Spin-dependent optical transitions in yttrium iron garnet

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Abstract
This study reviewed the electronic structure using density functional theory (DFT) and demonstrated the transmission of optical magnetic circular spectrum in probing spin-dependent optical transitions in yttrium iron garnet (YIG). DFT + U results suggested that the t 2 orbital of tetrahedral irons are polarized by exchange-splitting O(2p) bands. Such polarization was found to be essential for the kinetic exchange and magnetism in YIG. DFT + U results also identified the spin-polarized energy gaps in YIG. On the basis of the distinctions of Fe 3 O 4 [J. Chen et al, Phys. Rev. B, 98, 085 141 (2018)] and YIG in electronic band features along with their manifestations in an optical magnetic circular dichroism (OMCD) spectrum, a map of spin-dependent optical transitions in YIG is presented. Based on the analysis of OMCD spectra at room temperature, the majority-spin and minority-spin gap in YIG are determined to be 2.45 and 2.25 eV, respectively.

1. Introduction
When the optical chirality that is induced by applying a magnetic field is scanned with an incident photon, the measurement of optical magnetic circular dichroism (OMCD) at a given energy yields the difference in absorption between left- and right-circularly polarized light (LCP and RCP). Because of the spin selection rules governing a dipole transition, OMCD receives additional degrees of freedom in the unravelling of the spin-dependent channels of an optical absorption process. These make it possible to conduct a direct investigation of spin-polarized states in conjunction with calculations based on density-functional theory (DFT). The 'bulk sensitive' electronic structure can be accessed from the transmitted OMCD for an epitaxial thin film grown on a transparent substrate.

In earlier studies, the OMCD signal at the host band edge in a dilute magnetic semiconductor (DMS) has been used as a probe of magnetic contribution due to the localized state and its interaction with band electrons. In such a system, both the absorption and the OMCD spectrum exhibit similar amounts of blue shift with increasing carrier concentration, as produced by samples under reduced oxygen conditions [1, 2]. Magneto-optic signals are obtained by optically injecting a polarized electron into a Zeeman-split host conduction band [3]. This strategy has allowed researchers to conduct prospective in-line probes for spin-dependent chemical potential variation using OMCD measurement.

A test on the probing of the electronic structure using the OMCD technique was conducted in our previous study, [4] where we used a ferrimagnet (the magnetite Fe 3 O 4 ) that possessed different crystallographic sites with an asymmetric spin alignment. Fe 3 O 4 modeled as a 3d correlated oxide system. In a band picture, oxidation states merely indicate ion locations within a site (e.g., Fe 2+ and Fe 3+ in the B site of Fe 3 O 4 ) but not the real charge number. The crucial part in interpreting the optical absorption is determining the 2p covalence that is involved.

It was based on such a determination that the optical absorption in Fe 3 O 4 was recognized by a previous study as having the signature of Mott–Hubbard insulators; [5] this signature involves a transition from a Laporte-relaxed d–d charge transfer of lower energy to a higher p–d charge transfer that entered at 2.5eV and was determined to be the minority-spin optical gap from the OMCD spectrum. The term 'charge transfer' was originally adopted strictly for ionic complexes. In a band picture, the charge transfer is descriptively meaningful with regard to the
degrees of initial- and final-state wave function localization. Consequently, the dominant spin-dependent optical transitions can be mapped to the OMCD measurement on the Fe$_3$O$_4$ thin-film single crystal, and the previous study concluded that the transmission of an OMCD spectrum manifests the bare spin-polarized valence structure that is dominated by the majority-spin of the Fe site and minority spin of the 2p oxygen in Fe$_3$O$_4$ [4]. Such sensitivity was recently applied to a core–shell nanocomposite comprised of Fe$_3$O$_4$ and carbon, [6] in which both a magnetic enhancement (∼20%) and OMCD blue shift were observed. The map of spin-dependent optical transitions in Fe$_3$O$_4$ has elucidated the cause of unusual magnetic enhancement of the nanocomposite as lying in the interfacial spin-dependent charge transfer from amorphous carbon to the unoccupied states of the A site in Fe$_3$O$_4$.

