A microscopic model of oxygen vacancies in Ca-doped YIG

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Abstract. Annealing experiments carried out on calcium doped yttrium iron garnet (Ca:YIG) in an oxygen-reducing atmosphere, show dramatic decreases in the magnetisation over the entire temperature range. Simultaneously, the electric resistivity and the electric activation energy significantly increase. Within the framework of the iron-oxygen cluster model, we analyse and compare with each other two situations, in which compensating holes can be found. The first is their occupying hybridised eigen-energy levels of the cluster. In this case, it can be shown at which ions the holes tend to remain for a given energy level. It turns out that the active holes remain localised most at the oxygen ions. The other situation means the hole’s localisation in an attractive trap centre. The latter is created at the missing oxygen ion between the tetrahedral and octahedral iron-oxygen ionic clusters in the proximity of a doping Ca$^{2+}$ ion. For a sufficiently shallow traps, their localised states can be considered within the framework of hydrogen-like model. The ground state energy of the vacancy can thus be estimated, considering the dielectric constant of the host material and the hole’s effective mass as variational parameters. Communication between the tetrahedral and octahedral iron-oxygen clusters with missing oxygen between them, is assumed to be maintained via the $s – d$ hybridisation.

1. Introduction

There has recently been observed a great interest in creating semiconducting materials with permanent magnetic moment by an appropriate modification of those which already have magnetic long range order but do not necessarily conduct the electric current. Yttrium iron garnet (YIG) seems to be a good candidate for such a role as it is a ferrimagnet with high Curie temperature (550 K). Pure (YIG) is an almost ideal insulator, however, doped with valence uncompensated ions it becomes a semiconductor. In the last decades, many experiments have been carried out indicating that both the electric and magnetic properties of yttrium-iron garnets depend critically on the type and number of impurities included into the host structure. Our recent analysis is aimed at an understanding of a role of oxygen vacancies, which are present in all garnet structures. The empirical data concern thin films of yttrium-iron garnets doped with divalent calcium ions Ca$^{2+}$, which substitute trivalent yttrium [1-3]. Calcium is as diamagnetic as yttrium, so it basically leaves the magnetic moment untouched. Nevertheless, it can have significant effects on the magnetic moment of the system. Also, the electric properties of YIG are dramatically altered by the doping. Ca:YIG is a p-type semiconductor. Calcium ion introduces a local charge imbalance at the dopant site which is minimised by the creation of secondary induced charge centres of opposite sign. In our model, monovalent or completely missing...
oxygen ions immediately adjacent to the included $Ca^{2+}$ are considered as the principal charge compensating mechanism. The role of $O^-$ centres has been already discussed in a great detail elsewhere [4,5]. In the present paper, we concentrate on the question of oxygen vacancies which are oxygen sites with no oxygen ions but containing one ($V_O$ or two $V_O$) orbital compensating holes. In the first case, the vacancy compensates one adjacent $Ca^{2+}$, whereas the other vacancy compensates two calcium ions globally. It has been known that at temperatures below 100 K the magnetisation in Ca:YIG exhibits an anomalous decrease relative to that expected for pure YIG. Within the framework of our cluster model, we propose monovalent oxygen as an key instigator of this magnetisation anomaly. The lowering in magnetisation can be explained by a change of the local super-exchange interaction for ferromagnetic and a reduction of the tetrahedral cluster spin from $S = 5/2$ to $S = 2$ [4]. It has turned out that annealing in reducing atmosphere gives rise to even more dramatic decreases in the magnetisation of Ca:YIG over the entire temperature range. Furthermore, the observed shift in magnetisation for the $N_2$ annealed samples was linearly proportional to the change in crystal lattice constant[1,2]. The empirical results show conclusively that the magnetisation is related to the number of missing oxygen ions, which implicitly supports one of our most important previous conclusions [4] that actually compensating holes remain on the oxygen sites and only occasionally can hop at the iron sites, forming thereby $Fe^{4+}$ ions, the latter action being highly unfavourable from the energetic point of view as it involves the highest energy level of the iron-oxygen cluster. The organisation of the paper is as follows. In the next section, we briefly analyse a microscopic model of a pair of the octahedral ($a$) and tetrahedral ($d$) ionic clusters with the emphasis put on a key role which is played by the oxygen mutual site in determination of both the magnetic properties and the charge transport (see: for details, [4-6]). The analysis is aimed at a better understanding of a situation which occurs when the mutual oxygen vanishes. To achieve this objective, it seems to be necessary and sufficient to consider a pair of a and d ionic clusters, while only inducing influence of the remaining system in a form of certain mean-field parameters, such as the dielectric constant, or the effective mass of the compensating hole. In the third section, we focus on the properties of the vacancy with one or two compensating holes trapped in it as the topic requires obviously a deeper viewing. The oxygen vacancy is considered to be shallow and, consequently, treated as an hydrogen atom with the Coulomb attraction formed between a positive compensating hole and a resultant negative charge of $Ca^{2+}$ substituted for $Y^{3+}$. Assuming localisation of the hole at the empty oxygen site, we thereby determine the Bohr radius as being equal to the distance between the empty oxygen site and an $Ca^{2+}$ ion in its proximity, which means that its ground state energy is known, as well.

