FARADAY EFFECTS IN Rh^{4+} -AND Ir^{4+} -SUBSTITUTED MAGNETIC GARNETS

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Abstract- Large Faraday rotations are reported for Rh^{4+} -substituted magnetic garnets in the visible wavelength region, in comparison with those observed in Ir^{4+} substituted ones. Although rather strong absorptions are observed in the visible region, no absorption peaks corresponding to the Faraday rotation peaks are observed in the absorption spectra. In order to study the origin of the Faraday rotations, Rh^{4+} -and Ir^{4+} -substituted nonmagnetic garnet films are prepared by an LPE method and optical absorption spectra are measured. In addition, the electronic state calculation of $(\text{M}^{4+}\text{O}_6^{2-})^{8-}$ ($\text{M}=\text{Rh}, \text{Ir}$) octahedral clusters are performed by using the SCF-Unrestricted -SW $X\alpha$ method. From the observed absorption spectra in nonmagnetic garnets and the electronic state calculations, large Faraday rotations are assigned to the charge transfer transitions of an electron from O 2p to Rh 4d or Ir 5d orbitals, or $t_{1u}^n \rightarrow t_{2g}^*$ and $t_{2u}^n \rightarrow t_{2g}^*$ transitions.

KEYWORD : FARADAY ROTATION, GARNETS, Rh- AND Ir-SUBSTITUTION, ELECTRONIC STATE SCF-SW- $X\alpha$ METHOD

I. INTRODUCTION

There have been many studies on Faraday effects in magnetic garnets where Fe ions are partially substituted with transition metal ions. Among them, it has been known that the substitution of Co^{2+} ($3d^7$) ions induces a large Faraday rotation in the infrared region due to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ crystal field transition of Co^{2+} ion at tetrahedral sites in YIG^{1,2)}. Recently, it was reported that the substitution of Ir^{4+} ($5d^5$) ions also induces a large Faraday rotation at around $0.5 \mu\text{m}$, and the origin of this rotation is due to the charge transfer (CT) transition from O 2p to Ir 5d orbitals³⁾.

In this paper, we report the effect of Rh^{4+} ($4d^5$) -substitution on the Faraday rotation in YIG in comparison with that of Ir^{4+} ($5d^5$) -substitution. In addition, to make clear the origin of the Faraday rotation, we prepared Rh^{4+} -and Ir^{4+} -substituted nonmagnetic garnets by using an LPE (liquid phase epitaxy) method, and performed the electronic state calculations of $(\text{M}^{4+}\text{O}_6^{2-})^{8-}$ ($\text{M}=\text{Rh}, \text{Ir}$) octahedral clusters by SCF (self-consistent field)-Unrestricted-SW

(scattering wave)- $X\alpha$ method. As a result, it was found that large Faraday rotations observed in Rh^{4+} -and Ir^{4+} -substituted garnets in the visible region originate from the CT transitions from O 2p to Rh 4d or Ir 5d orbitals, or $t_{1u}^n \rightarrow t_{2g}^*$ and $t_{2u}^n \rightarrow t_{2g}^*$ transitions.

II. EXPERIMENT

The single crystalline magnetic garnet $(\text{Y}, \text{Ca}^{2+})_3(\text{Fe}, \text{Rh}^{4+})_5\text{O}_{12}$ and nonmagnetic garnet $(\text{Gd}, \text{Ca}^{2+})_3(\text{Ga}, \text{M}^{4+})_5\text{O}_{12}$ ($\text{M}=\text{Rh}, \text{Ir}$) films were prepared by the LPE method onto (111)-oriented GGG (gadolinium gallium garnets) substrates by using PbO and B_2O_3 fluxes. Table 1(a) and (b) show the melt composition used to prepare Rh^{4+} -substituted magnetic garnet films, and the Ir^{4+} -and Rh^{4+} -substituted GGG ones, respectively. In Table 1, the Ca contents in the melts were optimized so as to substitute Fe^{3+} or Ga^{3+} with Rh^{4+} or Ir^{4+} in a desired amount. Table 2(a) and (b) show growth temperature (Tg), dipping time (D.T.), thickness (d), and the lattice constant (a) of the films grown by using the melts in Table(a) and (b), respectively. The

melt compositions and the growth conditions for preparing the Ir⁴⁺-substituted magnetic garnet films have been shown in the reference 3. Film thickness was determined from the optical interference spectrum measured by UV-550 type spectrometer (JASCO) assuming the average refractive index of 2.15. Lattice constants were estimated from an (888) peak in the X-ray (Cu, K α) diffraction measurements. As shown in Table 2(a), the growth rates of the Rh⁴⁺-substituted films are very small in comparison with that of YIG, and decrease drastically with the increase of Rh contents in the melts, while the lattice constants of the Rh⁴⁺-substituted films are nearly equal to the lattice constant of YIG. Furthermore, it is seen that the growth rates of the nonmagnetic garnet films are also very small as shown in Table 2(a).

