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2001 J. Phys.: Condens. Matter 13 3607

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A space-symmetry approach to the p–d hybridization and direct p–p hopping in yttrium–iron garnets

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Received 1 September 2000, in final form 5 March 2001

Abstract

The first thorough symmetry analysis of the p–d hybridization and p–p hopping is performed for yttrium–iron garnets. Group-theoretical calculations of spin-independent p–d hybridization and p–p transfer-matrix elements allow us to determine symmetry-adapted ‘channels’ in the crystal unit cell. The results clearly indicate what role is played by each of the interactions in a possible charge transportation. The p–d hybridization turns out to be restricted to the small-sized octahedral and tetrahedral clusters of iron–oxygen neighbours; which results from the specific complex geometry of garnets. A propagation between the hybridizing clusters of the same type is realized by the p–p hopping to the second neighbours. The p–p hopping itself is shown to be restricted to small-sized oxygen clusters. Moreover, the second-neighbour p–p hopping between octahedral hybridizing clusters shows a strong anisotropy along the $\langle 111 \rangle$ axis. The p–p hopping between the nearest neighbours appears less important. An inter-sublattice charge motion may be mediated solely by the p–d hybridization since the nearest-neighbour hybridizing clusters share a common oxygen.

1. Introduction

Iron garnets and, in particular, the prototypical yttrium–iron garnet, $Y_3Fe_5O_{12}$ (YIG), have attracted much academic and also technological interest [1–4]. They have turned out to be extremely useful in applications in microwave, magnetic, optical and magneto-optical devices. The magnetic properties of magnetic garnets doped with rare-earth ions or charge-compensating diamagnetic ions have been intensively studied for quite a long time. Pure YIG is an insulating ferrimagnet. However, when the substituting ions have valency other than 3+, uncompensated garnets having semiconductor properties are produced, which form new materials with potential applications thanks to their unique electrical and magneto-optical properties. The Ca^{2+} -substituted yttrium–iron garnet (Ca^{2+} :YIG) is a good example showing

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charge-uncompensated doping. The mechanism of the electrical conduction process in the doped material has not yet found a truly satisfactory explanation [3, 4].

In this paper we present realistic symmetry calculations which, in our opinion, are necessary as a first step towards understanding the development of charge conductivity in both pure and doped iron garnets. It is well established that the electronic structure of yttrium–iron garnets has not been calculated with any standard band-structure theory. For a deeper interpretation of many fascinating properties of these materials, it seems, therefore, indispensable to clarify the microscopic role of the hybridization between the 3d states of iron and 2p states of oxygen, and also that of the direct inter-ion p–p hopping [5–7].

As is well known, the geometry of garnets is very complex (see, for example, [8]). The iron ions occupy 40 inequivalent crystal sublattices: 16 octahedral (a) and 24 tetrahedral (d). Its 24 dodecahedral sublattices (c) are occupied by trivalent yttrium ions with all their shells closed up. Each a-sublattice site is surrounded by six oxygen nearest neighbours, whereas each d site has four oxygens around it. The overall symmetry of the system is cubic. Two systems of electrons must be considered: 3d electrons on the iron ions which are treated in the strictly localized (atomic) limit, and the 2p electrons which are allowed to hop between different oxygen sites. In our approach, in order to maintain a coupling between the two subsystems we allow also inter-subsystem 3d–2p hopping which is called p–d hybridization, to distinguish it from the intra-subsystem oxygen–oxygen hopping.

The largest (cubic) contribution to the crystal field acting on each 3d electron, in the strong-field approximation, gives rise to a splitting of five 3d orbital states into the t_{2g} triplet and e_g doublet. For a 3d compensating hole, localized at an octahedral site, the ground state is the e_g doublet and at the tetrahedral site it is the t_{2g} triplet [9]. The energy difference between the excited and ground crystal-field energy levels is also different for the octahedral and tetrahedral sublattices [4]. The cubic crystal field does not split the t_{1u} triplet of the 2p orbital states [9].

It is obvious that the p–d hybridization and the p–p hopping play a crucial role in a determination of the electronic structure of the system (see, for example, [10, 15]). In the first-quantization representation, the two mechanisms can be expressed by the same well-known standard Hamiltonian:

$$\hat{H} = \sum \left(\frac{p_i^2}{2m} + V(r_i) \right) \quad (1)$$

where the summation is over all the electrons involved (i). The Hamiltonian consists of the kinetic and potential terms. The latter, apart from a single-site contribution, can comprise the electron correlations in the Hartree–Fock approximation.

It is then very important to choose states of proper symmetry for the perturbation calculus. In the first part of the paper, our attention is focused on the p–d hybridization. Even when considered in a single-particle approach, the p–d hybridization remains a global effect, i.e. affecting the whole system, so it seems natural to study the problem by means of space-group theory. In group-theoretical terms, the problem consists in a determination of the selection rules that govern whether the process is allowed or not. The wave function of the crystal unit cell can be approximated as a linear combination of all possible single-particle orbital and spin states, attached to each site of the cell [10]. In this LCAO (linear combination of atomic orbitals) approach, the following two contributions can be distinguished: one running through all of the iron sites (Ψ_{Fe}), and the other through all 96 oxygen sites (Ψ_O). The hybridization process is then governed by the value of the matrix element: $\langle \Psi_{Fe} | \hat{H}_{p-d} | \Psi_O \rangle$. In determining this selection rule the essential problem is that of establishing whether it is possible to show group theoretically when the matrix element must vanish. The orbital states can be assigned to the representations of the crystal-field point symmetry group, whereas the positions of the ions and the Hamiltonian are assigned to the various representations of the space symmetry

group (see, for instance, [10, 11]). Thus, in principle, the determination of this selection rule involves a Kronecker product of five representations of two different groups. The problem can be simplified, however, if one realizes that the hybridization Hamiltonian must be invariant with respect to all of the operators of the space group which means that it corresponds to the identity representation of the group. Moreover, since it is quite realistic to limit the p–d hybridization to iron–oxygen pairs of the nearest neighbours, we can define just two transitive representations of the space group, one which distributes the octahedral iron–oxygen pairs, and another which distributes the pairs consisting of tetrahedral iron and oxygen. Thus, finally it turns out that one has to consider only a double Kronecker product of two irreducible representations of a mutual subgroup of only two symmetry groups. Let us specify also exactly what we mean by a ‘hybridization channel’. It is a set of nearest-neighbour iron–oxygen pairs in the crystal unit cell which forms a basis of any irreducible representation of the space group. The appropriate orbital states are attached to each pair.

