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Investigation of Hardness, Chemical Shifts and Bonding of Rare Earth Iron Garnets

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The detailed chemical bond parameters of the rare-earth iron garnets were calculated using the chemical bond theory of complex crystals. Results indicated that RE-O bonds are ionic and Fe-O bonds possess higher covalency. The environment factor defined by electron polarizabilities and covalency was employed to predict spectra chemical shift and Mossbauer isomer shift of Fe ions. The hardness of yttrium iron garnet was predicted, which is in agreement with the experimental value.

Key Words: Hardness, Chemical shifts, Bonding, Rare earth, Iron, Garnets.

INTRODUCTION

Yttrium iron garnet (YIG) is a kind of synthetic garnet, with chemical composition $Y_3Fe_2(FeO_4)_3$ or $Y_3Fe_5O_{12}$. Yttrium iron garnet has high Verdet constant which is applied to the Faraday effect, high Q factor in microwave frequencies and very small linewidth in electron spin resonance. Yttrium iron garnet is a ferromagnetic material which is widely used in various microwave and optical-communication devices. Yttrium iron garnet is also transparent to wavelengths exceeding 600 nm, which makes it a good candidate for atom-optical purposes, in particular, for realizing new kinds of atom traps. In addition, yttrium iron garnet is used as a host material for solid-state lasers together with better-known yttrium iron garnet and YVO_4[1,2]. Its mechanical, spectra properties have been studied widely. However, the effect of chemical bond parameters on some important properties is not clear yet. In this paper we will employ the Phillips[3] dielectric theory of ionic-covalent bonding to study the bonding, polarization and spectrum properties of yttrium iron garnet and other rare earth iron garnets.

THEORETICAL METHOD

A chemical bond theory of complex structure crystals is proposed by Zhang[4,5]. Its crucial step is decomposing the complex crystal into pseudo binary crystals each containing only one type of chemical bond. For the multibond crystal $A_aB_b\ldots$, the subformula for any kind of chemical bond A-B can be expressed as:

$$\left[\frac{N(B-A)a}{N_{CA}}\right]A\left[\frac{N(A-B)b}{N_{CB}}\right]B \qquad (1)$$

where A, B, …, represent different elements or different sites of the same element in the crystal formula and a, b, …, represent numbers of the corresponding element, N(B-A) represents the number of B ions in the coordination group of A ion and N_{CA} represents the nearest coordination number of A ion. These binary crystals are related to each other and every binary crystal includes only one type of chemical bond. However, the properties of these psuedo-binary crystals are different from those of real binary crystals, although their chemical bond parameters can be calculated in a similar way.

Eqn. 1 can also be rewritten as another form,

$$\frac{N(B-A)a}{N_{CA}}AB_n \qquad (2)$$

and

$$n = \frac{N(A-B)bN_{CA}}{N(B-A)aN_{CB}} \qquad (3)$$

where the prefix $N(B-A)a/N_{CA}$ represents the ratio between the number of B ions and the total number of ions bonded to the central A ion and the subscript $[N(A-B)bN_{CA}]/[N(B-A)aN_{CB}]$ represents the ratio of the element B to A, n. According to eqn. 2, each type of bond has its corresponding subformula and the sum of all subformula equals the crystal formula, which is called the bond-valence equation.

On the analogy of the work of Phillips[3], the average energy gap E_g^μ for every μ bond in the psuedo binary crystals can be separated into homopolar E_h^μ and heteropolar C^μ parts. The homopolar gap E_h^μ can be interpreted as produced by the symmetric part of the total potential, while the ionic or charge-transfer gap C^μ results from the effect of the antisymmetric part. The average valence-conduction band gap is give by

