Magnetism in spinel and garnet structures

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ABSTRACT. The study of the building process of the magnetite leads to consider it as a normal spinel. This result suggests to attribute different magnetic moments to iron according to its crystallographic site in the $Ln_3Fe_5O_{12}$ garnets as in magnetite. The calculation of the magnetic moment of $Ln_3Fe_5O_{12}$ garnet is made in the framework of Dirac's theory. The coupling between the light or heavy rare earths and the iron lattice moments is the same but with a total contribution of the latter of $2.80\mu_B$ for europium and light rare earths garnets and $5.20\mu_B$ for the others.

RESUME. L'étude du procédé de construction de la magnétite conduit à la considérer comme un spinel normal. Ce résultat suggère d'attribuer différents moments magnétiques au fer suivant son site cristallographique dans les grenats $Ln_3Fe_5O_{12}$ comme dans la magnétite. Le calcul du moment magnétique des grenats est déterminé suivant la théorie de Dirac. Le couplage entre les moments des terres rares légères ou lourdes et le réseau du fer est le même mais avec une contribution totale de $2.80\mu_B$ pour l'europium et les terres légères et de $5.20\mu_B$ pour les autres.

1 Introduction

In view to explain the building process of the space of spinel structure we have shown in "Atoms and crystal structures" that the magnetite is a normal spinel [1]. In this approach, the atoms are neutral. A similar building process can been proposed for the garnet structure. This implies two different magnetic contributions for iron according to its site occupation in the same crystal. We will first recall the case of the magnetite and then discuss that of the garnets.

Now, magnetism generally uses the concept of spin. In fact Dirac's theory shows serious difficulties compared to the traditional approach of this concept. In particular, light and heavy rare earths correspond to the progressive filling of the two $4f_{5/2}$ and $4f_{7/2}$ subshells for the 4f layer. However, the energy levels of the two subshells of a same shell correspond to relativistic corrections of mass and nothing indicates that they correspond to states of spin-up and spin-down [2]. Further discussion concerning the notion of rotation is given in [3].

2 The spinel structure

A large number of compounds with the RM_2O_4 formula crystallize with the spinel structure. In this structure, the atoms of oxygen occupy the position of an almost perfect cubic close-packing arrangement. Notice that in the ionic approach, the oxygen ion has the largest volume and the lattice seems to be built on packing of these ions. In this fcc lattice the atoms of metals occupy two different sites: one atom in the A tetrahedral site and two atoms in the B octahedral site. The building process of the crystalline space from neutral atoms brings a new concept for the Fe_3O_4 magnetite where iron occupies the two sites of the metals. Notice that in this approach the iron atoms have the larger volume, about the double to that of the oxygen.

During the first attempts to interpret the spinel structure, the simplest seemed to attribute the tetrahedral site to the R metal and octahedral to M metal. However, there appear shortly difficulties concerning the size of the metal occupying the two sites. In this eventuality for $MgFe_2O_4$ and $MgAl_2O_4$, the magnesium the bigger of the two atoms or of the metallic ions would occupy the smallest site [4]. The study of the intensity of the rays of diffraction has led to suppose that magnesium occupies half of the B site for the two spinels. Consequently, when the R atom occupies the A tetrahedral site, the spinel is called normal and inverse if it occupies the B site with one of the two M atoms.

In the case of the Fe_3O_4 magnetite, the classical equilibrium of valence leads to distinguish two types of iron atoms: two Fe(III) trivalent iron atoms and one Fe(II) bivalent iron atom. In the ionic approach the ferrous iron being bigger than the ferric iron it is possible to propose an inverse spinel structure. With neutral atoms, the size of the volume to distinguish the two types of atoms or the intensity of the rays of diffraction does not allow to decide either the inverse or normal character of the spinel. We need a different approach. On the other hand, there is a need to understand how the crystalline space is built with the spinel structure for this compound.

