EFFECTS OF TETRAHEDRAL Co^{3+} ON INFRARED FARADAY ROTATION IN MAGNETIC GARNETS

T. SAITO, K. TAMANOI, K. SHINAGAWA, and T. TSUSHIMA

Dept. of Phys., Fac. of Sci., Toho Univeristy, Miyama, Funabashi, Chiba 274, Japan

ABSTRACT

Effects of the trivalent Co ion on the tetrahedral site of magnetic garnets on the Faraday rotation spectra (FRS) in the infrared region were investigated in the scheme of the crystal field theory (strong crystal field approximation), and the calculated FRS were compared with the experimentally obtained FRS in $(\text{Y}\text{Gd})_3(\text{Co}_x\text{Fe}_{5-x})\text{O}_{12}$ films grown by the conventional liquid phase epitaxy (LPE) method. The experimental FRS of Co doped magnetic garnets, having a dispersion-type shape, were well explained by the crystal field transition ${}^5\text{E} \rightarrow {}^5\text{T}_2$ taking into account the spin-orbit interaction (S.O.) and the tetragonally distorted field (S_4). From the calculations of the energy level splittings of ${}^5\text{T}_2$ excited state and ones of the FRS for Co^{3+} on the tetrahedral site, we found that the sign of S.O. and the magnitude of the low symmetry field (S_4) give a strong influence on the shape of FRS; only when S.O. is negative and a' , a measure of the low symmetry field (S_4), is larger than about 1000 cm^{-1} , the shape of FRS is of dispersive type as observed experimentally.

1. INTRODUCTION

Effects of Co ions on magneto-optical properties of some magnetic garnets have been studied experimentally since 1970s [1]-[4]. On substituting Co ions with tetravalent nonmagnetic ions for Fe^{3+} in magnetic garnets or various ferrites, the fairly large Faraday rotations are observed in the visible ($\lambda \sim 0.7\mu\text{m}$) and infrared ($\lambda \sim 1.5\mu\text{m}$) regions [1]-[7]. This Faraday rotation is well understood by the crystal-field (Td) transitions ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{P})$ and ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{F})$ with the spin-orbit interaction (S.O.) for tetrahedrally coordinated Co^{2+} [8]. Taking into consideration the tetragonally distorted crystal field (S_4), it is further explained why the infrared Faraday rotation spectrum (FRS) has such a broad absorption-type shape [4].

In the case of no charge compensation, the Co ions in garnets are primarily in trivalent state [9]. This Co^{3+} doped magnetic garnets also show the large Faraday rotation [1] as well as the magnetic garnets containing Co^{2+} on the tetrahedral site, though the shape of FRS seems to differ with each other (FRS of Co^{3+} has a dispersion-type shape), and the anomaly of FRS is shown only in the infrared region ($\lambda \sim 1.5\mu\text{m}$).

The origin of the large FRS of Co^{3+} about at $1.5\mu\text{m}$ is regarded as the crystal field (Td) transition ${}^5\text{E} \rightarrow {}^5\text{T}_2$ with the splitting of the excited state due to the S.O.. However, there are no detailed investigations about the origin of the FRS of Co^{3+} doped magnetic garnets as far as we know.

Taking account of the spin-orbit interaction and the low symmetry crystal field (S_4), we calculated in the framework of the strong crystal field approximation [10][11] the energy levels of the excited state for tetrahedral coordinated Co^{3+} and the parameters necessary for the calculation of FRS. We found that the FRS of tetrahedrally coordinated Co^{3+} is qualitatively well explained in this scheme and the sign of S.O. and the fairly large low symmetry field (S_4) are important in making the shape of FRS of tetrahedrally coordinated Co^{3+} dispersive.

In this paper, we report on the above results and the comparison between the calculated FRS and the experimentally obtained one in the Co doped uncompensated yttrium iron garnet (YIG) films grown by the LPE method.