Since the p–d hybridization involves no coupling between the orbital and spin degrees of freedom, the hybridizing states correspond to the same spin, which forms a first step towards actual factorization of the hybridization matrix. The latter splits into two identical submatrices with the spin up and spin down. The same is also true of the direct p–p hopping.

It is generally agreed that in many transition metal oxides, the electric charge transfer is mediated by the p–d hybridization (see [10] and references therein). As far as yttrium–iron garnets are concerned, we believe that the microscopic mechanism of the electric conduction is more complicated, involving not only p–d hybridization, but also direct p–p hopping. Therefore, we find it both important and instructive to perform a thorough symmetry analysis of these problems, with the use of advanced group-theoretical methods.

The organization of the paper is as follows. In the first section, the application of the space-group theory to the p–d hybridization is outlined. Also, the results of the actual calculations are gathered and thoroughly analysed, and conclusions are proposed. In the second section, we deal with the direct p–p hopping and, in particular, we present very interesting aspects of the effect resulting from the complex geometry of the system. Finally, in the last section, the general conclusions are proposed.

2. The space-group theory approach to the problem of the p–d hybridization in YIG

As mentioned before, the overall symmetry of garnets is cubic, with the space group O_h^{10} belonging to the bcc Bravais class.

Let us define the quotient group G :

$$G = O_h^{10} / T(a_i) \quad (2)$$

where $T(a_i)$ is the translational group generated by the minimum lattice vectors \vec{a}_i ($i = 1, 2, 3$), along the fourfold axes of the crystal, and the order of G is 96. G distributes all 64 cations and all 96 oxygen ions over the elementary cube which is the fourfold extended Bravais cell. Thus, hereafter, the group G will be referred to as a distributing group. The generating operators of group G are given in table 1, together with the information on their action on the vector (x, y, z) modulo $T(a_i)$ [11].

The origin of the Cartesian coordinate system is located at the site 1_a . The fourfold axes are along $\vec{i}, \vec{j}, \vec{k}$ which are parallel to the crystal axes. In the second column there are the symbols for the generating operators in the 96-element quotient group, after Bradley and Cracknell [11].

Let Ω_{Fe} be a set of all 40 iron ions of the elementary cube, and $P^{Fe}: G \otimes \Omega_{Fe} \rightarrow \Omega_{Fe}$ be the action realizing this distribution. Clearly, the action P^{Fe} , considered as a permutation

Table 1. The generating operators of the group G .

$\{C_{31}^+ 000\}$	g_{55}	z, x, y
$\{C_{2a} \frac{1}{4}\frac{1}{4}\frac{1}{4}\}$	g_{19}	$y - \frac{1}{4}, x + \frac{1}{4}, \bar{z} + \frac{1}{4}$
$\{I 000\}$	g_{25}	$\bar{x}, \bar{y}, \bar{z}$
$\{C_{2x} \frac{1}{2}\frac{1}{2}0\}$	g_{50}	$x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z}$
$\{C_{2z} \frac{1}{2}0\frac{1}{2}\}$	g_{52}	$\bar{x} + \frac{1}{2}, \bar{y}, z + \frac{1}{2}$

representation, decomposes into transitive representations:

$$P^{\text{Fe}} = \sum_{\beta \in I} R^{G:G^\beta} \quad (3)$$

and correspondingly the set Ω_{Fe} decomposes into orbits:

$$\Omega_{\text{Fe}} = \bigcup_{\beta \in I} \Omega_{\text{Fe}}^\beta \quad (4)$$

with $I = \{a, d\}$ being the set of the iron sublattices; the symbol G^β in the following equation denotes the stabilizer of the representation site $r_1^\beta \in \Omega_{\text{Fe}}^\beta$, i.e.

$$G^\beta = \{g \in G | P^{\text{Fe}}(g, \vec{r}_1^\beta) = \vec{r}_1^\beta\} \subset G. \quad (5)$$

The stabilizers of the two iron sites (a, d) are isomorphic with $S_6(G_6^1)$ and $S_4(G_4^1)$, respectively.

The notation in parentheses is after Bradley and Cracknell [11].

Analogously, let Ω_{O} be the set of all 96 oxygen sites of the elementary cube, and $P^{\text{O}}: G \otimes \Omega_{\text{O}} \rightarrow \Omega_{\text{O}}$ be the action realizing their distribution. In the case of the oxygen set, the action P^{O} , considered as a permutation representation, turns out to be the regular representation of the quotient group, i.e.

$$P^{\text{O}} = R^{G:\{E\}} \quad (6)$$

with $\{E\}$ denoting the trivial subgroup of G . Each set of all possible iron–oxygen pairs (i_β, f) , where: $\beta = a, d$; $i_a = 1, \dots, 16$; $i_d = 1, \dots, 24$; and $f = 1, \dots, 96$, decomposes naturally into orbits of equidistant pairs. From the physical point of view, it seems to be sensible and justifiable to consider only the orbits of nearest neighbours: one consisting of the pairs with iron of the cubic sublattice, i.e. Ω_a , and the other of those with iron of the tetrahedral sublattice, i.e. Ω_d . The numbers of pairs in the two are the same and equal to the number of the oxygen sites in the elementary unit cell. As already mentioned, the positions of oxygens are specified by successive appropriate elements of group G (cf. table 1) [8, 12]. The distribution of the pairs over the elementary unit cell is then realized by the following action: $G \otimes \Omega_\beta \rightarrow \Omega_\beta$ ($\beta = d, a$). The action defines two permutation representations which are identical to the transitive representations of G , T_β ($\beta = d, a$). Both T_d and T_a turn out to be the regular representations of the distributing group, G .

In order to determine the selection rules for the p–d hybridization, we now have to include orbital states of the electrons involved. To each site of the iron sublattices there is attached a fibre, isomorphic with the unitary linear space of e_g doublet and t_{2g} triplet 3d states [9, 14]. In the same way, a fibre isomorphic with the unitary linear space of the orbital 2p states of the cubic t_{1u} triplet is associated with each oxygen site [9, 14].

