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Ab initio calculation of structural, electronic and magnetic properties and hyperfine parameters at the Fe sites of pristine $ZnFe_2O_4$

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ABSTRACT

In this work we present an *ab initio* study of structural, electronic, magnetic and hyperfine properties of pristine Zn-ferrite ($ZnFe_2O_4$, ZFO). Density Functional Theory calculations were performed using the Full-Potential Linearized Augmented Plane Waves (FPLAPW) method in the framework of the Generalized Gradient (GGA) and the GGA+U approximations. In order to discuss the magnetic ordering and the electronic structure of the system we considered different spin arrangements. We found that ZFO presents an energy landscape characterized by a large number of metastable states separated by an energy barrier of about K_BT_F, being K_B the Boltzmann constant and T_F the freezing temperature, indicating that ZFO can be described as an spin-glass system at low temperature (<10.5 K). Our calculations also support the picture that below 10.5 K small ferromagnetic spin-clusters (short-range interactions) surrounded by similar spin-clusters with opposite spin orientations (long-range interactions) coexist. Finally, our calculations predict a band gap of normal ZFO of 2.2 eV and successfully describe the hyperfine properties (isomer shift, magnetic hyperfine field and electric field gradient tensor) at the Fe sites that are seen by Mössbauer Spectroscopy (MS) at 4.2 and 300 K. This comparison enables us to characterize the local spin structure around Fe atoms and to explain the origin of the two hyperfine interactions experimentally observed, giving support to the coexistence of short- and a long-range order below 10.5 K.

1. Introduction

Oxides with the spinel structure (XY_2O_4, with X: Zn, Co, Ni, Al Mg, Ti, and Y: Al, Ga, In, Ti, V, Cr, Fe, Co, Rh, Mg, Mn, Ni, Cu, etc., see Ref. [1]) comprise an important class of compounds with a variety of electronic and magnetic properties that make them interesting for different technological applications [2–5]. A particular subgroup of this family are the ferrites (XFe_2O_4), an important and interesting class of magnetic oxides and one of the most extensively studied magnetic materials. Due to their electronic characteristics (small band-gap semiconductors or insulators at low temperatures) they have been used in a number of technologically applications such as microwave devices, magnetic and magneto-optic recording, and electronic information mass storage [5–8].

In particular, the Zn-ferrite, $ZnFe_2O_4$ (ZFO) has been the subject of several studies because of its intriguing magnetic properties compared to other spinel ferrites [9]. The ZFO crystal structure is characterized by 8 tetrahedral *A* sites, occupied by Zn^{2+} and 16 octahedral *B* sites occupied by Fe^{3+} ions (normal spinel) [1]. The magnetic coupling between the Fe atoms on the *B* sublattice is due to superexchange via oxygen atoms and is weak. The Fe sites form a corner-sharing tetrahedral lattice that has the same atomic arrangement of pyrochlores and C15 Laves phase. These systems are characterized by geometrical frustration and unusual ground state phases (spin glass, spin ice, etc. [10]). Considering the similarity of the structures, topological frustration is expected in normal ZFO [11,12].

Different groups have studied the magnetic properties of ZFO using various experimental methods until now, but contradicting experimental results have been reported. Usually it is claimed that ZFO ferrite is a strongly paramagnetic substance with antiferromagnetic coupling only below $T_N = 10.5$ K (Neel temperature). But the situation is more complex. Neutron diffraction studies performed on high quality samples [13] have shown that even at

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temperatures of about 100 K, a short-range order (SRO) develops. Below 10.5 K long-range antiferromagnetic order (LRO) and SRO coexist and the system remains magnetically disordered even at temperatures as low as 1.5 K [13]. In consequence, the well-defined cusp-like anomaly at around 10.5 K in static susceptibility data does not correspond to the Neel Temperature in the ordinary meaning. Usa et al. [11,14] suggested that the LRO is driven by the quenched atomic disorder, allowing the interpretation of ZFO as an intrinsically frustrated spin system with nearest-neighbor antiferromagnetic interactions (Ref. [11] and references therein). On the other hand, from static magnetic susceptibility experiments, a positive Curie-Weiss (θ_{CW}) temperature of 120 K was estimated [11]. This result is in clear contradiction with the previously mentioned antiferromagnetic interaction between nearest-neighbors in normal ZFO, suggesting that the SRO is ferromagnetic like. This conclusion was supported by a theoretical analysis (based on a classical Heisenberg spin model) of neutron scattering experiments performed in single-crystal samples [10,11]. This work assumes a normal free-of-defects sample and predicts that ZFO is governed by an antiferromagnetic third-neighbor exchange interaction J_3 and a ferromagnetic first-neighbor one J_1 [11]. Based in these results, a magnetic configuration with ferromagnetically-coupled spins forming clusters and arranged antiferromagnetically with other clusters could be possible below the cusp temperature. Based on this idea Yamada et al. [11] and Tomiyazu et al. [15] proposed a molecular spin model that is consistent with the neutron scattering data [10]. A spin-molecule refers to a self-organized spin cluster. Correlation among the spins that form the spin-molecule is negligible in comparison to the intra-molecular correlation. The spins of one Fe-tetrahedron of the pyroclore-type ZFO structure are coupled ferromagnetically but antiferromagnetically with the spins of others Fe-tetrahedron [11,15].