In recent studies, spin-transport phenomena [7–10] in the heterojunction formed by nonmagnetic metals and any given ferrimagnetic insulator have drawn renewed attention to yttrium iron garnet (YIG). Studies have reported that the controllable variations in the magnetic properties and in the superexchange interaction can be achieved for off-stoichiometric YIG thin films [11–13]. In particular, a study reported that the saturation moment significantly increased by 20% when excess oxygen stoichiometry was created in a YIG unit cell [11].

In this study, we deduced the spin-dependent optical transitions in YIG, as indicated by OMCD features. Using the DFT-calculated electronic structure, we interpreted superexchange interactions in YIG from the $pd$ hybridization scheme. YIG thin films grown on (111)-oriented gadolinium gallium garnet (GGG) were deposited using pulsed-laser deposition with a pulsed solid-state Nd:YAG laser. The growth was achieved at a substrate temperature of 525 °C in an oxygen atmosphere of $3 \times 10^{-1}$ mbar at the laser wavelength of 266 nm and an energy fluence of 2.9 J cm$^{-2}$. Post-growth thermal annealing was conducted at 1050 °C for 4 h in ambient atmosphere. The resulting thin film was approximately 100 nm thick and had a circular shape of 5 mm in diameter.

For OMCD measurement, the optical source used was a 450-W xenon lamp with a wavelength precision of ±0.3 nm at 250–500 nm and ±0.8 nm at 500–800 nm. Both RCP and LCP light were generated from a 50-kHz photoelastic modulator in conjunction with a monochromat. Optical absorption was scanned at incident photon energy by applying a magnetic field that ran parallel ($I_\parallel$) and anti parallel ($I_\perp$) to the direction of sample thickness. The dominant absorptive spin channel could be indicated by the sign of the MCD signal ($I_\parallel - I_\perp$).

The crystal structure of YIG belongs to the space group Ia $\overline{3}$ d; the unit cell contains eight formula units Y(3)Fe$_{12}$O$_{18}$ for a total of 160 atoms (figure 1). Hereafter, Fe$_A$ and Fe$_B$ denote the iron atoms at the Wyckoff positions 16(a) and 24(d), respectively, at the sites octahedrally and tetrahedrally coordinated with oxygen in 96(h), respectively. The Fe$_B$ in each octant of the unit cell sharing a corner with Fe$_A$ form a body-centered cubic structure. From a simplified ionic perspective, each iron ions appear to be in a trivalent state at a 3$d^6$ electronic configuration. The magnetic moment at 0 K was found to be close to 5 $\mu_B$, which led to the conclusion that the origin of ferrimagnetism in YIG lies in the Fe$^{3+}_{B}$–O–Fe$^{3+}_{A}$ intersublattice superexchange interaction.
2. Electronic structure