The matrix elements of the p–d hybridization term are defined connecting the 3d and 2p orbital states, localized at the neighbouring ions. As stated before, a possible occurrence of non-zero matrix elements of \hat{H}_{p-d} requires second-order invariants to appear in a tensorial product of the two irreducible representations: one defined in the fibre space and the other in the

positional space. Let us discuss the problem separately for each of the two nearest-neighbour iron–oxygen orbits, Ω_β .

However, before we do that we have to overcome the difficulty of the formalism, which obviously arises at this point. It is connected with the point group O_h being only an isogonal subgroup of the quotient group G [13]. The largest point subgroup of G is S_6 , i.e. the stabilizer of any octahedral site a . The point group S_6 seems to be a natural choice for the orbit Ω_a with the origin of the coordinate system localized at the site 1_a . However, it is not the best choice for the other iron sublattice. So let us first discuss the problem for the octahedral orbit Ω_a .

Both groups considered so far must then be reduced to their mutual subgroup S_6 , and consequently the irreducible representations (irreps) of the distributing group G as well as those of the point group O_h become reducible. And, as such, they can all be decomposed into direct sums of the irreps of group S_6 . There are just six of them, all one-dimensional (see, for instance, [14]). The decomposition of each irrep of the point group O_h , after the restriction to the point group S_6 , can be expressed by the following formula:

$$\Theta_\mu^{O_h} \downarrow S_6 = \sum m(\Theta_\mu^{O_h} \downarrow S_6, \theta)\theta. \quad (7)$$

The summation in the formula is over the set of all six irreps θ of the point group S_6 .

The results of this procedure for the point group O_h are given below explicitly by the following formulae:

$$a_{1g}^{O_h} \downarrow S_6 = a_{2g}^{O_h} \downarrow S_6 = a_g^{S_6} \quad (8)$$

$$e_g^{O_h} \downarrow S_6 = e_g^{S_6} \oplus (e_g^{S_6})^* \quad (9)$$

$$t_{1g}^{O_h} \downarrow S_6 = t_{2g}^{O_h} \downarrow S_6 = a_g^{S_6} \oplus e_g^{S_6} \oplus (e_g^{S_6})^* \quad (10)$$

together with the corresponding formulae resulting from the replacement $g \rightarrow u$.

The character tables of the irreps of both subgroups, i.e. O_h and S_6 , can be found, for instance, in [14].

For the distributing group G , the analogous subduction equation takes the form

$$R_\gamma^G \downarrow S_6 = \sum m(R_\gamma^G \downarrow S_6, \theta)\theta \quad (11)$$

where again the summation is over all six irreps of the group S_6 . The results can be specified as follows:

$$R_1 \downarrow S_6 = R_3 \downarrow S_6 = a_g^{S_6} \quad R_2 \downarrow S_6 = R_4 \downarrow S_6 = a_u^{S_6} \quad (12)$$

$$R_5 \downarrow S_6 = e_g^{S_6} \oplus (e_g^{S_6})^* \quad R_6 \downarrow S_6 = e_u^{S_6} \oplus (e_u^{S_6})^* \quad R_7 \downarrow S_6 = a_g^{S_6} \oplus a_u^{S_6} \quad (13)$$

$$R_8 \downarrow S_6 = (e_g^{S_6})^* \oplus e_u^{S_6} \quad R_9 \downarrow S_6 = e_g^{S_6} \oplus (e_u^{S_6})^* \quad (14)$$

$$R_{10} \downarrow S_6 = R_{12} \downarrow S_6 = a_g^{S_6} \oplus e_g^{S_6} \oplus (e_g^{S_6})^* \quad (15)$$

$$R_{11} \downarrow S_6 = R_{13} \downarrow S_6 = a_u^{S_6} \oplus e_u^{S_6} \oplus (e_u^{S_6})^* \quad (16)$$

$$R_{14} \downarrow S_6 = a_g^{S_6} \oplus e_g^{S_6} \oplus (e_g^{S_6})^* \oplus a_u^{S_6} \oplus e_u^{S_6} \oplus (e_u^{S_6})^*. \quad (17)$$

The character table of the irreps of the distributing group G can be found in [11], on p 269.

As already stated, the fibre space of any iron–oxygen pair is a tensorial product of the 3d and 2p states. From equations (8)–(10), the tensorial products can be given in the form

$$(t_{2g}^{O_h} \otimes t_{1u}^{O_h}) \downarrow S_6 = (a_g^{S_6} \oplus e_g^{S_6} \oplus (e_g^{S_6})^*) \otimes (a_u^{S_6} \oplus e_u^{S_6} \oplus (e_u^{S_6})^*) \quad (18)$$

and analogously

$$(e_g^{O_h} \otimes t_{1u}^{O_h}) \downarrow S_6 = (e_g^{S_6} \oplus (e_g^{S_6})^*) \otimes (a_u^{S_6} \oplus e_u^{S_6} \oplus (e_u^{S_6})^*). \quad (19)$$

Moreover, the following relations are useful in further consideration:

$$a_g^{S_6} \otimes a_u^{S_6} = e_g^{S_6} \otimes (e_u^{S_6})^* = (e_g^{S_6})^* \otimes e_u^{S_6} = a_u^{S_6} \quad (20)$$

$$a_g^{S_6} \otimes e_u^{S_6} = e_g^{S_6} \otimes a_u^{S_6} = (e_g^{S_6})^* \otimes (e_u^{S_6})^* = e_u^{S_6}. \quad (21)$$

In the positional space of the nearest-neighbour hybridizing pairs Ω_a , the regular representation R^G decomposes into a direct sum of all the irreps of G with each irrep appearing in the sum as many times as its dimension. In order to investigate all of the quadratic products of the positional and fibre representations, we only need to take into consideration these positional irreps of G which, after the restriction of G to S_6 , decouple into sums containing $a_u^{S_6}$, $e_u^{S_6}$ and/or $(e_u^{S_6})^*$ (see equations (12)–(17)).

By resorting to the well-known projection procedure, one can determine all the bases of the relevant irreps of the point group S_6 in the standard fibre space of a hybridizing pair. For the irrep $a_u^{S_6}$ the results are displayed in table 2.