Table 1 Melt composition of magnetic garnet films.

(a) Magnetic garnet films

Sample	Melt composition (mol %)					
	Y ₂ O ₃	CaCO ₃	Fe ₂ O ₃	Rh ₂ O ₃	PbO	B ₂ O ₃
YIG	0.57	—	10.23	—	84.51	4.69
A	0.32	0.32	7.47	0.008	87.42	4.46
B	0.32	0.64	7.41	0.037	87.44	4.15

(b) Nonmagnetic garnet films

Sample	Melt composition (mol %)						
	Gd ₂ O ₃	CaCO ₃	Ga ₂ O ₃	IrO ₂	Rh ₂ O ₃	PbO	B ₂ O ₃
C	0.25	0.14	7.35	0.074	—	87.49	4.69
D	0.25	0.14	7.35	—	0.074	87.49	4.69

Table 2 The growth temperature(T_g), dipping time(D.T.), film thickness(d), and lattice constant(a).

(a) Magnetic garnet films

Sample	T _g (°C)	D.T. (min)	d (μm)	a (Å)
YIG	990	3	3.01	12.374
A	930	10	2.18	12.373
B	900	30	2.66	12.375

(b) Nonmagnetic garnet films

Sample	T _g (°C)	D.T. (min)	d (μm)	a (Å)
C	950	20	2.26	12.380
D	950	10	3.17	12.379

The compositions of the films were determined by the ICPS (Inductively Coupled Plasma Spectroscopy) method by using Perkin- Elmer Plasma II type apparatus, and the results are summarized in Table 3. From Table 3(a), it is seen that Rh contents in the magnetic films are less than 0.13 per formula unit, and Rh and Ir contents in the nonmagnetic films are 0.05 and 0.07 per formula unit, respectively, in the experiment. Furthermore, it is seen that Ca²⁺ contents are nearly equal to Rh and Ir ones in all films, indicating that Rh and Ir in the films are tetravalent states. Pb and Pt in Table 3 are impurities incorporated into the films from the flux and the Pt crucible used in the experiment.

Table 3 Film composition.

(a) Magnetic garnet films.

Sample	Composition (at./f.u.)					
	Y	Ca	Pb	Fe	Rh	Pt
YIG	3.00	—	0.00	5.00	—	0.00
A	2.94	0.05	0.01	4.94	0.05	0.01
B	2.84	0.15	0.01	4.85	0.13	0.02

(b) Nonmagnetic garnet films

Sample	Composition (at./f.u.)						
	Gd	Ca	Pb	Ga	Ir	Rh	Pt
C	2.92	0.08	0.00	4.92	0.07	—	0.01
D	2.95	0.05	0.00	4.94	—	0.05	0.01

Faraday rotation (FR) spectra were measured in the visible region by using J-250 type spectrometer (JASCO) under the magnetic field of 4.5kOe perpendicular to the film plane at room temperature and 120K. Optical absorption spectra were measured in the visible to the ultraviolet region by using UV-550 type spectrometer (JASCO) at room temperature.

III. EXPERIMENTAL RESULTS

Fig.1(a) and (b) show the Faraday rotation spectra of (Y,Ca)₃(Fe,M)₅O₁₂ films measured at room temperature and at 120K, respectively. Fig.2 shows Faraday rotation spectra of (Y,Ca)₃(Fe,Ir)₅O₁₂ films measured at 120K in comparison with those of Fig.1(b). From these results, it was found that 1) two large negative

Fig.1 Faraday rotation spectra of $\text{Y}_{3-x}\text{Ca}_x\text{Fe}_{5-x}\text{Rh}_x\text{CrO}_{12}$ films.

peaks at around 0.55 and at $0.9 \mu\text{m}$ appear with the Rh^{4+} -substitution, 2) Faraday rotation increases with the Rh contents in the films, 3) Faraday rotation depends strongly on the temperature, and Faraday rotation at $0.9 \mu\text{m}$ in the film of only 0.13 Rh per formula unit reaches about seven times as large as that in pure YIG at 120K , and 4) in comparison with the negative peaks in Ir-substituted magnetic garnets, those in Rh-substituted magnetic garnets shift to lower energies by about 0.5eV . Fig.3 shows the absorption spectra of $(\text{Y,Ca})_3(\text{Fe,Rh})_5\text{O}_{12}$ films measured at room temperature. It is seen that 1) the absorption strength increases with Rh content in the films, 2) there appear no peaks in the spectra at the positions corresponding to the Faraday rotation peaks, and 3) these characteristics in the absorption spectra are similar to those in the absorption spectra of $(\text{Y,Ca})_3(\text{Fe,Ir})_5\text{O}_{12}^{3)}$.