The \textit{ab initio} calculations were performed on 160 atoms of Y(24)Fe_3(16)Fe_A(24)O(96) (Ia 3 d) using generalized-gradient approximation [14] (GGA), as implemented in VASP, [15] where a 6 × 6 × 6 Monkhorst–Pack \( k \)-point grid and a 400-eV plane-wave cutoff were employed. The experimental lattice constant \( a = 12.376 \) Å [16, 17] was used. The coordinate was fully relaxed until all forces on the atoms were less than 0.01 eV Å\(^{-1}\). The energy tolerance was within 10\(^{-5}\) eV for static electronic relaxations. Table 1 presents the equilibrium positions. The parameter \( U \) of a simplified Dudarev's scheme [18] determines the orbital-dependent correction to the DFT energy. The effective on-site Coulomb energy, \( U_{\text{eff}} \), is the difference between the on-site Coulomb energy \( U \) and an approximation to the Stoner exchange parameter \( J \). Because the value of the energy gap strongly depends on the \( U_{\text{eff}} \), a series of calculations with \( U_{\text{eff}} \) varying from 0 to 5 eV for Fe 3d orbital have been conducted. Meanwhile, site-dependent \( U_{\text{eff}} \) were tested in response to the optical gaps determined from the OMCD spectrum. We finally employed \( U_{\text{eff}}^{A} = 4.7 \) eV and \( U_{\text{eff}}^{B} = 3.75 \) eV for Fe ions in A and B site, respectively. Figure 2 illustrates the electronic structure computed based on GGA and GGA + \( U \); both methods yielded predictions of the insulating ground state. The lowest unoccupied states (1) were the two 3d states of \( A(e, t_2) \) and \( B(t_{2g}, e_g) \) that possessed opposite spin polarizations (SP) and (2) comprised the nondegenerated subbands when projections to local symmetry were applied. [19] According to the GGA [figure 2(a)] results, the valence band (−6 to 0 eV) comprised the covalent mixing of the 3d and 2p bands. The valences of the dominant spin majority and spin minority were the A and B sites, respectively. The asymmetry in the SP of the 3d states at each site was the manifestation of the ferrimagnetism in YIG. The dominant electronic states in the vicinity of the \( E_{\text{g}} \) unaffected by any \( U \) correction, was the 2p valence edge with which the \( t_2 \) orbital is hybridized. In the GGA + \( U \) results [figure 2(b)], the 3d states were localized apart (≈−7 eV) from the 2p–band valence, which had the dominant spin majority in the vicinity of the \( E_{\text{g}} \), and transited to the opposite spin direction. The SP trend exhibited consistency between the \( t_2 \)– and 2p–band components in the valence, suggesting that \( t_2 \) was polarized by the 2p band, resulting in the \( t_2 \) spin minority (\( t_2 \downarrow \)), which was unaccounted for in the pure ionic picture (\( A \) site, \( e^{21} t_{2}^{1} \)). The same argument applies to the \( e \downarrow \) band. This consistency in SP also implied a stronger interaction with the 2p–oxygen for ions in the A–site than the B–site. The bond distances of O–Fe_A and O–Fe_B depicted in table 2 yield the same conclusion. The \( pd \) covalency redistributes the charge and spin density, causing (1) the spin–polarized charge density in the 2p band and (2) the reduction of spin moment in the d orbital [20]. The aforementioned findings explain the reduction in the magnetic moment of YIG [21, 22] relative to pure ionic Fe\(^{3+}\) (\( d^5 \)). The calculated A–site moment was always smaller than the B–site moment regardless of adjustments to \( U \) as shown in figure 3 (upper panel); this can be explained by the stronger \( pd \) interactions for the Fe_A ions than for the Fe_B ions in YIG. The moment contributed by yttrium was 2 orders of magnitude smaller than the moment contributed by all Fe ions.

In addition, the partial reoccupation of the 3d cations in the vicinity of the \( E_{\text{g}} \) by the nominal \( p \) electrons was also a signature of the kinetic superexchange. The band picture indicated that [23] the transition metal oxides forming 2p bands with a width of 4–5 eV covalently mixed with the localized 3d states. Considering the preceding results, we conclude that the inhibition of 3d cations by the on-site Coulomb interaction \( U \) explains the upward trend of the computed magnetic moment shown in figure 3. This trend also suggested a stronger \( pd \) covalency for the A–site ions, as indicated by the calculated A–site moment being always smaller than the B–site. These therefore evinced the electron correlation effect on ferrimagnetic superexchange in YIG [24, 25].