2. EXPERIMENT

The magnetic garnet films $(\text{Y}\text{Gd})_3(\text{Co}_x\text{Fe}_{5-x})\text{O}_{12}$ were grown on (111) plane of gadolinium gallium garnet (GGG) substrates by the LPE using $\text{PbO-B}_2\text{O}_3$ as the flux. Gd was employed to have a good matching of the lattice constant of the garnet film with that of GGG. R_1 and R_3 parameters of the melts were both 14.0, where $R_1 = ([\text{Fe}_2\text{O}_3] + [\text{CoO}]) / ([\text{Y}_2\text{O}_3] + [\text{CoO}])$ and $R_3 = [\text{PbO}] / [\text{B}_2\text{O}_3]$. These parameters were determined by referring to the experimental results of Hibiya [12] and Ito et al. [2]. Growth temperature (T_g) and substrate rotation of garnet films used in the FRS measurements were fixed at 950°C and 100rpm, respectively. Chemical compositions analyzed by an EPMA technique were $(\text{Y}_{2.72}\text{Gd}_{0.24}\text{Pb}_{0.04})\text{Fe}_5\text{O}_{12}$, $(\text{Y}_{2.76}\text{Gd}_{0.21}\text{Pt}_{0.03})(\text{Co}_{0.03}\text{Fe}_{4.95}\text{Pt}_{0.02})\text{O}_{12}$, $(\text{Y}_{2.73}\text{Gd}_{0.23}\text{Pb}_{0.04})(\text{Co}_{0.07}\text{Fe}_{4.91}\text{Pt}_{0.02})\text{O}_{12}$, and $(\text{Y}_{2.75}\text{Gd}_{0.22}\text{Pb}_{0.03})(\text{Co}_{0.10}\text{Fe}_{4.88}\text{Pt}_{0.02})\text{O}_{12}$. Pb and Pt ions originate from the flux and the platinum crucible for LPE, respectively.

The FRS were measured by the polarization modulation method at room temperature.

3. ELECTRONIC STATES OF Co^{3+} IONS ON TETRAHEDRAL SITES IN MAGNETIC GARNETS

3.1 Tetrahedral Crystal Field (Td group)

Co^{3+} has $(3d)^6$ electronic configuration. When the ion occupies a tetrahedral site, the ground and the first excited states become $|t_2^3e^3({}^5\text{E})\rangle$ and $|t_2^4e^2({}^5\text{T}_2)\rangle$ (high spin states), respectively.

The two states have the same Coulomb energies $-12B$ [10] in terms of Racah parameter B_2 , then the energy level of 5T_2 state relative to that of 5E (set equal to zero) is $10Dq$.

3.2 Spin-Orbit Interaction (S.O.)

In terms of the operator equivalent method [10], the S.O. of the excited state (5T_2) can be written as $\mathcal{H} = \lambda(\alpha {}^5T_2) \mathbf{S} \cdot \mathbf{L}$, where α is the electronic configuration (t_{2e}^2) and $\mathbf{S}, \mathbf{L}$ are the total spin angular momentum and the orbital one, respectively. From the similarity between 5T_2 state and 5P state ($L=1$) [10], it is seen that 5T_2 level splits into three sublevels as shown in Fig.1.

The value of $\lambda(t_{2e}^2 {}^5T_2)$ obtained theoretically is $-\zeta/4$ [10], where ζ is the spin-orbit interaction parameter for 3d electrons. Though ζ of Co^{3+} is not known, Sturge et al. [13] obtained experimentally $\lambda = -110\text{cm}^{-1}$ from an ESR measurement on a crystal of Co^{3+} doped YGG. This value of λ is close to the above theoretical one -133cm^{-1} assuming that ζ of Co^{3+} and that of Co^{2+} have the same value which is known as 533cm^{-1} [11].

3.3 Tetragonally Distorted Crystal Field (S_4)

The symmetry of the tetrahedral site (Td) in garnets is really reduced to the lower symmetry S_4 having two unequal oxygen distances [9]. The additional potential term of the low symmetry field to the cubic one is characterized by a spherical harmonic function aY_0^4 , where a is a coefficient.

This low symmetry field gives rise to the another splittings of energy levels in the excited state as shown schematically in Fig.1.

3.4 Calculation of Energy Levels for 5T_2 State in an S_4 Field

By diagonalizing the matrix of $\mathcal{H}(S.O. + S_4)$, the energy levels for the excited state 5T_2 state were obtained. For $\lambda = -110\text{cm}^{-1}$, we show in Fig.2 the energy splittings of 5T_2 state as a function of a' which is defined as $a' = a \langle \alpha L=1 || Y_0^4 || \alpha L=1 \rangle$ where $\langle \alpha L=1 || Y_0^4 || \alpha L=1 \rangle$ is a reduced matrix for the electronic configuration $\alpha(t_{2e}^2)$ and $L=1$; the reduced matrix is a constant in 5T_2 state, therefore, we used the a' as a measure of the departure from the cubic field (Td). In Fig.2, the parent 5T_2 state is set to zero.