### 2. A microscopic model of a pair of the a and d iron-oxygen clusters with the oxygen vacancy

Electronic properties of the single tetrahedral (d) and octahedral (a) ionic clusters are determined by the five 3d electrons localised at the central iron ions and the six 2p electrons at each neighbouring oxygen site. Considering systems with their charge transport maintained by positive compensating holes it seems quite natural to analyse their electronic structure in terms of orbital holes rather than electrons. We thereby start with the Anderson Hamiltonian in the atomic limit rewritten for the pair of the different ionic clusters, in terms of the orbital 3d and 2p holes [4]:

$$\hat{H} = \hat{H}_{3d} + \hat{H}_{2p} + \hat{H}_{d-d}$$

where

$$\hat{H}_{3d} = E_a \sum_{i,m} \hat{n}_{i,m} + E_d \sum_{j,m} \hat{n}_{j,m} + \frac{U}{2} \sum_{i,m} \hat{n}_{i,m}\hat{n}_{i,-m} + 1/2U \sum_{j,m} \hat{n}_{j,m}\hat{n}_{j,-m}$$

$$\hat{H}_{2p} = \frac{1}{2} \sum_{i,m} \hat{n}_{i,m}$$

$$\hat{H}_{d-d} = \frac{1}{2} \sum_{j,m} \hat{n}_{j,m}$$
Figure 1. The hybridised single-hole energy levels of the octahedral ($E_a$) (dashed line) and tetrahedral ($E_d$) (solid line) clusters vs the $p-d$ hybridisation parameter ($V$) for the following values of the on-site energies: $E_a = -1.5\text{eV}, E_d = -0.44\text{eV}, E_p = 2.5\text{eV}$ and $U = 8\text{eV}$.

and

$$\hat{H}_{2p} = E_p \sum_{\sigma,m} \hat{n}_{\sigma,m}$$

(3)

The communication between the two systems of the orbital holes is maintained by the $p-d$ hybridisation which is assumed to take the following simple form:

$$\hat{H}_{p-d} = \sum_{l,\sigma} (V(l,m|\sigma,m) \hat{d}^+_l \hat{c}_{\sigma,m} + h.c.)$$

(4)

where $E_a$ and $E_d$ are the energy levels of all five holes localised either at the octahedral or tetrahedral iron site, and $U$ is the on-site Coulomb repulsion parameter. $E_a$ and $E_d$, in general, can differ from each other. The summations $i, j, l$ run over five orbital $d$ eigenstates, and $m$ is the spin state. $E_p$ is the energy of all six spin orbitals at the oxygen ions. $\hat{d}^+$ and $\hat{c}^+$ ($\hat{d}, \hat{c}$) are the fermion creation (annihilation) operators. The hybridisation parameters are reduced to one, being equal to $V_{pd}$.

In the first step of our procedure, the original Hamiltonian is projected onto each ionic cluster separately and diagonalised with only the inter-cluster hybridisation considered, which enables us to determine properly original single-hole eigenstates of the system within the framework of the LCMO approximation. The eigenstates of the octahedral cluster are linear combinations of appropriate 3d atomic orbitals, localised at the central iron site, with 2p atomic orbitals, localised at each of the six oxygen sites. Analogously, the eigenstates of the tetrahedral cluster are linear combinations of iron 3d orbitals with 2p states at each of its four oxygen neighbours. In the first case, the orbital eigenstates of the cluster are labelled by irreducible representations of the point group $S_6$ (octahedral) [7], whereas in the second case, the eigenstates are determined by irreducible representations of the point group $S_4$ (tetrahedral). The clusters’ eigenstates with mutually opposite spins are separated because of the on-site Coulomb repulsion at the iron sites. For our further discussion, it is sufficient to consider only a set of four eigenstates per a cluster. Of course, such a set must be labelled by the same irreducible representation. We select linear combinations of the 3d and 2p states with the largest value of the matrix element of $\hat{H}_{pd}$ between them. An illustration of our results is provided in Fig.1, where the hybridised energy levels of the clusters are given as functions of the hybridisation parameter. For different eigenstates of the clusters, there can be also determined probabilities of localisation both at the iron and oxygen sites. They are determined by the 3d and 2p contributions to the appropriate eigenfunctions.
Figure 2. The superexchange integral $J_{ad}$ between spins attached to the ground orbital eigenstates of the $a$ and $d$ clusters vs the hybridisation parameter $V$, for pure (the solid line) and doped (the dotted curve) system. The relevant model parameters take the following values: $U = 8eV$, $E_a = -1.5eV$, $E_d = -0.44eV$ and $E_p = 2.5eV$.