Table 2. Bases of the irrep $a_u^{S_6}$ for a standard fibre of any iron–oxygen (i_a – f) pair of nearest neighbours.

	$a_u^{S_6}$	
$e_g^{O_h}(i_a) \otimes t_{1u}^{O_h}(f)$	$\frac{1}{\sqrt{6}}(\theta(i_a) + i\varepsilon(i_a))(z(f) + \omega^*x(f) + \omega y(f))$	$\frac{\sqrt{6}}{2}V_a$
	$\frac{1}{\sqrt{6}}(\theta(i_a) - i\varepsilon(i_a))(z(f) + \omega x(f) + \omega^*y(f))$	$\frac{\sqrt{6}}{2}V_a$
	$\frac{1}{3}(\xi(i_a) + \eta(i_a) + \zeta(i_a))(x(f) + y(f) + z(f))$	$2\sqrt{3}V_d$
$t_{2g}^{O_h}(i_a) \otimes t_{1u}^{O_h}(f)$	$\frac{1}{3}(\zeta(i_a) + \omega^*\eta(i_a) + \omega\xi(i_a))(z(f) + \omega^*x(f) + \omega y(f))$	$-\sqrt{3}V_d$
	$\frac{1}{3}(\zeta(i_a) + \omega\eta(i_a) + \omega^*\xi(i_a))(z(f) + \omega x(f) + \omega^*y(f))$	$-\sqrt{3}V_d$

In the first column, the original Cartesian products of the irreps of O_h are given. In the second column, all possible bases of $a_u^{S_6}$ are gathered, according to the successive products in equation (20). The values of the matrix elements of \hat{H}_{p-d} are presented in the third column.

As seen from the table, all five $a_u^{S_6}$ singlets turn out to be bonding. The values of the matrix elements of \hat{H}_{p-d} are not equal to one another as might easily have been expected. Also, two different hybridization parameters (V_a and V_d) have been introduced to express the difference in hybridization between the original 2p states and those of 3d belonging to e_g or t_{2g} , which is dependent on the wave functions involved.

Analogously we can find all the bases for the irreps $e_u^{S_6}$ and $(e_u^{S_6})^*$. The result turns out, however, to be less promising, since all of the matrix elements of the hybridization Hamiltonian are equal to zero, which means that all the $e_u^{S_6}$ singlets are non-bonding. The result for the complex-conjugate irrep $(e_u^{S_6})^*$ is the same.

Let us now repeat the procedure presented for a hybridizing pair of the orbit Ω_d . In this case, a natural point group is the stabilizer of each tetrahedral iron site, i.e. the group S_4 . Let us consider specifically the tetrahedral site 9_d since it is one of the six tetrahedral nearest neighbours of the octahedral site 1_a . All necessary information on the stabilizer of the site 9_d is gathered below in table 3.

The second column of the table presents symbols for the operators in the distributing group G with the origin of the Cartesian coordinate system at the iron site 9_d which means that

$$x' = x - \frac{1}{4} \quad y' = y + \frac{1}{8} \quad z' = z. \quad (22)$$

With the origin of the coordinate system localized at the octahedral site 1_a , the stabilizer of any tetrahedral site cannot be a point subgroup of group G since its operators contain fractional

Table 3. The stabilizer $S_4(G_4^1)$ of the site 9_d and its action on the vector (x', y', z') .

$\{E 000\}$	g'_1	x', y', z'
$\{C_{2y} 000\}$	g'_3	\bar{x}', y', \bar{z}'
$\{S_{4y}^-, 000\}$	g'_{86}	\bar{z}', \bar{y}', x'
$\{S_{4y}^+, 000\}$	g'_{89}	z', \bar{y}', \bar{x}'

translations. This is the case for any unsymmorphic space group, and after a transformation of the coordinate system, the tetrahedral stabilizer can become a point subgroup of the distributing group $O_h^{10}/T(a_i)$.

The scheme presented in detail for the former case is followed. The decomposition of the irreps of the group O_h after its restriction to the group S_4 can be expressed by the formulae

$$a_{1g}^{O_h} \downarrow S_4 = a_{2u}^{O_h} \downarrow S_4 = a^{S_4} \quad a_{2g}^{O_h} \downarrow S_4 = a_{1u}^{O_h} \downarrow S_4 = b^{S_4} \quad (23)$$

$$e_g^{O_h} \downarrow S_4 = e_u^{O_h} \downarrow S_4 = a^{S_4} \oplus b^{S_4} \quad (24)$$

$$t_{1g}^{O_h} \downarrow S_4 = t_{2u}^{O_h} \downarrow S_4 = a^{S_4} \oplus e^{S_4} \oplus (e^{S_4})^* \quad (25)$$

$$t_{2g}^{O_h} \downarrow S_4 = t_{1u}^{O_h} \downarrow S_4 = b^{S_4} \oplus e^{S_4} \oplus (e^{S_4})^*. \quad (26)$$

The character tables of both point groups can be found, for instance, in [14].

For the distributing group G , the decomposition can be expressed as follows:

$$R_1 \downarrow S_4 = R_4 \downarrow S_4 = a^{S_4} \quad R_2 \downarrow S_4 = b^{S_4} \quad (27)$$

$$R_5 \downarrow S_4 = R_6 \downarrow S_4 = a^{S_4} \oplus b^{S_4} \quad (28)$$

$$R_7 \downarrow S_4 = R_8 \downarrow S_4 = R_9 \downarrow S_4 = e^{S_4} \oplus (e^{S_4})^* \quad (29)$$

$$R_{10} \downarrow S_4 = R_{13} \downarrow S_4 = a^{S_4} \oplus e^{S_4} \oplus (e^{S_4})^* \quad (30)$$

$$R_{11} \downarrow S_4 = R_{12} \downarrow S_4 = b^{S_4} \oplus e^{S_4} \oplus (e^{S_4})^* \quad (31)$$

$$R_{14} \downarrow S_4 = 2a^{S_4} \oplus 2b^{S_4} \oplus e^{S_4} \oplus (e^{S_4})^*. \quad (32)$$

We can now alternate appropriately the formulae for the tensorial products of the 3d and 2p cubic crystal-field states.