3. Optical transitions

The GGA + \( U \) results (figure 2(b)) indicate the formation of energy gaps by 2p–3d. It can therefore be expected that the ligand–to–metal charge transfer (LMCT), \( 2p^6 3d^5 \rightarrow 2p^5 3d^6 \), dominates the optical transition in YIG. In figure 3 (lower panel), the \( U_{\text{eff}} \) value of 4.5 eV yielded a reasonable estimate of the \( pd \) gap, including the corresponding experimental results of the 2.4 eV photoconductivity onset in [26] and the 2.8 eV electrical band.
gap in [27]. This photoconductive threshold has an energy that is higher than the energy of the ligand field transitions (LFTs) of single Fe$^{3+}$ ions. This structure is common for ferrimagnetic garnets and $\alpha$-$\text{Fe}_2\text{O}_3$, which are distinguished only by slight energy shifts. Notably, the GGA $+ U$ results had predicted spin-dependent gaps that were left unexplored; the majority gap became larger than the minority gap as $U$ increased.

Through the use of transmitting OMCD, optical gaps in inverse-spinel-ferrite Fe$_3$O$_4$ ($Fd\bar{3}m$) were resolved into the majority gap of 2.35 eV and the minority gap of 2.5 eV [4]. The gaps border the major transitions in Fe$_3$O$_4$: the energy below and above the gaps were the intervalence charge transfer (IVCT) and LMCT, respectively. IVCT applied to the interband transition involved two cations of different oxidization states (sites), and the LMCT was the pd charge transfer introduced at 2.5eV in the optical absorption process. In Fe$_3$O$_4$, the spin majority was the $B$ site, comprising the Fe$^{2+}$ and Fe$^{3+}$ configurations $t_{2g}^{1} e_{g}^{1}$, $t_{2g}^{1} e_{g}^{1}$, $t_{2g}^{1} e_{g}^{1}$, and $t_{2g}^{1} e_{g}^{1}$, respectively, whereas that in Y$_3$Fe$_5$O$_{12}$ was the $A$ site ($e_2^{\uparrow} t_{2g}^{\downarrow}$). In a band picture, the oxidation states mentioned in this study refer to the location of the $B$-site cations but not the real charge. Because of the time-reversal odd property, the MCD sign is expected to invert when the dominant spin-channel changes. This sign reversion can be a rule of thumb for feature assignments in the OMCD spectrum through comparative analysis, as discussed in the subsequent sections. Figure 4 presents the computed valence band electronic structure and the OMCD spectra of both ferrites.

### 3.1. Fe$_3$O$_4$

In Fe$_3$O$_4$, the spin majority in the valence band arises from the strong mixing of the $e_g$ $\uparrow$ and 2$p$ $\uparrow$ bands; the spin minority primarily comprises the 2$p$ $\downarrow$ band. A majority $d$-$d$ charge transfer, mediated by 2$p$ oxygen, and a minority pd $LMCT$ were inferred. The charge transfer is conventionally termed the intersublattice charge transfer (ISCT) because it occurs between the $B$-site $e_2$ band [$B(e_2) \uparrow$] and the $A$-site empty 3$d$ states [$A(e_2^c t_2) \uparrow$]. The LMCT in Fe$_3$O$_4$ is the minority charge transfer from 2$p$ $\downarrow$ to the $B$-site empty 3$d$ states [$B(t_{2g} e_2^c) \downarrow$]. The two
channels give rise to the paramagnetic and diamagnetic responses in the OMCD spectrum of Fe$_3$O$_4$, namely, the main rising slope (feature C, 2.7–3.0 eV) and falling slope (band ω, 3.5–4.5 eV), as shown in figure 4(c). The onsets of the main rising and falling slopes define the optical gaps in Fe$_3$O$_4$. The minority gap setting in the LMCT was determined to be 2.5 eV, at which the 2p component of the absorption process is initiated. This channel was overwhelmed by the paramagnetic ISCT channel and was apparent until the absorption energy became excessively high (at > 3.5 eV). These gaps were determined to be the optical gaps in Fe$_3$O$_4$ bordering the IVCT and LMCT can be observed at a close-up scan interval. The optical gaps γ ↑ and δ ↓, as depicted in figure 4(d), and the IVCT of $t_{2g} \rightarrow e_g$ which is depicted in feature B of figure 4(d).