In the next step of the perturbation procedure, the inter-cluster p-d hybridisation is considered to yield single-hole states of the $a$-$d$ pair of the clusters. For each pair their mutual oxygen ion is crucial as a bridge of the inter-cluster p-d hybridisation. By taking into account non-zero matrix elements of the hybridisation Hamiltonian between the tetrahedral $3d$ states and the octahedral $2p$ states of the mutual oxygen ion as well as between the octahedral $3d$ states and the tetrahedral $2p$ states at the oxygen, we can obtain a $8 \times 8$ transfer matrix for the $a$–$d$ pair of the clusters. Its matrix elements take the following form:

$$
(\hat{H}_{pd})^{ad}_{i,j} = \langle \Psi^a_i , \hat{H}_{pd} \Psi^d_j \rangle \delta(m,m')
$$

where $\Psi^a_i$ and $\Psi^d_j$ with $i, j = 1, 2, 3, 4$ are the single-particle eigenstates of the clusters $a$ and $d$, corresponding to the energy levels $E^a_i$ and $E^d_j$, and the spins $m, m'$, respectively. In the inter-cluster $2p$–$3d$ hybridisation, the specific oxygen site, shared by the two clusters, plays an essential role and, consequently, the oxygen parts of the eigenstates of the two clusters ($\Psi^a_i$, $\Psi^d_j$), are reduced to their respective components, which are localised at the mutual site. Since the hybridisation is spin conserving, its matrix elements are non-zero only between the clusters’ orbital states with the same spin, the transfer matrix is different for the case of parallel and anti-parallel orientations of the spins attached to the ground orbital states of the clusters. Consequently two different sets of eight energy levels of the pair are obtained. A parameter of superexchange interaction between spins of the clusters can be estimated as a difference in the magnetic energy of the pair for the parallel and anti-parallel orientation of their spins.

Within the framework of the simplified cluster model of only four hybridised eigenstates per a cluster, pure and doped yttrium-iron garnets can be distinguished from one another by a number of the holes localised at each cluster. In the case of pure YIG the number of the holes per a cluster is 1 and per a pair of the $a$ and $d$ clusters it is 2. In the case of $Ca : YIG$ the number of holes per a cluster can increase to 2 for certain clusters, which means also that for certain $a$–$d$ pairs the number of the holes is 3. Assuming that each doping $Ca^{2+}$ introduces one extra hole we can roughly determine a fraction of the clusters, whose population gets doubled in the process. On the basis of a straightforward analysis of the low-temperature anomaly in the behaviour of the magnetisation of $Ca : YIG$, it seems to be sensible to attribute the anomaly to a presence of the holes localised at certain oxygen ions and thereby increasing the latter’s valency from $O^2$ to $O^-$. As already mentioned, the low-temperature anomaly in magnetisation of $Ca : YIG$ can be interpreted as an effect of the hole’s localisation at the oxygen ions. Since the inter-cluster antiferromagnetic superexchange interaction is then changed for ferromagnetic, it must
give rise to a canting of the certain tetrahedral spins and consequently, to a moderate reduction of the resultant magnetic moment. The effect is more pronounced in the low-temperature range since at higher temperatures, the holes are prone to move. In Fig.2, the inter-cluster exchange interaction is presented vs the hybridisation parameter. The interaction change its sign for certain magnitude of the parameter. An occurrence of an oxygen vacancy at the site shared by the octahedral and tetrahedral clusters requires a revision and a modification of our original approach. As mentioned before, the oxygen vacancy with a trapped hole is described in terms of an hydrogen atom. Only the ground state of the atom is taken into account. To maintain a contact of the clusters, hybridisation between the 1s states of the vacancy and the 3d states at the octahedral and tetrahedral iron ions must be assumed. Possible hybridisation of the vacancy with the 2p states at the remaining oxygen ions of the clusters, is neglected as the oxygen-oxygen distance is considerably larger than that between oxygen and iron ions. Let us then reconsider a pair of the a and d clusters with a vacancy at their mutual corner. It is obvious that the inter-cluster transfer matrix must be completely changed. However, since there is only one missing oxygen neighbour out of the octahedral six and tetrahedral four oxygen ions, we find it justifiable to start our analysis of the problem with a modified version of our simplified cluster model. It is assumed that the p – d hybridisation is maintained between the 3d states of at the central iron ions and the 2p states at all their nearest neighbours, save the one, which is missing. It suggests that in order to adapt the former LCMO hybridised single-cluster eigenstates to the present physical conditions, they should only have their oxygen contributions to multiplied by factor of $\sqrt{6/5}$ in the case of the octahedral cluster and by $\sqrt{4/3}$ in the case of the tetrahedral one. For the pair of the clusters, the original basis of its Hilbert space of the eigenstates consists of ten following wave-functions $\Psi_{i,m}, \Psi_{j,m'}, \phi_{1s,m}, \phi_{3s,-m}$, where $i, j = 1, 2, 3, 4$ and $m, m'$ are the spin states.