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \quad (4)$$

The ionicity and covalency of any type of chemical bond is defined as follows

$$f_i^\mu = \frac{(C^\mu)^2}{(E_g^\mu)^2} \quad (5)$$

$$f_c^\mu = \frac{(E_h^\mu)^2}{(E_g^\mu)^2} \quad (6)$$

and $\quad E_h^\mu = \frac{39.74}{(d^\mu)^{2.48}} \ (eV) \quad (7)$

where d^μ = bond length. For any binary crystal, *i.e.*, AB_n type compounds, the heteropolar C^μ part is defined as

$$C^\mu = 14.4 b^\mu [(Z_A^\mu)^* + \Delta Z_A^\mu - n(Z_B^\mu)^*] e^{-k_s^\mu r_0^\mu} / r_0^\mu \ (EV) \ (8)$$

$$r_0^\mu = d^\mu / 2$$

$$k_s^\mu = (4 k_F^\mu / \pi a_B)^{1/2} = 1.551 (k_F^\mu)^{1/2} \quad (9)$$

$$(k_F^\mu)^3 = 3\pi^2 N_e^\mu \quad (10)$$

$$N_e^\mu = (n_e^\mu)^* / v_b^\mu \quad (11)$$

$$(n_e^\mu)^* = [(Z_A^\mu)^* / N_{CA}^\mu + (Z_B^\mu)^* / N_{CB}^\mu] \quad (12)$$

$$v_b^\mu = (d^\mu)^3 / \sum_\nu [(d^\nu)^3 N_b^\nu] \quad (13)$$

where v_b^μ = bond volume, $(n_e^\mu)^*$ = number of effective valence electrons per μ bond, N_e^μ = number of valence electrons of μ bond per cubic centimeter. k_F^μ and k_s^μ are Fermi wave number and Thomas-Fermi screening wave number of valence electron in binary crystal composed of only one type of bond μ, respectively. a_B = Bohr radius and n = ratio of element B to element A in the subformula. $(Z_A^\mu)^*$ and $(Z_B^\mu)^*$ are the number of effective valence electrons of the A and B ions, respectively and $(Z_A^\mu)^* = Q_{AB}^\mu \cdot N_{CA}^\mu$, $(Z_B^\mu)^* = [(Q_{AB}^\mu \cdot N_{CB}^\mu) / (8 - Z_B^\mu)] \cdot Z_B^\mu$, Q_{AB}^μ is Pauling bond valence of A-B bonds, Z_B^μ is the number of valence electrons of the B atoms. ΔZ_A^μ is correction factors from d electron effects such as the crystal field stable energy and Jahn-Teller effect, *etc.*[6,7]. b^μ is proportional to the square of the average coordination number N_c^μ

$$b^\mu = \beta (N_c^\mu)^2 \quad (14)$$

$$N_c^\mu = \frac{N_{CA}^\mu}{(1+n)} + \frac{n N_{CB}^\mu}{(1+n)} \quad (15)$$

where b^μ depends on a given crystal structure. The typical value of β is $0.089 \pm 10\ \%$[8].

If the dielectric constant of the crystal is known, the value of β can be deduced from the Kramers-Kronig relation of dielectric function at the long wave limit, which is written as

$$\chi^\mu = \left[\left(\frac{4\pi N_e^\mu e^2}{m} \right) \frac{D^\mu}{(E_g^\mu)^2} \right] \left(1 - \frac{E_g^\mu}{4 E_F^\mu} + \frac{(E_g^\mu)^2}{48 (E_F^\mu)^2} \right) \quad (16)$$

$$\varepsilon(\infty) = 1 + \chi = 1 + \sum_\mu F^\mu \chi^\mu \quad (17)$$

where χ = macroscopic linear susceptibility, χ^μ = total macroscopic susceptibility of a binary crystal composed of only one type of bond μ, E_F^μ = Fermi energy, F^μ = fraction of the binary crystal composing the actual complex crystal. D^μ = periodic dependent constants given in work of Levine[8].