Fig.2 Faraday rotation spectra of $\text{Y}_{3-x}\text{Ca}_x\text{Fe}_{5-x}\text{Ir}_x\text{O}_{12}$ films at 120K .

Fig.3 Optical absorption spectra of $\text{Y}_{3-x}\text{Ca}_x\text{Fe}_{5-x}\text{Rh}_x\text{O}_{12}$ films at room temperature.

Fig.4 Optical absorption spectra in $\text{Gd}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{M}_x\text{O}_{12}$ ($\text{M}=\text{Rh}, \text{Ir}$) films at room temperature.

Fig.4 shows absorption spectra measured in nonmagnetic $(\text{Gd}, \text{Ca})_3(\text{Ga}, \text{M})_5\text{O}_{12}$ ($\text{M}=\text{Rh}, \text{Ir}$) films. It is seen that 1) there appears a weak peak at around $0.5 \mu\text{m}$ in the absorption spectrum of Rh-substituted nonmagnetic garnet, and 2) a relatively strong peak at around $0.3 \mu\text{m}$ and a shoulder at around $0.5 \mu\text{m}$ appear in Ir-substituted nonmagnetic garnet. It should be noted that these weak transitions in the absorption spectra are attributable to the large Faraday rotations in magnetic garnets.

IV. CALCULATION

In order to make clear the origin of the observed large Faraday rotation, we calculated the electronic states of $(\text{M}^{4+}\text{O}_6^{2-})^{8-}$ ($\text{M}=\text{Rh}, \text{Ir}$) octahedral clusters, cut out from the surrounding of M^{4+} ion in YIG, by using the SCF-Unrestricted-SW- $X\alpha$ method⁴⁾. The Metal-Oxygen distance was assumed to be 3.815 a.u. (1 a.u.=0.529167 Å) equal to the average Fe-O distance in a $(\text{Fe}^{3+}\text{O}_6^{2-})^{9-}$ octahedral cluster in YIG⁵⁾. The atomic sphere radii of M^{4+} and O^{2-} were assumed to be 1.815 and 2.000 a.u., respectively. In addition, the outer sphere was assumed that encloses and just touches the atomic spheres. The exchange parameters of $\alpha=0.7026$, 0.6931, and 0.7445 were assumed for Rh, Ir and O, respectively, and weighted average values of $\alpha=0.7356$ and 0.7335 for the interatomic and the extracuster (an outside of the outer sphere) regions for the $(\text{Rh}^{4+}\text{O}_6^{2-})^{8-}$ and $(\text{Ir}^{4+}\text{O}_6^{2-})^{8-}$ clusters, respectively⁶⁾. In addition, to account for the neighbors of the clusters approximately, we used Watson spheres with the same positive charges as the negative ones of the cluster. Furthermore, the orbitals except 4s, 4p, and 4d for Rh, 5s, 5p, and 5d for Ir, and 2s, 2p for O were assumed for simplicity to be the core orbitals in our calculations. Fig.5 shows the one electron energy levels, the electron configuration of the ground state and the allowed charge transfer (CT) transitions (vertical arrows) of $(\text{M}^{4+}\text{O}_6^{2-})^{8-}$ ($\text{M}=\text{Rh}, \text{Ir}$) clusters. It should be noted that only the down-spin energy levels are shown in Fig.5. As seen in this figure, both Rh^{4+} (4d)⁵ and Ir^{4+}

(5d)⁵ are in the low-spin states with one hole in the down-spin t_{2g}^* level, and as shown by the vertical arrows in Fig.5, three CT transitions to the t_{2g}^* level are allowed from oxygen 2p-like t_{1u} or t_{2u} level by the symmetry consideration. From the Slater transition state calculations, we can obtain the transition energies of these CT transitions, and the results are summarized in Table 4. From Table 4, it is seen that 1) the CT transitions in $(\text{Rh}^{4+}\text{O}_6^{2-})^{8-}$ cluster appear in the visible wavelength region, 2) the transition energies in $(\text{Ir}^{4+}\text{O}_6^{2-})^{8-}$ cluster shift to higher energies by about 0.5eV, in comparison with those in $(\text{Rh}^{4+}\text{O}_6^{2-})^{8-}$ cluster.

Fig.5 One electron energy levels and down spin electron configurations of $(\text{Ir}^{4+}\text{O}_6^{2-})^{8-}$ and $(\text{Rh}^{4+}\text{O}_6^{2-})^{8-}$ in the ground state and the allowed charge transfer transitions.