Within this basis a new $10 \times 10$ transfer matrix $\hat{H}_{ad}$ can be obtained. It corresponds to the original Hamiltonian $\hat{H}$ extended by the the $1s – 3d$ hybridisation term $\hat{H}_{sd}$, and projected onto the 10-dimensional Hilbert space of eight selected eigenstates of the clusters, and two eigenstates of the vacancy. From the ten diagonal matrix elements of the transfer matrix, four are equal to the energies of the octahedral cluster($E_{i}^{s}$), and four to the energies of the tetrahedral cluster ($E_{j}^{d}$), and two to the energy ($E_{1s}$ corresponding to the ground state of the vacancy, being a spin-orbital doublet.

Non-zero off-diagonal matrix elements of $\hat{H}_{ad}$ take either the form:

$$
(\hat{H}_{ad})_{k,l} = (\Psi_{i,m}, \hat{H}_{sd}\phi_{1s,m'})\delta(m, m')
$$

(6) where for $k = 1, \ldots, 4$, $i$ takes the same values, and $l = 5, 6$ for $m', -m'$, respectively, or, the following analogous form:

$$
(\hat{H}_{sd})_{k,l} = (\Psi_{j,m}, \hat{h}t\hat{H}_{sd}\phi_{1s,m'})\delta(m, m')
$$

(7) where for $k = 7, \ldots, 10$, $j$ is equal to $j = 1, \ldots, 4$, $m$ and $m'$ are the respective spin states of the clusters ($m$) and the vacancy ($m'$). The approach, presented here, has one more advantage. It provides information about localisation of the hole either at one of the central iron or at their respective oxygen neighbours. The transfer matrix elements take larger values than those of the second option.

Likewise, in the case of the p – d hybridisation, all possible parameters of the s – d hybridisation are reduced to only one, $V_s$. Diagonalisation of the transfer matrix yields ten energy levels of the pair of the clusters with the oxygen vacancy localised at their mutual site. Again we can assume either a parallel or an anti-parallel mutual orientation of spins attached to the orbital ground states of clusters a and d. It turns out, however, that the orientation of the spins has no effect what-so-far on the form of the transfer matrix. Both ferromagnetic and
anti-ferromagnetic transfer matrices are identical which further means that possibly the oxygen vacancy can totally destroy super-exchange interaction between spins localised at the iron sites. This conclusion remains in remarkable agreement with the empirical data on the YIG-derivative samples annealed in oxygen-reducing atmosphere and containing oxygen vacancies. Magnetic measurements indicate dramatic changes in the temperature behaviour of their magnetisation [1,2]. All the results we have obtained are expressed in terms of several characteristics of the system, which are the on-site energies $E_a, E_d, E_p$ and $U$, the $p - d$ hybridisation parameter, $V$, as well as the parameters, which describe the vacancy itself, such as the ground state energy $E_{1s}$, and the parameter of the $1s - 3d$ hybridisation, $V_s$. A deeper insight into the problem of an $a - d$ pair of the clusters with an oxygen vacancy requires more information about mutual relation between the two types of the system’s parameters. Thus, in order to determine more precisely the characteristics of the vacancy, we need a closer look at the microscopic model of it.