RESULTS AND DISCUSSION

The rare-earth iron garnets (RE_3Fe_5O12, RE = rare earth or yttrium) crystallize in space group Ia3d with eight formula units per cell. The cell dimension is 12.376 Å for YIG at room temperature. In YIG, the five iron(III) ions occupy two octahedral and three tetrahedral sites, with the yttrium(III) ions coordinated by eight oxygen ions in an irregular cube. The structure of YIG is shown in Fig. 1a.
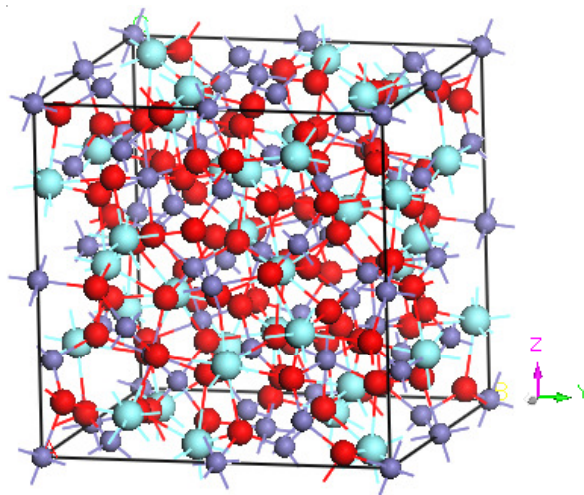
(a)
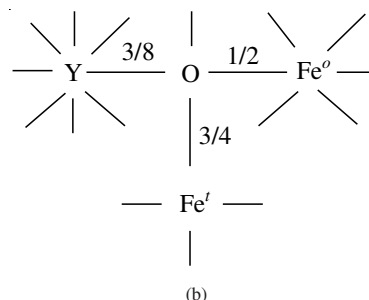
(b)

Fig. 1. (a) Crystal structure (b) Pauling bond valences

According to theory[4,5], the crystal formula of YIG can be converted into a subformula equation (a bond-valence equation) as follow:

$$Y_3Fe_5O_{12} = Y_3Fe_2^o(Fe^tO_4)_3$$

$$= \left[\frac{N(O-Y)a}{N_{CY}} \right] Y \left[\frac{N(Y-O)b}{N_{CO}} \right] O$$

$$+ \left[\frac{N(O-Fe^o)a}{N_{CFe^o}} \right] Fe^o \left[\frac{N(Fe^o-O)b}{N_{CO}} \right] O$$

$$+ \left[\frac{N(O-Fe^t)a}{N_{CFe^t}} \right] Fe^o \left[\frac{N(Fe^t-O)b}{N_{CO}} \right] O$$

$$= \frac{8 \times 3}{8} Y \frac{2 \times 12}{4} O + \frac{6 \times 2}{6} Fe^o \frac{1 \times 12}{4} O + \frac{4 \times 3}{4} Fe' \frac{1 \times 12}{4} O$$

$$= 3YO_2 + 2Fe^oO_3 + 3Fe'O \quad (18)$$

From Fig. 1b, it is seen that the Pauling bond valence Q_{AB}^μ of the Y-O, Fe^o-O, Fe^t-O bonds are 3/8, 1/2 and 3/4, respectively. For YO_2, $(Z_A^\mu)^* = Q_{AB}^\mu \cdot N_{CA}^\mu = (3/8) \times 8 = 3$,

$(Z_B^\mu)^* = [(Q_{AB}^\mu \cdot N_{CB}^\mu)/(8 - Z_B^\mu)] \cdot Z_B^\mu = [((3/8) \times 4)/(8\text{-}6)] \times 6$
$= 9/2$. For $Fe^oO_{3/2}$, $(Z_A^\mu)^* = Q_{AB}^\mu \cdot N_{CA}^\mu = (1/2) \times 6 = 3$, $(Z_B^\mu)^*$
$= [(Q_{AB}^\mu \cdot N_{CB}^\mu)/(8 - Z_B^\mu)] \cdot Z_B^\mu = [((1/2) \times 4)/(8\text{-}6)]\,6 = 6$. For
$Fe^oO_{3/2}$, $(Z_A^\mu)^* = Q_{AB}^\mu \cdot N_{CA}^\mu = (3/4) \times 4 = 3$, $(Z_B^\mu)^* =$
$[(Q_{AB}^\mu \cdot N_{CB}^\mu)/(8 - Z_B^\mu)] \cdot Z_B^\mu = [((3/4) \times 4)/(8\text{-}6)] \times 6 = 9$.

The refractive index[9], n, at 4.0 μm of YIG is 2.148. Its dielectric constant, $\varepsilon = n^2 = 4.6$. Using the dielectric constant of YIG, we can calculate its bond parameters and linear optical susceptibilities of individual bonds. They are listed in Table-1.