In the case of the orbit Ω_d , the following results are obtained:

$$(t_{2g}^{O_h} \otimes t_{1u}^{O_h}) \downarrow S_4 = (b^{S_4} \oplus e^{S_4} \oplus (e^{S_4})^*) \otimes (b^{S_4} \oplus e^{S_4} \oplus (e^{S_4})^*) \quad (33)$$

and

$$(e_g^{O_h} \otimes t_{1u}^{O_h}) \downarrow S_4 = (a^{S_4} \oplus b^{S_4}) \otimes (b^{S_4} \oplus e^{S_4} \oplus (e^{S_4})^*). \quad (34)$$

As before, in the case of the orbit Ω_a , in our further discussion we will make use of the following relations:

$$b^{S_4} \otimes b^{S_4} = e^{S_4} \otimes (e^{S_4})^* = a^{S_4} \quad (35)$$

$$a^{S_4} \otimes b^{S_4} = e^{S_4} \otimes e^{S_4} = b^{S_4} \quad (36)$$

$$a^{S_4} \otimes e^{S_4} = b^{S_4} \otimes (e^{S_4})^* = e^{S_4}. \quad (37)$$

For the irrep $(e^{S_4})^*$, a relation analogous to that for e^{S_4} can be found.

Again, the standard projection procedure provides all the bases of the four irreps of the point group S_4 , in the fibre space of the tetrahedral iron–oxygen hybridizing pair. Knowing

the bases, we can easily determine the matrix elements of the Hamiltonian \hat{H}_{p-d} . The irrep a^{S_4} turns out to be non-bonding; i.e., all the matrix elements are equal to zero.

The irreps b^{S_4} and e^{S_4} are bonding and the information on them is provided in tables 4 and 5, respectively.

In table 4, in the first column, the original Cartesian products of the irreps of O_h are given. All of the possible bases of the irrep b^{S_4} are presented in the second column, whereas values of the matrix elements of \hat{H}_{p-d} are gathered in the last column. As can be seen, the choice of the bases determined by b^{S_4} makes the hybridization possible.

Table 4. Bases of the irrep b^{S_4} for a standard fibre of any tetrahedral iron–oxygen (i_d-f) pair of nearest neighbours.

	b^{S_4}	Matrix elements of \hat{H}_{p-d}
$e_g^{O_h}(i_d) \otimes t_{1u}^{O_h}(f)$	$\frac{1}{\sqrt{2}}(\theta(i_d) + \sqrt{3}\epsilon(i_d))y(f)$	$-V_a$
$t_{2g}^{O_h}(i_d) \otimes t_{1u}^{O_h}(f)$	$\frac{1}{2}(\xi(i_d) + i\zeta(i_d))(x(f) + iz(f))$	$i\sqrt{3}V_d$
	$\frac{1}{2}(\xi(i_d) - i\zeta(i_d))(x(f) - iz(f))$	$-i\sqrt{3}V_d$

In table 5, the first column gives the two possible Cartesian products of the appropriate irreps of O_h . The bases of e^{S_4} are in the second column, and the hybridization matrix elements in the third one.

Table 5. Bases of the irrep e^{S_4} for a fibre of the tetrahedral iron–oxygen (i_d-f) pair.

	e^{S_4}	Matrix elements of \hat{H}_{p-d}
$e_g^{O_h}(i_d) \otimes t_{1u}^{O_h}(f)$	$\frac{1}{2\sqrt{2}}(\theta(i_d) + i\epsilon(i_d))(x(f) + iz(f))$	$\frac{1}{2\sqrt{2}}V_a(1+i)$
	$\frac{1}{2\sqrt{2}}(\sqrt{3}\theta(i_d) - \epsilon(i_d))(x(f) - iz(f))$	$-\frac{1}{2}\sqrt{\frac{3}{2}}V_a(1+i)$
$t_{2g}^{O_h}(i_d) \otimes t_{1u}^{O_h}(f)$	$\frac{1}{\sqrt{2}}\eta(i_d)(x(f) - iz(f))$	$\sqrt{\frac{3}{2}}V_d(1-i)$
	$\frac{1}{\sqrt{2}}(\xi(i_d) - i\zeta(i_d))y(f)$	$\sqrt{\frac{3}{2}}V_d(1-i)$

From the physical point of view, the question of the irreps of S_4 and S_6 seems to be particularly important; after the extension of these point groups into the distributing group $O_h^{10}/T(a_i)$, they induce the same irrep of the distributing group. We are going to return to this problem in our further discussion.

In either orbit of the nearest-neighbour iron–oxygen pairs, bases of all relevant irreps of the distributing group G can be found by the standard projection method. Some general conclusions can be drawn immediately. Firstly, the two orbits spontaneously split into hybridizing clusters each consisting of the iron site surrounded by its six (the octahedral sublattice) or four (the tetrahedral sublattice) oxygens. No oxygen sites are shared by hybridizing clusters of the same type. However, there are common oxygen sites for the nearest a-sublattice and d-sublattice clusters. It seems natural then for the hybridizing clusters of either type to be labelled according to their central iron ions.

The final result can be described by the following formula:

$$|R_\gamma, \mu_\gamma, \nu\rangle = N_\gamma^{-1} \sum_{i_\beta} \check{C}(R_\gamma, \mu_\gamma, \nu; i_\beta) \sum_f C(R_\gamma, \mu_\gamma, \nu; f)(i_\beta, f). \quad (38)$$

The summation over pairs (i_β, f) of each orbit Ω_β ($\beta = a, d$) is performed in two steps. The first summation runs over all 16 hybridizing clusters of the type a or 24 clusters of the type d.

In the second step, the summation is performed inside each cluster running through either all six oxygens which are the nearest neighbours of the central octahedral iron or the four oxygen neighbours of the tetrahedral site. The inter-cluster relations are expressed in terms of the coefficients $\check{C}(\mathbf{R}_\gamma, \mu_\gamma, \nu; i_\beta)$. The intra-cluster situation is described by the coefficients $C(\mathbf{R}_\gamma, \mu_\gamma, \nu; f)$ where in this case f labels oxygen sites of the cluster. As an example, we present below (in tables 6–9) the results of the projection procedure for the first vector of each space belonging to the successive relevant irreps of the transitive group G .