3.5 Molecular Field (M.F.)

In the ferrimagnetic state, each level obtained as above is affected by the M.F.. It is schematically shown on the right side of Fig.1; however, only the related parts to the calculations of FRS are indicated in this figure. (The magnitude of the M.F. is not strictly considered.)

The ground state may become $\Gamma_2(S_4)$ which is corresponding to $S_z = \pm 2$ under the influence of M.F.

4. CALCULATIONS OF FARADAY ROTATION

4.1 Faraday Rotation of Co^{3+} in S_4

As indicated on the right side of Fig.1, the selection rules are different between the right-circularly polarized light ($S_z=2 \rightarrow J_z=3$ ($\Gamma_2 \rightarrow \Gamma_3$); P_+ (solid line)) and the left-circularly one ($S_z=2 \rightarrow J_z=1$ ($\Gamma_2 \rightarrow \Gamma_4$); P_- (broken lines)), where P_+ and P_- are the electric dipole moments corresponding to each of circularly polarized lights. This causes the Faraday rotation in the infrared region for magnetic garnets containing Co^{3+} on the tetrahedral sites.

It is seen in Fig.1 that this Faraday rotation can be decomposed into three Faraday rotations which have different transition strength P_i^2 and the splitting width Δ_i for each pair of φ_i and φ_+ excited states. (In this figure, the ground state and the excited states are denoted as $\varphi_0, \varphi_1, \varphi_2, \varphi_3$ and φ_+ , respectively.) The transition strength P_i^2 is defined using the above symbols as

$$P_i^2 = | \langle \varphi_i | P_- | \varphi_+ \rangle |^2 \quad (i=1,2,3,+), \quad (1)$$

then the relation that $P_+^2 = P_1^2 + P_2^2 + P_3^2$ must be satisfied, and the splitting width Δ_i is defined as $E(\varphi_+) - E(\varphi_i)$ where E is the energy of the state.

Each Faraday rotation θ_i originating from each transition in Fig.1 can be written [14] as

$$\theta_i \propto P_i^2 \Delta_i \frac{\omega}{\omega_0} \frac{(\omega_0 - \omega)^2 - \gamma_0^2}{\{(\omega_{0i} - \omega)^2 + \gamma_{0i}^2\}^2} \quad (2).$$

Fig.1 Energy level diagram of Co^{3+} on the tetrahedral site of magnetic garnets.

Fig.2 Splitting of 5T_2 energy level (set to zero) due to S_4 field. a' is a parameter proportional to S_4 .

Here, ω is the frequency, ω_{0_i} the transition frequency defined as $(E(\varphi_+) + E(\varphi_-))/2$, and γ_{0_i} the width of the absorption.

We note that the sign of the Faraday rotations θ_1 and θ_2 is negative, whereas that of θ_3 is positive because the sign of Δ_1 and Δ_2 is negative though that of Δ_3 is positive (see Fig.1 and eq.(2)). This fact suggests that though each θ_i has the absorption-type shape, the total FRS may have the dispersion-type shape similar to the experimentally observed one in Co^{3+} doped magnetic garnets.

Fig.3
(a) Effects of S_4 on the centers of the absorption frequencies ω_{0_i} of excited three pair levels in Fig.1.
(b) Effects of S_4 on the product of the transition strength P_i^2 and the splitting width Δ_i .

4.2 Effects of Low Symmetry Field S_4 on FRS

In Fig.3(a) and (b), ω_{0_i} and $|P_i^2 \Delta_i|$ are represented as a function of a' (magnitude of the S_4 field) for $\lambda = -110 \text{ cm}^{-1}$. $|P_i^2 \Delta_i|$ is a factor proportional to the magnitude of each FRS (see eq.(2)). ω_{0_i} was calculated by the energy levels shown in Fig.2.

From these figures 3(a) and (b), it can be seen that the low symmetry field S_4 plays an important role in determining the shape of FRS as follows;

- 1) when a' exceeds about 1000 cm^{-1} , the shape of the total FRS may change from the absorptive type to the dispersive type, because the Faraday rotation component arises from the transition (3) in Fig.1, having plus sign, is very small against the other transitions (1) and (2) having minus sign when a' is small (less than 1000 cm^{-1}) as shown in Fig.3(b);
- 2) with increasing a' , ω_{0_i} is separated gradually into two groups as shown in Fig.3(a). This also affects the shape of the total FRS; the width of the total FRS may become broader as known in the case of tetrahedrally coordinated Co^{2+} [4].

