents a magnetic resultant in consequence of structural distortion characteristic of R3c structure. The employment of theoretical approaches based on DFT possibilities the proposal of new material to technological purpose based in the magnetism as well as provides a complete description of magnetic, structural and electronic properties in a short time period.

Despite the challenge dealing with magnetic materials, theoretical simulations, mainly DFT-based, can be used to clarify the unusual phenomena's commonly observed in such materials, as well as to predict new candidates with singular properties, improving the perspective of materials design.

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