In the first of the tables (table 6), one standard cluster of the type a (1_a) is subjected to all operators of all of the relevant irreps of the group G . In table 7, the same is done with the

Table 6. Non-zero coefficients $C(\mathbf{R}_\gamma, \mu_\gamma, \nu; f)$ for the first vectors ($\nu = 1$) of all the relevant irreps (\mathbf{R}_γ) of the quotient group, G , projected onto a standard cluster (e.g. $i_\beta = 1_a$) of the iron–oxygen nearest-neighbour orbit (Ω_a). Moreover, μ_γ labels subspaces of Ω_a belonging to the same irrep \mathbf{R}_γ .

\mathbf{R}_γ	μ_γ	$f \in 1_a$					
		1	5	9	25	29	33
\mathbf{R}_2		1	1	1	$\bar{1}$	$\bar{1}$	$\bar{1}$
\mathbf{R}_7	1	1	1	1	1	1	1
	2	0	0	0	0	0	0
\mathbf{R}_{11}	1	1	0	0	$\bar{1}$	0	0
	2	0	1	0	0	$\bar{1}$	0
	3	0	0	1	0	0	$\bar{1}$
\mathbf{R}_{14}	1	1	0	0	0	0	0
	2	0	1	0	0	0	0
	3	0	0	1	0	0	0
	4	0	0	0	1	0	0
	5	0	0	0	0	1	0
	6	0	0	0	0	0	1

Table 7. Non-zero coefficients $C(\mathbf{R}_\gamma, \mu_\gamma, \nu; f)$ for the first vectors ($\nu = 1$) of irreps \mathbf{R}_2 of the quotient group, G , projected onto a standard cluster (e.g. $i_\beta = 9_d$) of the iron–oxygen nearest-neighbour orbit (Ω_d).

\mathbf{R}_γ	μ_γ	$f \in 9_d$			
		1	3	86	89
\mathbf{R}_2		1	1	$\bar{1}$	$\bar{1}$
\mathbf{R}_7	1	1	$\bar{1}$	0	0
	2	0	0	1	$\bar{1}$
\mathbf{R}_{11}	1	1	$\bar{1}$	0	0
	2	0	0	0	0
	3	0	0	1	$\bar{1}$
\mathbf{R}_{14}	1	1	$\bar{1}$	0	0
	2	0	0	0	0
	3	0	0	0	0
	4	0	0	1	$\bar{1}$
	5	0	0	0	0
	6	0	0	0	0

Table 8. Non-zero coefficients $\check{C}(R_\gamma, \mu_\gamma, \nu; i_a)$ for the first vectors ($\nu = 1$) of all the relevant irreps (R_γ) of the quotient group, G , for all the iron–oxygen clusters (i_a) of the orbit Ω_a where μ_γ labels subspaces of Ω_a , belonging to the same irrep R_γ .

R_γ	μ_γ	$i_a \in \Omega_a$							
		$\frac{1_a}{9_a}$	$\frac{2_a}{10_a}$	$\frac{3_a}{11_a}$	$\frac{4_a}{12_a}$	$\frac{5_a}{13_a}$	$\frac{6_a}{14_a}$	$\frac{7_a}{15_a}$	$\frac{8_a}{16_a}$
R ₂		1	1	1	1	1	1	1	1
R ₇	1	1	1	1	1				
	2					1	1	1	1
R ₁₁	1	1	1	1	1	1	1	1	1
	2	1	1	1	1	1	1	1	1
	3	1	1	1	1	1	1	1	1
R ₁₄	1	1	$\bar{1}$	1	$\bar{1}$	1	$\bar{1}$	1	$\bar{1}$
	2	1	$\bar{1}$	$\bar{1}$	1	1	$\bar{1}$	$\bar{1}$	1
	3	1	1	$\bar{1}$	$\bar{1}$	1	1	$\bar{1}$	$\bar{1}$
	4	1	$\bar{1}$	1	$\bar{1}$	$\bar{1}$	1	$\bar{1}$	1
	5	1	$\bar{1}$	$\bar{1}$	1	$\bar{1}$	1	1	$\bar{1}$
	6	1	1	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	1	1

Table 9. Non-zero coefficients $\check{C}(R_\gamma, \mu_\gamma, \nu; l_d)$ for the first vectors ($\nu = 1$) of all the relevant irreps (R_γ) of the quotient group, G , for all the iron–oxygen clusters (l_d) of the orbit Ω_d , where μ_γ labels subspaces of Ω_d , belonging to the same irrep R_γ .

R_γ	μ_γ	$l_d \in \Omega_d$											
		$\frac{1_d}{13_d}$	$\frac{2_d}{14_d}$	$\frac{3_d}{15_d}$	$\frac{4_d}{16_d}$	$\frac{5_d}{17_d}$	$\frac{6_d}{18_d}$	$\frac{7_d}{19_d}$	$\frac{8_d}{20_d}$	$\frac{9_d}{21_d}$	$\frac{10_d}{22_d}$	$\frac{11_d}{23_d}$	$\frac{12_d}{24_d}$
R ₂		1	1	1	1	1	1	1	1	1	1	1	1
R ₇	1	1	1	1	1	1	1	1	1	1	1	1	1
	2	1	1	1	1	1	1	1	1	1	1	1	1
R ₁₁	1			1	1		1	1		1	1		1
	2	1	1		1	1		1	1		1	1	
	3		1	1		1	1		1	1		1	1
R ₁₄	1			1			1			1			1
	2	1			1			1			1		
	3		1			1			1			1	
	4			1			1			1			1
	5	1			1			1			1		
	6		1			1			1			1	

tetrahedral cluster 9_d which is the nearest neighbour of the cluster 1_a . These selected clusters share one oxygen site (1).

Since it has become apparent that only five $a_u^{S_6}$ (see table 2), three b^{S_4} (see table 4) and four e^{S_4} (see table 5) states allow p–d hybridization, from now on we are going to discuss only these irreps of the quotient group, G , which, after the restriction of G to S_6 , decouple from the irrep $a_u^{S_6}$, and also, after the restriction of G to S_4 , decouple from b^{S_4} and e^{S_4} (see equations (12)–(17) and equations (26)–(31)).