In Fe$_3$O$_4$, the divalent Fe ions of the B site set the partially occupied $t_{2g}$ band (figure 4(a)) and govern the finite conductivity at room-temperature. Because the 2p covalency and B-site distortion relax the parity selection, divalent Fe ions appear in the IVCT interband transition: $t_{2g} \downarrow \rightarrow e_g$ ↓ [28]. This spin-minority IVCT channel usually has stronger oscillator strength and larger bandwidth compared with the LFTs for spinel-type ferrites [29]. The IVCT of $t_{2g} \rightarrow e_g$ (feature B in figure 4(d)) is also associated with the DFT + U-computed energy separations of $t_{2g}$ ↓ and $e_g$ ↓. These findings agree with those in the literature [29–31]. The majority gap γ ↑ (2.35 eV) setting of the ISCT in Fe$_3$O$_4$ was associated with a negative paramagnetic feature within the IVCT region. This finding accords with the opposite spin-directions of IVCT and ISCT. The minority gap δ ↓ setting of the LMCT was assigned to 2.5 eV, at which the slope changed at the paramagnetic ISCT. The assignment of δ ↓ indicated a reentrant spin-minority transition at that energy position because the spin directions of IVCT and LMCT are identical.

### 3.2. Y$_3$Fe$_5$O$_{12}$

For YIG, because all iron ions are trivalent, the Fe$^{3+}$ LFTs are expected to dominate the optical transition below the LMCT threshold. A simple ionic picture for LFT in magnetic-coupled Fe$^{3+}$ cations was obtained. For high-spin Fe$^{3+}$ in either an octahedral or tetrahedral coordination, the ground ligand quintet state $^6$A$_{1g}$ ($S = \frac{3}{2}$) arises from the configuration $t_{2g}^{3/2} e_g^{1/2}$. The first possible excited configuration is $t_{2g}^{1} e_g^{1} t_{2g}^{1}$, which provides the terms $^4T_1$ and $^4T_2$. Other higher ligand states result from $t_{2g}^{2} t_{2g}^{0} e_g^{2}$ and $t_{2g}^{1} e_g^{1} t_{2g}^{1}$. These ligand field states are quartets ($S = \frac{3}{2}$) and rarely have increasing absorption energies because of the onset of strong LMCT bands. Because the transition of quintet ($^6$A$_{1g}$) to quartets are spin forbidden, magnetic superexchange in YIG is important in the observations of LFT. Hence, the selection rules for the magnetic coupled Fe$^{3+}$–Fe$^{3+}$ pair, but not a single Fe$^{3+}$ ion, must be considered.[32] For this case, the spin Hamiltonian $J S_1 \cdot S_2$ acts as a perturbation to the ligand field.