The comparison between the volumes of the monochalcogenides of rare earths and of the *3d* metals shows the tetravalent character of different metals including iron and the existence of metal-metal bonds responsible of the valence [1]. This result points out that metals with metal-metal bonds play an important role in the building process of the space. As a result of the short metal-metalloid distance, the tetrahedral coordination can be considered as more stable than the octahedral coordination with larger metal-metalloid distances. The existence of numerous radicals with the tetrahedral coordination as PO_4, SO_4, and VO_4 also strengthens this supposition. Consider the inverse spinel $NiFe_2O_4$ [5]-[6], the iron with two *3d* electrons less than nickel has windows on the nucleus more attractive imposing its tetrahedral coordination and leaving to nickel and to the other half of iron the octahedral site. Thus we are led to suppose that the space is built by the $[FeO_4]$ covalent groups and between them the other atoms of metal make cement. In this view one has to consider the magnetite as a normal spinel with from this result the valence four for the tetrahedral iron and two for the octahedral iron. The interpretation of the Curie constant is coherent with this approach [7]; it leads in Kemu/gat unit to two times the $C(Fe_B) = 5.55$ value and one time the $C(Fe_A) = 3.12$ value giving $C(Fe_3O_4) = 14.22$ as theoretical value for an experimental value of 14.2 and a value of 11.76 according to the classical model. The calculation of the μ magnetic moment to saturation to zero Kelvin degree is equally in agreement with this approach; supposing with Néel [8] an antiparallel coupling between the A and B sites it comes:

$$\mu_{th} = 2\,\mu(Fe_B) - \mu(Fe_A). \tag{1}$$

In our work on magnetism with Georges Lochak [2], we have supposed that the individual magnetic momentum of an electron of a hydrogen atom remains in a complex atom, despite the strength of the perturbation. It follows that the magnetic moment of an atom is the sum of the magnetic moments of the electrons, which make their contribution. The magnetic moment of an electron is:

$$\mu_e = \mathrm{g} u \mu_B \quad \textit{with} \quad \mathrm{g} = k(k + ½)^{-1} \tag{2}$$

where: μ_B is the Bohr magneton, *u* the projection of the total angular momentum on the direction of the magnetic field, g is the factor of Landé, *k* is Dirac's q. n. homologous with Schrödinger's q. n. ℓ. In a same layer it takes the values $k = \ell$ and $k = -\ell - 1$.

The magnetic moment of iron in the oxides can vary according to the electrons contributing [9]. For the magnetite and the nickel ferrite inverse spinel, the moments to consider are $\mu(Fe_B) = 4{,}6\mu_B$ and $\mu(Fe_A) = 5\mu_B$.

In Dirac's theory, $5\mu_B$ for iron corresponds to the sum of the contributions of the four electrons on the first $3d_{3/2}$ subshell that is $3.2\mu_B = 2\times 1.2\mu_B + 2\times 0.4\mu_B$ to which is added $1.8\mu_B$ the contribution of Fe electron of iron after Mn [1]. For the magnesium ferrite it comes $\mu(Fe_B) = 4{,}2\mu_B$ and $\mu(Ni_B) = 2{,}6\ \mu_B$. The change of $0{,}4\mu_B$ between two iron moments correspond to the contribution of one $3d_{3/2}$ electrons.

Table I. Magnetic moments in spinels.

RFe_2O_4	μ_{th}	μ_{exp}	$\mu_{th\text{-}Néel}$
Fe_3O_4	4.20	4,118	4
$NiFe_2O_4$	2.20	2,22	2
$MgFe_2O_4$	0.80	0,86	0

In table (1), for $\mu(Fe_3O_4)$ the experimental value of 4,118 μ_B is that obtained by Pauthenet en 1983 on single crystal in the direction of easy magnetization and with magnetic field up to 180Koe [10]. The other experimental values are also those from the thesis of Pauthenet [11]. The moment μ_{th} of the model of Néel is the sum of the contribution of one electron in Bohr magneton by single electron.

3 The garnet structure

In the classical model, the net magnetic moment observed for $Ln_3Fe_5O_{12}$ garnets, called LnIG, is explained in terms of coupling between the rare earths and the iron sublattice moments. The results in Table 2 are for supposing the antiparallel coupling for heavy and parallel for light rare earths. This model, the µth-P values, does not corroborate with many experimental results shown in table 2.

The magnetization curves of various garnets shows that their Curie temperature stays close to 560°K [4]. This allows supposing that the contribution of the iron is the most stable with just one type of coupling for light and heavy Ln.