Table 8 displays coefficients expressing the contributions of the a-sublattice clusters to all the first vectors of the irreducible subspaces of the orbit Ω_a , corresponding to the relevant irreps of the transitive group. The remaining vectors of the subspaces can be easily obtained within the framework of the same projection procedure. For the orbit Ω_d , analogous information is given in table 9.

The results for the irrep R_{13} are not given in tables 6–9 as they all turn out to be identical with those for R_{11} . For each irrep of the tables, the number of different linear combinations of hybridizing clusters in the crystal unit cell is equal to the square of the irrep's dimension. However, as seen from tables 8 and 9, these combinations often do not run through all the clusters of either Ω_a or Ω_d , but select certain subsets. Also, inside the clusters some oxygens may not contribute to the hybridization (see tables 6 and 7). For each representation, finally, all possible selections cover the whole of the pair space. For example, in the case of R_2 , only one linear combination of all the hybridizing clusters is obtained in Ω_a and Ω_d , with five possible $a_u^{S_6}$ singlets (Ω_a) or three possible $b_u^{S_4}$ singlets (Ω_d) associated with every pair of the respective clusters.

By considering crystal-field effects, we come to the conclusion that in the orbit Ω_a the favoured ones are the representations which contain the 3d states of the doublet $e_g^{O_h}$, whereas in Ω_d the cubic crystal field selects 3d singlets constructed from the states of $t_{2g}^{O_h}$.

Because of our interest in a possible mechanism of charge transport both in YIG and its derivatives, we emphasize one conclusion again. With respect to the p–d hybridization, each pair space separates into 16 (Ω_a) or 24 (Ω_d) single hybridizing clusters consisting of the central iron ion surrounded by its six (sublattice a) or four (sublattice d) oxygen nearest neighbours. In each pair space, no sites are shared by the clusters. Mutual oxygen sites occur only for clusters belonging to different orbits: Ω_a and Ω_d . So, it seems that each pair space can be considered as a set of well-separated hybridizing clusters [7], and there arises a question of how the charge can move between them. It can be shown that compensating holes can be transferred between clusters of the same type due to the direct p–p hopping (see the next section), whereas the transport between neighbouring a-sublattice and d-sublattice clusters can be mediated solely by the p–d hybridization. In order to make this happen, we must consider what symmetry conditions have to be fulfilled. The formalism demands two matrix elements of the Hamiltonian \hat{H}_{p-d} to be non-zero: that between the tetrahedral 3d states and oxygen 2p states, and that between the octahedral 3d states and the appropriate oxygen 2p states. As already stated before, this can be achieved when the respective irreps of both stabilizers, i.e. S_4 and S_6 , induce the same irrep of the distributing group G .

3. The direct p–p hopping in YIG

In order to investigate the p–p hopping in YIG we start with identification of all oxygen neighbours of each single oxygen site in the crystal unit cell, up to the fifth order of the neighbourhood. As mentioned before, the oxygen sites are labelled by 96 successive elements of the transitive group G . The oxygen site labelled as 1 has the coordinates of its positional vector equal to (x, y, z) with respect to the centre of the Cartesian coordinate system located at the iron site 1_a . After some simple geometrical estimation, the actual values of the coordinates can be easily found.

The oxygen neighbours of the site 1 (labelled by the first element of the transitive group G) are identified up to the fifth zone of neighbourhood [8, 12]. This information is gathered in table 10.

Positions of the oxygen sites are given in parentheses with respect to the iron site 1_a .

Table 10. Successive neighbours of the first oxygen site (1) of the crystal unit cell up to the fifth zone of neighbourhood.

Neighbourhood zones	
Zone I	5 = (z, x, y) 9 = (y, z, x)
Zone II	68 = ($\bar{y} + \frac{1}{4}, \bar{x} + \frac{1}{4}, \bar{z} + \frac{1}{4}$)
Zone III	3 = ($\bar{x} + \frac{1}{2}, y, z$)
Zone IV	70 = ($\bar{x} + \frac{1}{4}, z - \frac{1}{4}, y + \frac{1}{4}$)
Zone V	29 = ($\bar{z}, \bar{x}, \bar{y}$) 33 = ($\bar{y}, \bar{z}, \bar{x}$)

On the basis of the information gathered in table 10 and by using all of the elements of G , we obtain the neighbours of all of the oxygens in the crystal unit cell. The result of this procedure turns out to be quite interesting, especially with respect to the problem of the p–p hopping. Thirty six three-site closed-up clusters of common nearest neighbours are found. The second neighbours form forty eight two-site clusters and so forth. This conclusion is partly illustrated in table 11 where the first and second zones of neighbourhood are specified for several selected oxygen sites.

Table 11. The first and second zones of neighbourhood for several selected oxygen sites.

Oxygen sites	The neighbours	
	I	II
1	5, 9	68
5	1, 9	71
9	1, 5	72
68	71, 72	1
71	68, 72	5
72	68, 71	9

The result suggests that no continuous charge motion in the crystal can be expected to be mediated solely by the p–p hopping even if more distant hops are considered.

Let us consider now the p–p hopping by taking into account both the octahedral (S_6) and tetrahedral (S_4) point symmetries.

In the first case, the irreducible representation $t_{1u}^{O_h}$ associated with each oxygen site, after the restriction of O_h to its subgroup S_6 , becomes reducible and as such it decomposes as indicated in equation (10).

Thus in the fibre space of each oxygen pair, we have to consider square Cartesian products of each ungerade irrep of S_6 . The useful results take the following form:

$$a_u^{S_6} \otimes a_u^{S_6} = e_u^{S_6} \otimes (e_u^{S_6})^* = a_g^{S_6} \quad (39)$$

and

$$a_u^{S_6} \otimes e_u^{S_6} = e_u^{S_6} \otimes e_u^{S_6} = (e_g^{S_6})^*. \quad (40)$$

Again within the framework of the projection procedure, all possible states corresponding to the three gerade irreps of S_6 can be found. The question of their occurrence in the space of all possible oxygen–oxygen pairs is analysed for successive neighbours of the oxygen 1. The detailed results are given below, in table 12.

Table 12. Bases of the irreps $a_g^{S_6}$ and $e_g^{S_6}$ for the fibre space for selected oxygen pairs with fixed $f = 1$.