Firstly, we may employ the calculated chemical bond parameters to predict hardness of these materials. The hardness of psuedo binary compound composed of μ-type bond can be calculated as follows[10,11]:

$$H_\nu^\mu(GPa) = 8.82(N_e^\mu)^{2/3} E_h^\mu e^{-1.191 f_i^\mu}$$

$$= H_\nu^\mu = \frac{350(N_e^\mu)^{2/3} e^{-1.191 f_i^\mu}}{(d^\mu)^{2.5}} \qquad (19)$$

The hardness H_ν of complex crystals should be calculated by a geometric average of all bonds as follow:

$$H_\nu = \left[\prod^\mu (H_\nu^\mu)^{n^\mu}\right]^{1/\Sigma n^\mu} \qquad (20)$$

where n^μ = number of bond of type μ composing the actual complex crystal. As shown in Table-1, the calculated hardness of the Y-O, Fe^o-O, Fe^t-O bonds are 5.1, 15.8 and 37.5 GPa, respectively. The average hardness of the YIG can be calculated as follows:

$$H_\nu = \left[\prod^\mu (H_\nu^\mu)^{n^\mu}\right]^{1/\Sigma n^\mu}$$

$$= \{[H_\nu^\mu(YO)]^{\{N(Y).n(Y)\}} \cdot H_\nu^\mu(Fe^tO)]^{[N(Fe^t).n(Fe^t)]}$$

$$\cdot[H_\nu^\mu(Fe^oO)]^{[N(Fe^o).n(Fe^o)]}\}^{1/[N(Y).n(Y).N(Fe^t).n(Fe^t)+N(Fe^o).n(Fe^o)]}$$

$$= (5.1^{8\times3} \times 15.6^{4\times3} \times 37.0^{6\times2})^{1/(8\times3+4\times3+6\times2)} = 11.1\,(GPa)$$

where, N(Y), N(Fe^t) and N(Fe^o) are the coordination number of the Y, Fe^t and Fe^o atoms, respectively. n(Y), n(Fe^t) and n(Fe^o) are the number of the Y, Fe^t and Fe^o atoms in a YIG, respectively. Our calculated values of average hardness for YIG, 11.2 GPa, is in good agreement with the available experimental one[12].

The chemical bond parameters can also be applied to the study on nephelauxetic effect, which mean that the parameter values of the interelectron repulsion are smaller in the solid than in the corresponding free ion. It is known that the nephelauxetic effect depends on covalency and the polarizabilities of ligands. Jørgensen[13] found that the nephelauxetic effect can be factored into a function of just a ligand and the centre metal:

$$B/B_0 = 1 - k \text{ (centre ion)} h_e \text{ (ligand)} \qquad (21)$$

where B and B_0 are the Racah parameters of free ions and the ions in crystals, respectively.

We introduce the chemical environmental factor, h_e, presented as[14].

$$h_e = \left(\sum_\mu \alpha_L^\mu f_c^\mu\right)^{1/2} \qquad (22)$$

TABLE-1
CHEMICAL BOND PARAMETERS AND HARDNESS OF RARE-EARTH IRON GARNETS. WHERE $H_{\nu\,av.}$ AND $H_{\nu\,exn.}$ ARE CALCULATED AND EXPERIMENTAL VICKERS HARDNESS RESPECTIVELY. $\delta_{calcd.}$ ARE CALCULATED ISOMER SHIFTS WITH RESPECT TO α-Fe AT ROOM TEMPERATURE. $\delta_{exp.}$ ARE EXPERIMENTAL ISOMER SHIFTS WITH RESPECT TO α-Fe AT ROOM TEMPERATURE, WHICH IS EQUAL TO THE ISOMER SHIFTS WITH RESPECT TO STAINLESS STEEL SUBTRACT 0.09 cm/s