V. DISCUSSION

From the results of the transition energies of the CT transitions in Table 4 and the observed absorption spectra in Rh^{4+} - and Ir^{4+} -substituted nonmagnetic garnets, we could

Table 4 The transition energies of the charge transfer (CT) transitions in $(\text{M}^{4+}\text{O}_6^{2-})^{8-}$ cluster ($\text{M}=\text{Ir}, \text{Rh}$).

CT trans.	$(\text{Ir}^{4+}\text{O}_6^{2-})^{8-}$	$(\text{Rh}^{4+}\text{O}_6^{2-})^{8-}$
$t_{1u}^n \rightarrow t_{2g}^*$	2.04 eV (0.61 μm)	1.54 eV (0.80 μm)
$t_{2u}^n \rightarrow t_{2g}^*$	2.66 eV (0.47 μm)	2.04 eV (0.60 μm)
$t_{1u} \rightarrow t_{2g}^*$	3.41 eV (0.36 μm)	2.84 eV (0.44 μm)

assign the observed peak at around 0.3 μm and a shoulder at around 0.5 μm in Ir-substituted nonmagnetic garnet to $t_{1u} \rightarrow t_{2g}^*$, $t_{2u}^n \rightarrow t_{2g}^*$ and $t_{1u}^n \rightarrow t_{2g}^*$, in energy order, respectively, and the observed peak at around 0.5 μm to $t_{1u} \rightarrow t_{2g}^*$ in Rh^{4+} -substituted nonmagnetic garnet, while two transitions with lower energies are too weak to be observed as shown in Fig.4. If these assignments are reasonable, then it is considered that the large Faraday rotations observed in Rh^{4+} -substituted magnetic garnets in the visible region are induced by the two lower energy weak CT transitions of $t_{1u}^n \rightarrow t_{2g}^*$ and $t_{2u}^n \rightarrow t_{2g}^*$, as suggested in the Faraday rotation of Ir-substituted magnetic garnets³⁾. It has been known that weak transitions such as these CT transitions may have significant contributions to the Faraday rotations^{3),7),8)}. As shown in Fig.6, the ground state and the CT excited state in the $(\text{Rh}^{4+}\text{O}_6^{2-})^{8-}$ cluster are $[(t_{2g}^*)^5(t_{1u}^n)^6]^2T_{2g}$ and $[(t_{2g}^*)^6(t_{1u}^n)^5]^2T_{1u}$ or $[(t_{2g}^*)^6(t_{2u}^n)^5]^2T_{2u}$, respectively. They are split by the spin-orbit (S.O.) interaction of 4d electrons in Rh^{4+} and the molecular field (M.F.) from the Fe sublattices in magnetic garnets. The Faraday rotation originates from the difference of the selection rules for the transitions for a right circularly polarized light and for a left one from the lowest ground level at low temperatures, if we assume that the splitting of the ground state due to the molecular field is too large to promote an electron to the upper ground level at room temperature³⁾. Therefore, the effects of the

spin-orbit interaction of 4d or 5d electrons and the molecular field on the ground state are more important factors for a large Faraday rotation than the strengths of the transitions.

VI. CONCLUSION

In conclusion, two large Faraday rotation peaks were observed at around 0.55 μ m and 0.9 μ m in Rh⁴⁺-substituted magnetic garnets, corresponding to those observed at around 0.5 μ m in Ir⁴⁺-substituted magnetic garnets. From the absorption spectra in Rh⁴⁺-and Ir⁴⁺-substituted nonmagnetic garnets and the electronic state calculations of the (M⁴⁺O₆²⁻)⁸⁻ (M=Rh,Ir) octahedral clusters by using the SCF-Unrestricted-SW-X α method, these large rotations were attributable to the charge transfer transitions of an electron from O 2p to Rh 4d or Ir 5d orbitals or $t_{1u}^n \rightarrow t_{2g}^*$ and $t_{2u}^n \rightarrow t_{2g}^*$. Finally, it was suggested that the effects of the spin-orbit interaction of 4d or 5d electrons in Rh⁴⁺ or Ir⁴⁺, respectively, and the molecular field from Fe sublattices in the magnetic garnets on the [(t_{2g}^{*})⁵(t_{1u}ⁿ)⁶]²T_{2g} ground state are important factors for the large Faraday rotations in Rh⁴⁺-and Ir⁴⁺-substituted magnetic garnets.

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Fig.6 Energy level diagram of the ground and excited states in (Rh⁴⁺O₆²⁻)⁸⁻ cluster and the allowed transitions for P₊ and P₋ polarization.