		Oxygen pair (f, f')	Matrix element of H_{p-p}
$a_g^{S_6}$	$\frac{1}{3}(x(f) + y(f) + z(f))(x(f') + y(f') + z(f'))$	$f' = 5$	t_1
		$f' = 9$	t_1
		$f' = 68$	$-t_2$
$e_g^{S_6}$	$\frac{1}{3}(z(f) + \omega^*x(f) + \omega y(f))(z(f') + \omega^*x(f') + \omega y(f'))$	$f' = 68$	$-t_2$

In the first and second columns, two successive bonding bases are explicitly shown, according to the formulae (38) and (39). In the third column, the specific oxygen pairs are given, with the appropriate matrix elements of \hat{H}_{p-p} in the fourth column. Finally, t_1 and t_2 denote the hopping parameters for the first and second neighbours, respectively.

It seems that, from the physical point of view, the second-neighbour hopping is more important than hopping to the nearest neighbours. Let us consider possible charge motion between clusters of the type a.

The three oxygen mutually nearest neighbours belong to the same hybridizing cluster. But, if the next-nearest neighbours are involved, then the p–p hopping joins the nearest a-sublattice clusters. And, what is even more interesting, from six nearest clusters, the p–p next-nearest-neighbour hopping selects only two. For example, in the case of the 1_a cluster, the motion is possible only to either 5_a or 13_a clusters. From the cluster 5_a the charge can only get to either 1_a or 9_a . Positions of the central irons of these clusters single out the axis $\langle 111 \rangle$ [8, 12]. Consequently, the whole set of all 16 clusters of the type a splits into four quasi-one-dimensional subsets along the threefold crystal axes.

Actually, there is some experimental evidence for anisotropy of the charge transportation in the doped garnets [19].

The charge motion in the tetrahedral superlattice of iron–oxygen clusters may also be mediated by the p–p hopping between the second oxygen neighbours. In the case of the tetrahedral orbit Ω_d , the cubic irrep $t_{1u}^{O_h}$ decomposes into a sum of the irreps of the point group S_4 as shown before. Therefore for each pair of oxygen neighbours, we have to consider square Cartesian products of b^{S_4} , e^{S_4} and $(e^{S_4})^*$. In our further consideration, equations (32)–(36) turn out to be extremely useful. As can be easily concluded, all possible bases are already known. Below, in table 13, all information is gathered on the second-neighbour p–p hopping. Again, like in the case of the octahedral sublattice, the second-neighbour hopping is more important than that between first oxygen neighbours. Again like in the former case, the p–p hopping between the second neighbours connects the nearest tetrahedral hybridizing clusters with one another. In contrast, however, to the situation supposed to occur in the space of the octahedral clusters, no crystal axis seems to be favoured so far.

4. The final conclusions

Let us draw some final conclusions from the above results. The symmetry analysis of the two important processes which probably occur in both pure and doped yttrium–iron garnets clearly suggests possible microscopic mechanisms for the charge transportation. It seems that the complex specific geometry of garnets is responsible for the fact that both p–d hybridization and direct p–p hopping are limited in their influence to small-sized clusters of neighbours [5–7].

Table 13. Bases of the irreps a^{S_4} , b^{S_4} and e^{S_4} for the fibre space the second-neighbour oxygen pair: $f = 1$, $f' = 68$.

	The basis	Matrix elements of \widehat{H}_{p-p}
a^{S_4}	$y(f)y(f')$	0
	$\frac{1}{\sqrt{2}}(x(f) + iz(f))\frac{1}{\sqrt{2}}(x(f') - iz(f'))$	$-t_2/2$
b^{S_4}	$\frac{1}{\sqrt{2}}(x(f) + iz(f))\frac{1}{\sqrt{2}}(x(f') + iz(f'))$	$t_2/2$
	$\frac{1}{\sqrt{2}}(x(f) - iz(f))\frac{1}{\sqrt{2}}(x(f') - iz(f'))$	$t_2/2$
e^{S_4}	$y(f)\frac{1}{\sqrt{2}}(x(f') - iz(f'))$	$-t_2/\sqrt{2}$
	$\frac{1}{\sqrt{2}}(x(f) - iz(f))y(f')$	$-t_2/\sqrt{2}$

In order to explain any continuous charge motion in the crystal, three possible mechanisms must be considered:

- (i) Intra-sublattice motion in the octahedral sublattice (a). Its occurrence requires a combination of the p–d hybridization with the p–p hopping between the second oxygen neighbours. As seen from our discussion so far, the three oxygen nearest neighbours belong to the same hybridizing cluster. The next-nearest-neighbour p–p hopping brings the charge to the nearest hybridizing cluster. And, what is even more interesting, the symmetry limits possible motion to two of the six nearest octahedral hybridizing clusters. The p–p hopping to the second neighbour gives rise to motion between the p–d hybridizing clusters which are nearest neighbours to one another. The threefold crystal axes are singled out and actually a possible conduction anisotropy is backed by some experimental evidence [19]. The whole superlattice of 16 octahedral clusters spontaneously splits into four subsets along the four threefold crystal axes.
- (ii) Intra-sublattice motion in the tetrahedral sublattice (d). Like the motion among the a-sublattice hybridizing clusters, it is mediated both by the p–d hybridization and the p–p hopping between the next-nearest neighbours. However, unlike in the former case, the motion among the tetrahedral hybridizing clusters is isotropic.
- (iii) Inter-sublattice motion between the a- and d-sublattice hybridizing clusters can be attained solely by p–d hybridization since each two nearest a- and d-sublattice clusters share one common oxygen site. The necessary condition for this to occur is that the irreps of the respective point groups S_6 and S_4 , which determine the hybridization channels in the crystal, induce the same irrep of the distributing group G . The most probable choice seems to be the one-dimensional irrep R_2 of the distributing group which is reduced to the irrep $a_q^{S_6}$ in the octahedral orbit Ω_a , and to the irrep b^{S_4} in the tetrahedral orbit Ω_d .

Acknowledgments

Our especial thanks are due to Professor Gillian A Gehring of the University of Sheffield for words of encouragement and her extremely helpful comments.

Professor Philip E Wigen and his collaborators at the Ohio State University have inspired us to perform this symmetry analysis and we express here our gratitude to them.

Thanks are also due to Professor Ryszard J Wojciechowski and Professor Roman Micnas for critically reading the article.

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