### Table 2. Interatomic distances in YIG.

| Ion       | Nearest-neighbor | Distances (Å) |
|-----------|-----------------|---------------|
|           |                 | GGA           | LDA           | Exp. [16, 17] |
| Fe$^{3+}$ |                 |               |               |
| Fe$_{\alpha}$ | 4O$^{2-}$   | 1.87          | 1.88          | 1.87          |
|           | 6Y$_{\beta}$  | 3.09          | 3.09, 3.79    | 3.09(2), 3.79(4) |
|           | 4Fe$_{\alpha}$ | 3.46          | 3.46          | 3.46          |
|           | 4Fe$_{\beta}$  | 3.79          | 9.79          | 3.79          |
| Fe$_{\beta}$ | 6O$^{2-}$     | 2.02          | 2.01          | 2.01          |
|           | 6Fe$_{\alpha}$ | 3.46          | 3.46          | 3.46          |
|           | 2Y$_{\beta}$  | 3.46          | 3.46          | 3.46          |
| O$^{2-}$  |                 |               |               |
| Fe$_{\alpha}$ | 1.87          | 1.88          | 1.87          |
| Fe$_{\beta}$ | 2.02          | 2.01          | 2.01          |
|           | 2Y$_{\beta}$  | 2.36, 2.43    | 2.37, 2.43    | 2.37, 2.43    |
|           | 9O$^{2-}$     | 2.69, 2.69    | 2.68(2), 2.81, 2.84 | 2.81, 2.87 |
|           |               | 3.01, 2.97    | 2.96, 2.99(2), 3.14, 3.59 | 3.16(2) |
| Y$_{\beta}$ | 8O$^{2-}$     | 2.36, 2.43    | 2.37, 2.43    | 2.37(4), 2.43(4) |
|           | 6Fe$_{\alpha}$ | 3.09          | 3.09, 3.79    | 3.09(2), 3.79(4) |
|           | 4Fe$_{\alpha}$ | 3.46          | 3.46          | 3.46          |
|           | 4Fe$_{\beta}$  | 3.79          | 3.79          | 3.79(4)      |
states of the Fe$^{3+}$ cations, yielding the pair-state energy $E = \frac{1}{2} [S_{\text{tot}}(S_{\text{tot}} + 1) - S_1(S_1 + 1) - S_2(S_2 + 1)]$. Considering that both Fe$^{3+}$ cations are quintet $^6A_1$ states, the total spin is $S_{\text{tot}} = 0, 1, 2, 3, 4, 5$. If one Fe$^{3+}$ cation in the pair is excited to a quartet state, the total spin of the Fe$^{3+}$ pair gives $S'_{\text{tot}} = 1, 2, 3, 4$. Furthermore, if both Fe$^{3+}$ cations are excited to a quartet state where $S_1 = S_2 = \frac{3}{2}$, the pair excitation resulting from magnetic coupled cations is such that $S'_{\text{tot}} = 0, 1, 2, 3$. In both cases, the transition from the ground state to the excited pair states will includes $\Delta S_{\text{tot}} = S'_{\text{tot}} - S_{\text{tot}} = 0$. The spin selection becomes possible through the magnetic coupling of electronic spin of the next-nearest-neighboring Fe$^{3+}$ cations [21].

In YIG, because all Fe ions are trivalent, the major 3d states of both sites are well separated below the 2p band. As depicted in figure 4(b), the valence band is dominated by the 2p-band that possesses the positive SP near the $E_F$ and transits to the opposite direction away from $E_F$. Therefore, both optical gaps in YIG are of the LMCT type, and the energy position of the gaps is expected to border LMCT and LFTs.

As depicted in figure 4(d), the characteristic features in YIG accorded with those in [33]; these features are a broad band of negative MCD (1.6–1.9 eV), two positive paramagnetic components denoted as A (2.0 eV) and $A'$ (2.2 eV), and a pit (2.4 eV) next to a strong rising peak Y. The energy position shifted little when YIG was cooled to a low temperature, and these features sharpened and became more distinguishable. Per [33], as summarized in table 3, the assignment of the low-lying broad band (1.6–1.9 eV) was the $B$-site LFT. Because of the parity selection rule, one expects tetrahedral cations to have more intense LFT relative to the corresponding components for octahedral cations of the same trivalent states. Consequently, the stronger positive paramagnetic $A$ and $A'$ in YIG assigned to the $A$-site Fe$^{3+}$ LFT (i.e., $^5A_1 \rightarrow ^3T_1$ and $^5A_1 \rightarrow ^3T_2$) were in general agreement with findings in the literatures [33–36]. The corresponding energy positions were located between the $B$-site LFT and the stronger rising peak Y (2.55 eV).
4. Spin-dependent optical transitions in YIG