Later, M. A. Hakim et al. [16] reported that field cooled and zero field cooled DC magnetizations display a divergence at low temperature. This result indicates that there is a frozen state with freezing temperature $T_F = 21$ K, suggesting that ZFO presents a spin-glass phase at low temperatures and it is not a canted antiferromagnet. A spin-glass is a magnetically disordered system with high magnetic frustration in which each spin freezes in a random orientation below T_F [17]. A spin-glass contains many metastable states separated by an energy barrier of about K_BT_F [18].

In order to elucidate the magnetic ground state and the electronic structure of pristine normal ZFO, we have performed an *ab initio* study of the structural, electronic and magnetic properties of this oxide. The calculations used the Full-Potential Linearized Augmented Plane Waves method (FPLAPW). The Generalized Gradient (GGA) and the GGA+U approximations were used to describe the exchange and correlation potential. We discuss the validity of both approaches and the dependence of the results with the value of U. To find the lowest energy spin configuration, we considered the ferromagnetic and different antiferromagnetic spin configurations. For all cases, we computed the total energies, the band structures and hyperfine parameters (isomer shift, quadrupole splitting, quadrupole shift and hyperfine magnetic field) at the Fe sites. From the lowest total energy obtained the equilibrium structure and the ground state of pristine ZFO is found. The hyperfine parameters at the Fe sites for the different magnetic configurations studied were compared with the experimental ones, obtained in Mössbauer Spectroscopy (MS) experiments performed on high quality samples of normal ZFO. As we will show, the two different interactions experimentally detected at 5 K can be associated to Fe nucleus in two different magnetic environments, one ferromagnetic and the other antiferromagnetic, in agreement with the spin-glass phase and the formation of small ferromagnetic spin-clusters surrounded by clusters with opposite spin orientation.

2. The system under study

The spinel ferrites (XFe_2O_4) are isostructural with the mineral $MgAl_2O_4$ (spinel) [1] and belong to the space group *Fd*3*m* (*Oh7)*. Ferrites crystallize in a face-centered cubic lattice with a close-packed arrangement of oxygen ions, with X and Fe ions at two different crystallographic sites (sites *A* and *B*). These *A* and *B* sites have O_4 (tetrahedral) and O_6 (octahedral) oxygen coordination, respectively [1]. The unit cell contains eight formula units. Two types of ferrites can be distinguished: the normal and inverted ferrites. In the normal ferrites, the X ions occupy the *A* sites and the Fe atoms the *B* sites. In the inverted ferrites, eight Fe atoms are located at the *A* sites and the X and Fe metal ions occupy the *B* sites in equal proportions. Inverted ferrites can be described by the formula $Fe[FeX]O_4$.

The spinel structure is characterized by two parameters, the lattice constant *a* and the oxygen positional parameter *u*. For an ideal spinel *u* has the value of 0.25 for the -3*m* origin [1]. Generally, *u* is often found to be higher than the above value for all the spinels. The spinel ferrite investigated here, $ZnFe_2O_4$ (ZFO), adopts the normal spinel structure. However, depending on the procedure under which ZFO is growth, partial inversion can occur. For ZFO, different values of the lattice parameter *a* have been reported, ranging from 8.43 to 8.46 Å [13,19–22]. A lattice parameter $a = 8.52$ Å at ambient temperature was determined using x-ray powder diffraction by K. Kamazawa et al. [10]. The authors claim that this value (slightly larger than those previously reported) is more accurate since it was obtained from a high-quality sample. In normal ZFO the Zn atoms are located at tetrahedral *A*-sites (Wyckoff position 8*a* (1/8, 1/8, 1/8)), whereas the Fe atoms (which carry a magnetic moment due to the partially filled 3*d* shell) occupy the octahedral *B*-sites only (16*d*, (1/2, 1/2, 1/2)). The Fe-O and Zn-O bond lengths are 2.04 and 2.00 Å, respectively. The O atoms are at 32*e* (*u*,*u*,*u*) positions of the fcc structure ($u = 0.258$, Ref. [22]).

3. Computational aspects

3.1. Computational methods

Ab initio electronic structure calculations were employed to determine the self-consistent potential and the charge density inside the cell of ZFO. From the charge density structural, electronic, magnetic and hyperfine properties of ZFO were obtained. The calculations were performed with the WIEN2K [23] implementation of the FPLAPW method [24–26] in a scalar relativistic version. Exchange and correlation effects were treated within density-functional theory using the Wu and Cohen parameterization of the generalized gradient approximation (GGA) [27]. Since the exchange and correlation effects included in GGA are insufficient to describe 3-*d* transition oxides, GGA plus the Hubbard *U* term (GGA+U) in the self-interaction correction (SIC) scheme was employed [28]. GGA+U is not a fully *ab initio* method, because we have to select *a priori* the on-site Coulomb energy *U* [29]. In this study we took $U = 5$ eV for the 3*d*-Fe orbitals. This value was selected after the study of a set of Fe oxides ($FeTiO_3$, $TiFe_2O_4$, FeO, Fe_2O_3, Fe_3O_4) as a function of *U* in the range from plain GGA calculations ($U = 0$) to $U = 7.0$ eV. For $U = 5$ eV, we correctly reproduce the structural properties, band gaps, magnetic moments and experimentally reported hyperfine parameters at the Fe sites for the set of Fe-oxides studied (see next section). Based on this, we “transferred” the value of *U* to ZFO. For some selected systems, we also studied the effect of adding a *U* value for the 3*d* levels of Zn. As we will show, none of the results presented here are affected by this additional correction.

In the FPLAPW method, the unit cell is divided into non-overlapping spheres with radius R_i and the interstitial region. The