	Bond type	d^μ (Å)	ν_b^μ (Å^3)	N_e^μ (Å^{-3})	ΔZ_A^μ	E_h^μ (eV)	C^μ (eV)	f_i^μ	χ^μ	h_e	$\delta_{calcd.}$ (cm/s)	$\delta_{exn.}$[18] (cm/s)	H_ν^μ	$H_{\nu av.}$ (GPa)	$H_{expt.}$ (GPa)
YIG	YO	2.395	6.427	0.233	0.000	4.556	-13.761	0.901	1.359	0.519	–	–	5.110	11.2	12 [12]
	Fe^{o}O	2.019	3.850	0.519	0.897	6.958	-12.358	0.759	3.352	0.797	0.406	0.4	15.807	–	–
	Fe^{t}O	1.866	3.040	0.987	0.399	8.460	-9.498	0.558	8.451	0.952	0.203	0.23	37.546	–	–
SmIG	SmO	2.441	6.744	0.222	0.000	4.346	-13.125	0.901	1.524	0.553	–	–	4.719	10.6	–
	Fe^{o}O	2.039	3.931	0.509	0.897	6.790	-12.044	0.759	3.461	0.812	0.397	0.45	15.220	–	–
	Fe^{t}O	1.875	3.057	0.981	0.399	8.360	-9.359	0.556	8.641	0.959	0.198	0.2	37.020	–	–
EuIG	EuO	2.434	6.710	0.224	0.000	4.377	-13.231	0.901	1.506	0.549	–	–	4.768	10.7	–
	Fe^{o}O	2.011	3.784	0.528	0.897	7.027	-12.440	0.758	3.363	0.793	0.408	–	16.173	–	–
	Fe^{t}O	1.888	3.132	0.958	0.399	8.218	-9.227	0.558	8.699	0.970	0.191	–	35.742	–	–
TbIG	TbO	2.412	6.556	0.229	0.000	4.476	-13.533	0.901	1.471	0.538	–	–	4.953	10.9	–
	Fe^{o}O	2.014	3.817	0.524	0.897	7.001	-12.419	0.759	3.347	0.794	0.407	–	16.008	–	–
	Fe^{t}O	1.879	3.099	0.968	0.399	8.316	-9.344	0.558	8.573	0.963	0.196	–	36.406	–	–
DyIG	DyO	2.400	6.468	0.232	0.000	4.532	-13.696	0.901	1.454	0.533	–	–	5.061	11.0	–
	Fe^{o}O	2.031	3.920	0.510	0.897	6.857	-12.196	0.760	3.385	0.805	0.401	0.42	15.381	–	–
	Fe^{t}O	1.864	3.030	0.990	0.399	8.482	-9.521	0.558	8.433	0.951	0.204	0.20	37.729	–	–
YbIG	YbO	2.376	6.209	0.242	0.000	4.647	-13.950	0.900	1.461	0.526	–	–	5.341	11.6	–
	Fe^{o}O	2.007	3.742	0.534	0.897	7.062	-12.469	0.757	3.383	0.791	0.409	0.44	16.394	–	–
	Fe^{t}O	1.861	2.984	1.006	0.399	8.516	-9.513	0.555	8.550	0.948	0.207	0.19	38.386	–	–
LuIG	LuO	2.355	6.161	0.243	0.000	4.750	-14.349	0.901	1.385	0.512	–	–	5.482	11.5	–
	Fe^{o}O	2.019	3.882	0.515	0.897	6.958	-12.400	0.761	3.304	0.796	0.407	0.43	15.698	–	–
	Fe^{t}O	1.868	3.075	0.976	0.399	8.437	-9.508	0.559	8.359	0.955	0.202	0.24	37.080	–	–

in which α_L^μ = polarizability of ligand in μ bond, f_c^μ represents the covalency of μ bond. For the μth bond, the polarizable coefficient α_0^μ can be obtained from the Lorentz-Lorenz equation:

$$\alpha_0^\mu = \left(\frac{3}{4\pi}\right)\frac{(\varepsilon^\mu - 1)}{(\varepsilon^\mu + 2)} \qquad (23)$$

where ε^μ = low-frequency dielectric constant of a binary crystal composed of only one type of μ bond. The polarizabilities of the bond volume are

$$\alpha_b^\mu = \alpha_0^\mu V_b^\mu \qquad (24)$$

and the electron polarizabilities of the ion volume in the μth bond are

$$\alpha_A^\mu = \left\{\frac{(r_A^\mu)^3}{[(r_A^\mu)^3 + (r_B^\mu)^3]}\right\} a_b^\mu \qquad (25)$$

$$\alpha_B^\mu = \left\{\frac{(r_B^\mu)^3}{[(r_A^\mu)^3 + (r_B^\mu)^3]}\right\} a_b^\mu \qquad (26)$$

here r_A^μ and r_B^μ are effective radius of A and B ions[15], respectively.

The effect of the centre ion is expressed as[14]

$$k = \left[\frac{(Z + 2 - S)}{5}\right]^2 \qquad (27)$$

where Z = valence of the ion, S = spin of the electron configuration of the ion.