The assignments in table 3 were based on the assumption that all transitions were LFTs in origin. In [36] and [34], the $2p - 3d$ charge transfer was introduced by a localized $d$-electron model explicitly incorporating a band picture with the electronic correlation accounted for. However, that only accounted for absorption energies $>3.3$ eV. Prominent unoccupied states of the opposite spin to which the $2p$ band was transferred was ostensibly concealed. Analogous to the case of Fe$_3$O$_4$, when we assigned the majority-spin gap ($\gamma^\uparrow$) at the onset of the raising peak $Y$, the majority LMCT of $2p^\uparrow \rightarrow (t_{2g}; e_{g})^\uparrow$ was determined. Peak $Y$ at 2.55 eV must reflect the unoccupied $3d$ states of the $B$ site. The falling slope $C$ ($2.5 – 3.3$ eV) manifesting the diamagnetic response of $2p^\downarrow \rightarrow (t_{2g}; e_{g})^\downarrow$ should be followed. This explains the opposite value for both the MCD sign and slope of edge $C$ because the $A$-site empty states in Fe$_3$O$_4$ and YIG had opposite spin directions. Subsequently, the minority gap of YIG ($\delta^\downarrow$) should be backtracked along the diamagnetic response $C$ at an energy position bordering the LFT and LMCT. Hence, the minority LMCT channel of $2p^\uparrow \rightarrow t_{2g}^\uparrow$ was located by the minority gap $\delta^\downarrow (2.3$ eV), at which the diamagnetic response was set next to the positive $A$-site LFT. The assignment also matched the band gap, as observed from the hard x-ray photoelectron spectroscopy spectra of a YIG bulk single crystal [37]. This channel was impaired by the opposite LMCT channel $Y$ and was apparent until the falling edge $C$. Table 4 presents a summary of the dominant spin-dependent optical transitions in YIG along with Fe$_3$O$_4$ in [4].

The assignment of optical gaps agree with the predicted larger gap size of the spin majority in YIG. According to figure 5 (lower panel), the DFT+$U$ computed gaps were correlated with the $U$ values. This led us to consider
the site–dependent $U$ correction ($U_{\text{eff}}^A = 4.7$ eV and $U_{\text{eff}}^B = 3.75$ eV) that is responsible for the determined optical gaps in YIG. Figure 5 shows the computed projected density of states and the corresponding subtractive difference of the computed unoccupied total density of states. As clearly indicated in figure 5(b), the main features $Y$ and $C$ in the OMCD spectra can be matched from the subtractive difference of the computed

| Table 3. Position of MCD features listed versus line shape and assignment. Reprinted with permission from [33]. Copyright (1975) by the American Physical Society. |
|---|---|---|---|
| Energy (cm$^{-1}$) | Line shape | Ligand field transition |
| | (eV) | Paramagnetic | Diamagnetic |
| 10400 | 1.29 | + | $^6A_{1g} \rightarrow ^4T_{1g}$ |
| 10920 | 1.35 | + | |
| 11420 | 1.42 | + | |
| 13500 | 1.67 | + | $^6A_{1g} \rightarrow ^4T_{2g}$ |
| 14090 | 1.75 | — | |
| 14870 | 1.84 | — | |
| 16050 | 1.99 | + | $^6A_1 \rightarrow ^4T_1$ |
| 16500 | 2.03 | + | |
| 16840 | 2.09 | — | |
| 17380 | 2.15 | + | |
| 18200 | 2.26 | + | |
| 18550 | 2.30 | + | |
| 19100 | 2.37 | — | $^6A_1 \rightarrow ^4T_2$ |
| 19600 | 2.43 | + | |
| 20700 | 2.57 | + | $^6A_1 \rightarrow ^4E; ^1A_1$ |
| 21500 | 2.67 | + | $^6A_{1g} \rightarrow ^2Eg; ^4A_{1g}$ |
| 22500 | 2.79 | + | $^6A_{1g} \rightarrow ^4T_{2g}$ |
| 23250 | 2.88 | — | pair excitation or |
| 25200 | 3.12 | — | Fe$^{3+}$-Fe$^{3+}$ |
| 27500 | 3.41 | — | charge transfer |