4.3 Effects of the Sign of λ on FRS

The above results hold only for the negative λ . If $\lambda > 0$, the three FRS components have the same sign (positive) because the order of the energy levels split from the 5T_2 parent state due to S.O. is reversed though the order of split levels due to S_4 field remains as they were. Therefore, the shape of the total FRS, in this case, keeps the absorptive type even if a' changes. The similar situation arises in the case of Co^{2+} on the tetrahedral site [4].

5. COMPARISON WITH EXPERIMENTAL RESULT

5.1 Experimental Result

The symbols in Fig.4 indicate the experimental results of $(\text{Ygd})_3(\text{Co}_x\text{Fe}_{5-x})\text{O}_{12}$ subtracted the FRS of the $(\text{Ygd})_3\text{Fe}_5\text{O}_{12}$ in order to get the pure effect of Co^{3+} . (The chemical composition of these samples were described in Sec.2). The amplitude of FRS at about $1.5 \mu\text{m}$ increases proportionally to the concentration of Co ions. The large anomaly of FRS occurs mostly in the infrared region and the shape of FRS is dispersive type; these results are in accordance with the results of GdIG single crystals containing Co^{3+} ion [1].

Judging from the fact that no large rotational anomaly can be seen at about $0.7 \mu\text{m}$, which is characteristic of the FRS of tetrahedral coordinated Co^{2+} [1]-[7], we attributed the large FRS in Fig.4 mainly to Co^{3+} ions on the tetrahedral sites in the magnetic garnets.

On the other hand, at $\lambda \lesssim 1.2 \mu\text{m}$ FRS decreases with increasing contents of Co ions. This may originate from the Pb^{2+} ions [1].

5.2 Comparison of Calculated FRS with Experimentally Obtained FRS

Solid lines in Fig.4 indicate the calculated FRS by the procedure described in the previous section. It is seen in Fig.4 that the experimental results are well reproduced qualitatively except the region $\lambda \lesssim 1.2 \mu\text{m}$. The parameters used in calculating FRS of $x=0.07$ in Fig.4 are listed in Table 1. The other FRS in Fig.4 were also well explained by the same parameters except the proportional constant of eq.(2) (denoted as C in Table 1); C was almost proportional to the Co contents.

One reason that the experimental FRS have larger negative values than the calculated one at $\lambda \lesssim 1.2 \mu\text{m}$ is probably the effect of Pb^{2+} as mentioned in the previous sub-section.

6. CONCLUSION

The experimentally obtained FRS in magnetic garnet films $(\text{Ygd})_3(\text{Co}_x\text{Fe}_{5-x})\text{O}_{12}$ grown by LPE method were well understood qualitatively in terms of the crystal field transition $^5E \rightarrow ^5T_2$ with the spin-orbit interaction and the tetragonally distorted crystal field (S_4). The dispersion-type shape of the FRS of the tetragonally coordinated Co^{3+} was explained by the negative λ and the fairly

Fig.4 Calculated FRS in the infrared region for tetrahedral coordinated Co^{3+} (solid lines). The symbols denote experimental data on $(\text{YGd})_3(\text{Co}_x\text{Fe}_{5-x})\text{O}_{12}$ thin films grown by an LPE method. They are subtracted values by $(\text{YGd})_3\text{Fe}_5\text{O}_{12}$.

TABLE 1. Parameters used in calculation of FRS ($x=0.07$) in Fig.4. Parameters for the three components of FRS (1), (2) and (3) are listed. ($a' = 4500\text{cm}^{-1}$)

	P_i^2	$\Delta_i (\text{cm}^{-1})$	$\omega_{0i} (\text{cm}^{-1})$	$\gamma_{0i} (\text{cm}^{-1})$	C_i
(1)	0.0540	- 450	7926	1250	-5800
(2)	0.2291	- 234	7819	1400	-5800
(3)	0.0502	2268	6576	1600	-5800

large low symmetry field (about $a' = 4500\text{cm}^{-1}$). From the calculations such as energy levels split from the parent $^5\text{T}_2$ state and the FRS for the tetrahedrally coordinated Co^{3+} , it was found that the shape of FRS turns into the absorption type if λ is positive or a' is less than about 1000cm^{-1} .

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