3. Microscopic model of the oxygen vacancy
The simplest microscopic approach to a shallow point defect in semiconductors consists in an application of the hydrogen model [8]. The oxygen vacancy is a point defect, the question whether it is also shallow, however, requires further analysis.
At the present moment, the hydrogen model is merely assumed. And, we have to realise that the specific geometry of garnets gets lost as the accepted model is characterised by spherical symmetry. Nevertheless, it serves well as a point of departure for our dealing with the problem. It is hoped that only the ground state of the vacancy is necessary in the process. To this objective, the text-book formula for the ground state $1s$ energy of the original hydrogen atom must be re-written in the following way:

$$E_{1s} = m_h Z^2 e^4 / (2\pi \hbar^2 (4\epsilon)^2)$$  \hspace{1cm} (8)

the effective Bohr radius can be introduced, as well:

$$a^* = 4\pi \hbar^2 \epsilon / (e^2 m_h)$$  \hspace{1cm} (9)

where $m_h$ is the effective mass of the hole and $\epsilon$ is a ratio of the dielectric constant of the host material to that of vacuum ($\epsilon_0$). These two parameters are especially important since they characterise the host material, in which the impaired pair of the clusters is embedded. Within the framework of our cluster model, they can be varied to account for the actual experimental results.

Since we are especially interested in compensating holes localised at the oxygen vacancies, the length of the effective Bohr radius should be fixed to remain comparable with the distance between the vacancy and its dodecahedral neighbour, which is occupied by the doping $Ca^{2+}$ ion. Consequently, possible delocalisation of the hole can be interpreted as its excitation to one of the non-occupied $a$ or $d$ cluster energy levels. The excited hole gains an access to all the oxygen sites of the hybridised cluster and can continue its motion farther on. Thus, within the framework of the cluster model, the difference in energy between the highest occupied localised level of the vacancy and the lowest non-occupied level of either of the clusters should respond to the activation energy, $E_{act}$. The latter was measured, in the annealed samples of $Ca:YIG$, at room temperature, and found to be in the range of $0.2 - 0.4eV$ [1-3]. A position of $E_{1s}$ is thus automatically determined relative to the energy spectra of the clusters.

In order to maintain a proper relation between the ground state energy of the vacancy and its fixed distance from the nearest dodecahedral neighbour, we still have two variational parameters for further manipulation. Those are the effective relative dielectric constant $\epsilon/\epsilon_0$, and the effective relative hole mass $m_h/m_e$, where $m_e$ is the electron mass.

In Fig.3, the relative dielectric constant vs ratio of the activation energy to the ionisation energy of the hydrogen atom (13.6eV), is presented for the vacancy with one hole ($Z = 1$) and that with two holes ($Z = 2$). The hole’s effective mass was assumed to be equal to $0.1m_e$. The same value of the mass was used in experimental analysis. The measurements on $Ca:YIG$ thin films suggest the dielectric constant between 16 and 18. However, at this point, we cannot attain desired compatibility with the empirical data as $\epsilon$ turns out to be much lower and equal to 2.61. By assuming larger values for the effective mass such as the relative mass of the order of 10, one can obtain the microscopic results which remain in reasonably good agreement with the experimental data.

For the sake of this discussion, the following formula can be useful:

$$\epsilon/\epsilon_0 = Z \sqrt{E_{1s}/E_{act}} \sqrt{m_h/m_e}$$  \hspace{1cm} (10)

For two different values of the relative dielectric constant, we determine the effective hole’s mass as a function of the activation energy. The results are gathered and presented in Fig. 4. Again two cases are considered with one hole or two holes trapped in the vacancy. Our assumption of heavy mass of the hole corresponds with the assumption of its fixed position and thus it finds an experimental confirmation.
In order to summarise the results presented in this paper, we wanted to include an occurrence of the oxygen vacancies in the ionic cluster model of garnets, to re-interpret the empirical data in terms of the model quantities, and so achieve compatibility of the both aspects of the problem. It turns out that the magnetic properties of different derivatives of YIG, and in particular, those of Ca : YIG, as well as charge-transfer processes in these systems, interpreted within the framework of the ionic cluster model, result from an interplay of the two mutually opposite tendencies. Doping ions, such as Ca$^{2+}$ in Ca : YIG introduce compensating holes, which are positive charge carriers in the system and, when localised, they can change magnetic interaction between spins. On the other hand, oxygen vacancies tend to trap the holes, destroying thereby the antiferromagnetic inter-cluster coupling and simultaneously reducing effectively the number of the mobile charge carriers. Moreover, localisation of the hole results in a reduction of the resultant spin in the system. The mechanism of the charge transfer, as based on the hybridisation of the orbital states of the clusters, is simultaneously spin-polarised.

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