| Table 4. Spin-dependent optical transition in YIG. (LF: ligand field transition, LMCT: ligand-to-metal charge transfer, IVCT: inter-valence charge transfer, ISCT: inter-sublattice charge transfer). Based on the first derivative of the OMCD signal, features were assigned to a peak $\frac{d\Delta}{dE} = 0$, the band of diamagnetic response $\frac{d\Delta}{dE} < 0$, and the band of paramagnetic $\frac{d\Delta}{dE} > 0$ response. |
|---|---|---|---|---|---|---|
| Features | Energy (eV) | Main Transition | Type | $f(E)$ | $\frac{df}{dE}$ |
| | | YIG | Fe$_3$O$_4$ (Chen et. al.) | | |
| $A$ | 1.95 | $^6A_1 \rightarrow ^4T_1$ | — | LF$^a$ | + | 0 |
| $A'$ | 2.25 | $^6A_1 \rightarrow ^4T_2$ | — | LF | + | 0 |
| $B$ | 2.1 | — | $t_{2g} \downarrow \rightarrow e_g \downarrow$ | IVCT | — | 0 |
| $\gamma \uparrow$ | 2.45 | $2p \uparrow \rightarrow t_{2g} \uparrow$ | — | LMCT$^b$ | — | + |
| | 2.35 | $e_g \uparrow \rightarrow (e, t_2) \uparrow$ | — | ISCT | — | + |
| $\delta \downarrow$ | 2.25 | $2p \downarrow \rightarrow e \downarrow$ | — | LMCT$^b$ | — | + |
| | 2.5 | — | $2p \downarrow \rightarrow t_{2g} \downarrow$ | LMCT | — | + |
| $Y$ | 2.55 | $2p \uparrow \rightarrow e \uparrow$ | — | LMCT$^b$ | — | + |
| $Y'$ | 2.7 | $2p \uparrow \rightarrow e_g \uparrow$ | — | LMCT | — | 0 |
| $C$ | 2.7-3.3 | $2p \uparrow \rightarrow (e, t_2) \uparrow$ | — | LMCT | — | — |
| | — | $e_g \uparrow \rightarrow (e, t_2) \uparrow$ | — | ISCT | + | + |
| $\omega$ | 3.5 - 6.0 | $2p \downarrow \rightarrow t_{2g} \downarrow$ | — | LMCT | — | — |
| $D$ | 3.9 | $t_{2g} \downarrow \rightarrow (e, t_2) \downarrow$ | $2p \uparrow \rightarrow (e, t_2) \uparrow$ | LMCT | — | + |

$^a$ Tetrahedral Fe$^{3+}$ crystal field transition

$^b$ Optical gap of spin majority

$^c$ Optical gap of spin minority
unoccupied total state dominated by the 3d character. This verified that Y and C reflect the unoccupied 3d band above the E_F, each having the final-state characteristics of $2p \uparrow \rightarrow t_{2g}$ and $2p \uparrow \rightarrow t_2$, respectively. For those uncovered OMCD areas, including $Y'$, $\omega$ (2.9–3.5 eV) and $D$ (3.9 eV) have an initial-state character in a $2p - 3d$ dipole-transition. Hence, the analysis concluded that (1) features Y and C are A- and B-site Fe characters, respectively, and (2) the uncovered area in $\omega$ and D is of an oxygen character.

5. Conclusion

We investigated the spin-dependence optical transition in YIG. GGA + U-predicted spin-dependent gaps were deduced from the transmitting OMCD spectrum of a PLD-grown single crystal thin films. Optical gaps were resolved into the spin majority of 2.45 eV and the spin minority of 2.25 eV. The energy below the gaps applies to the interband transition involving two cations of trivalent states, and the energy above the gaps was the $p - d$ charge transfer introduced at 2.25 eV in the optical absorption process.
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Data availability

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

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