For LnIG: there are 3Ln in the dodecahedral sites, 2Fe in the octahedral sites and 3Fe in the tetrahedral sites. Like in the building process of the spinels, we suppose that the [FeO4] covalent groups build the space, and that between them the atoms of the other metals act as a cement, build the space. This leads to suppose two different magnetic moments for iron in the octahedral and tetrahedral sites.

YIG has a saturation moment around $5\mu_B$. This value was interpreted in terms of a net contribution of the iron of $5\mu_B$ in its two crystallographic sites, the moments on these two sites being antiparallel. The existence of a compensation point and the fast decrease of μ(LnIG) with temperature for several garnets of the heavy rare earth, leads to suppose that the total contribution of iron [14] for these garnets must be subtracted from that of the rare earths giving:

$$\mu(\text{LnIG}) = 3\,\mu(\text{Ln}) - 3\mu(\text{Fe-tétra}) + 2\mu(\text{Fe-octa}). \quad (3)$$

Table 2. The magnetic moment of LnIG in μ_B: μth according to this work, μth-P according to Pauthenet supposing the quenching of the angular momentum [11]. Experimental values [17-21].

	Gd	Tb	Dy	Ho	Er	Tm	Yb
μth	16.23	17.51	17.06	14.09	9.80	-1.33	-0.07
μex	15.93	18.2	16.85	13.90	9.62	-1.20	0.00
μth-P	16.00	13.00	10.00	7.00	4.00	1.00	2.00

	Pr	Nd	Sm	Eu	Y	Lu
μth	10.51	9.22	5.37	2.80	5.20	5.20
μex	9.89	9.05	5.43	2.78	5.03	5.07
μth-P	7.00	8.00	10.00	13.00	5.00	5.00

Thus we have to find two different iron magnetic moments giving a value equal or close to $5\mu_B$ according to the relation (4). Taking μ(Fe-tétra) = $3.2\mu_B$ and μ(Fe-octa) = $2.2\mu_B$ it comes:

$$3\mu(\text{Fe-tetra}) - 2\mu(\text{Fe-octa}) = 5.2\mu_B. \qquad (4)$$

For the others LnIG, where Ln stands for Eu, Sm, Pr or Nd, the iron moment is supposed to be in the octahedral site $\mu(\text{Fe-octa}) = 5\mu_B$ and in the tetrahedral site $\mu(\text{Fe-tetra}) = 2.40\mu_B$.

$$2\mu(\text{Fe-octa}) -3\mu(\text{Fe-tetra}) = 2.8\mu_B. \qquad (5)$$

The magnetic moment of the rare earths of LnIG are determined in the same way as in our previous work on the subject [9]. Using the relations (3) and (4) for the heavy rare earths and (3) and (5) for light rare earths we obtain the results given in the table (2). For Dy, Ho and Er there are two possible μ_{th} values differing of $0.43\mu_B$ with the experimental value μ_{ex} between them. The highest reported in the table 2 is also the closest to μ_{ex}. Comparing to our previous study [9], this new approach with two different iron moments for the heavy rare earths LnIG, as for the light rare earths, improve the coherency with the experiment for most of them.

Furthermore, the experimental values of $5.03\mu_B$ and $5.07\mu_B$ obtained for YIG and LuIG are explained with the theoretical value of $5.20\mu_B$ higher than the previous expected value of 5.0μB.

Table 3. The magnetic contribution of the rare earths in LnIG.

	Gd	Tb	Dy	Ho	Er	Tm
$\mu(4f_{5/2})$	4.29	3.00	1.71	1.29	0.43	1.29
$\mu(4f_{7/2})$	2.86	4.57	5.71	5.14	4.57	0.00
μLn	7.14	7.57	7.42	6.43	5.00	1.29

	Yb	Pr	Nd	Sm	Eu
$\mu(4f_{5/2})$	0.00	2.57	2.14	0.86	0.00
$\mu(4f_{7/2})$	1.71	0.00	0.00	0.00	0.00
μLn	1.71	3.86	2.14	0.86	2.57

4 Conclusion

To calculate the magnetic moments in magnetite and LnIG we have used the covalent building group [FeO_4], involving different magnetic moments for octahedral and tetrahedral sites. The process improves the coherency between experimental and theoretical magnetic moments with accuracy of an order of the percent. This work should shed light on the mechanism allowing a filled subshell to have different magnetic contributions according to the element and the crystallographic structure.

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