Yttrium iron garnet is a antiferromagnetic phase at room temprature. The magnetic structure is probably $Fe^o(S = 5/2, \uparrow)_2 Fe^t(S = 5/2 \downarrow)_3$. The antiferromagnetic exchange interactions Fe^o_2-O-Fe^t_2 would lead to the reduction of the spin S of Fe^o. Since the angle of Fe^o-O-Fe^t is only 126.6°, not 180°, the coupling between Fe^o and Fe^t may be not complete. A effective spin S of Fe^o may be estimated as: S = (5/2) (1-cos (180° - 126.6°)) = 1.009. Thus, the k value of Fe^o ions is calculated as 0.637. For Fe^t ions, S = 5/2 and k = 0.25. the Racah parameters of free Fe3+ (S = 5/2) ion, B_0, is 928 cm^{-1} [16]. The environmental factor h_e for Fe sites in YIG crystals is obtained using eqn. 22. According to eqn. 21, the calculated Racah parameters B(Fe^o site) and B(Fe^t site) are 457 and 707 cm^{-1}, respectively. They are in good agreement with the experimental values: B(Fe^o site) = 460 cm^{-1} and B (Fe^t site) = 700 cm^{-1} [17].

Besides the spectra red shifts, another chemical shift is Mossbauer isomer shift. It has been known that the ^{57}Fe isomer shift can provide extensive and valuable information about the local chemical environment of iron. For a given oxidation state, a correlation between the isomer shift δ and the chemical environmental factor h_e is found[7]. This can be written as:

$$\delta(^{57}Fe) = \delta_0 + bh_e$$

(mm s^{-1}, relative to α-Fe at room temperature) (28) where, b = -0.7. When h_e is equal to zero, $\delta = \delta_0$, which is the isomer shift of the free-ion state. For an isolated high-spin $Fe^{3+}(d^5)$, δ_0 is 0.87 mm s^{-1}.

Neglecting relativistic effects, only *s*-electrons possess a non-zero probability of entering the nuclear volume of $Fe^{3+}(d^5)$ and therefore the isomer shift is a good approximation proportional to the s-electron density at the nucleus, $|\Psi_s(0)|^2$. Since the nuclear radius of ^{57}Fe in the first excited state is smaller

than that in the ground state, an increasing δ implies a decreasing *s*-electron density at the absorbing nuclei. In YIG, the supercharge between 3d electrons of two Fe^o and two Fe^t could result in a enhancing shield for 4*s*-electron density. In other words, this shield could lead to decreasing s-electron density at the Fe^o nucleus. We may suggested a so-called superexchange shield factor, η, which can be estimated by the Slater shield constant as follow:

$\eta = \sigma(Fe^{3+}, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5)/\sigma^*(Fe^{3+}, 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 \_3d^{5*})$

$= (10 \times 1 + 13 \times 0.85)/(10 \times 1 + 18 \times 0.85) = 0.832.$

In YIG, the isomer shift of the Fe^o nucleus may be calculated as $\delta(Fe^o) = 0.87 - 0.7\eta h_e$ (mm s^{-1}, relative to α-Fe at room temperature) = 0.40 cm^{-1}, the isomer shift of the Fe^t nucleus $\delta(Fe^t) = 0.87 - 0.7h_e = 0.20$ cm^{-1}. The results of rare-earth iron garnets are shown in Table-1. From Table-1, it is clearly seen that the calculated results of Mossbauer isomer shifts in two crystallographic positions are in good agreement with their experimental values[18]. This also shows that the calculated chemical bond parameters here are reasonable.

Conclusion

The detailed chemical bond parameters of the rare earth iron garnets were calculated using the chemical bond theory of complex crystals. Results indicated that RE-O bonds are ionic and Fe-O bonds possess higher covalency. The environment factor defined by electron polarizabilities and covalency was employed to predict spectra chemical shift and Mossbauer isomer shift of Fe ions. We revealed theoretically that the antiferromagnetic superexchange interaction of 2Fe^o-O-2Fe^t could result in the partly reduction of the spin of Fe^o ions and the superexchange shield effect for isomer shift of Fe^o ions. The hardness of yttrium iron garnet was predicted, which is in agreement with the experimental value. The same model may be easily applied to other systems.

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