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Optical Absorption Spectra in Cobalt-Substituted Epitaxial Magnetic Garnet Films Measured with Photothermal Deflection Spectroscopy

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Optical absorption spectra were measured at room temperature by means of photothermal deflection spectroscopy (PDS) in Co^{2+}-substituted or Co^{3+}-substituted magnetic garnet films prepared by liquid phase epitaxial technique. We compared the PDS results with theoretical absorption spectra calculated for Co^{2+} and Co^{3+} ions using the ligand-field theory. A satisfactory agreement has been obtained between the calculation and the observation especially for the case of Co^{2+}-substituted films.

KEYWORDS: optical absorption spectrum, photothermal deflection spectroscopy, transmission spectroscopy, cobalt-substituted magnetic garnet films, ligand-field transition, calculation of absorption spectrum

Recently, cobalt-substituted magnetic garnet films are intensively studied as materials for magneto-optical devices[1-4] since they are known to show a large Faraday rotation in the infrared wavelength region. Both Co^{2+} and Co^{3+} ions have been known to introduce absorption in the so-called window region of the host crystal. However, there have been no reports on the details of the absorption structures in cobalt-substituted magnetic garnet films. Absorption spectrum associated with Co^{2+} and Co^{3+} in tetrahedral site of the garnet structure is only available for cobalt diluted in a nonmagnetic bulk crystal.[5] This is due to the difficulty in accurate determination of small absorption coefficient in thin films by the conventional transmission spectroscopy. It is for such a case, PDS (photothermal deflection spectroscopy) technique can show its ability. This technique has proved to be a sensitive tool for evaluating an entirely low optical absorption bands such as those introduced by defect states in a-Si:H films.[6,7]

In this study, we evaluated the optical absorption spectra in Co^{2+}-substituted, Co^{3+}-substituted and unsubstituted YIG films in infrared region using a PDS apparatus constructed for characterization of photo-CVD a-Si:H films[8] and compared those experimental results with theoretical analyses.

The samples were grown on (1 1 1) plane of GGG ($Gd_3Ga_5O_{12}$) substrate by LPE (liquid phase epitaxy) method. Table I shows a summary of film parameters of these films. Cobalt ions substituting the tetrahedral iron are supposed to become trivalent, while they are assumed to become divalent if germanium ions are doped together as compensator. To obtain a better lattice matching substitution of yttrium by a suitable amount of gadolinium was also carried out.

The principle of the PDS measurement is as follows: A monochromatic light absorbed by a sample causes a temperature gradient in the medium adjacent to the sample surface by the heat flow brought by a non-radiative relaxation process of the excited states. A He-Ne laser beam grazing the sample surface is deflected by the variation of the refractive index. The deflected beam is detected by a position sensitive photodiode, the output of which is amplified by a lock-in amplifier.

The exciting source for the PDS measurement was a 150 W xenon arc lamp chopped at 11 Hz. The light was lead to an entrance slit of a JASCO CT25A monochromator. The exit monochromatic light was focused to a width of 2 mm by a concave mirror on the surface of a sample immersed in a deflecting medium. We used CCl_4 as the deflecting medium which has a temperature coefficient of refractive index thousand times larger than air. In order to extend the length of interaction between the exciting beam and the probe beam, we laid the monochromator vertical, so that the image of the slit can be turned sideways.

The PDS signal was corrected for the spectral response using the incident light intensity monitored simultaneously with a thermopile detector. All measurements were carried out at room temperature.

It has been reported that for the low absorption wavelength region the optical absorption coefficient α is given by (Jackson *et al.*[6])

$$\alpha = -(1/d)\ln(1 - S/S_{sat}), \quad (1)$$

where S is the deflection signal, d the film thickness, S_{sat} the saturated PDS signal. We estimated the absorption coefficient from this equation.

Table I. Thickness and composition of magnetic garnet films $Y_3(Fe_{5-x-y}Co_xGe_y)O_{12}$ used in the present experiment.

Sample	Film thickness (μm)	Film composition x	y
unsubstituted	9.85	0	0
Co^{3+}-substituted	6.42	0.2	0.2
Co^{2+}-substituted	10.12	0.07	0

A conventional transmission spectrum was measured by means of a single beam method with a halogen-tungsten lamp as a light source, the same monochromator as used for the PDS measurement, a Si or Ge photocell as a detector and a lock-in detection system. The transmittance T was obtained by taking the ratio of transmitted lights for the sample and the blank. Absorption coefficient is calculated by the following formula,

$$\alpha(\omega) = -\ln T(\omega)/d, \tag{2}$$

where d is the sample thickness. Here we paid no consideration of the surface reflection and the mutiple reflection effect.

Absorption spectra obtained by both measurements are plotted together in Figs. 1 and 2. Figure 1 illustrates the absorption spectra in the unsubstituted YIG film, with absorption coefficient scaled in logarithmic way. The similar shape of absorption band is observed in both spectra. However, the absorption coefficient at the foot of the absorption band evaluated by the transmission spectroscopy appears about one order of magnitude greater than one deduced from PDS. This is caused by the neglect of the correction for surface reflection. We tried to make a correction for the effect using the reported value of refractive index. However, such correction often gave improper value of absorption coefficient due to unreliable evaluation of refractive index. On the contrary, the PDS signal is proportional to the absorbed light itself and suffers less influence of surface reflection except that the PDS signal intensity is reduced. Therefore, we regard the spectra obtained by PDS as more reliable for YIG films. For unsubstituted YIG film it is important to evaluate the absorption coefficient at the window wavelength region for the characterization of the films. The value is found to be about 10 cm^{-1}, which is reasonable for film samples, although it is much larger than that observed in bulk crystals.

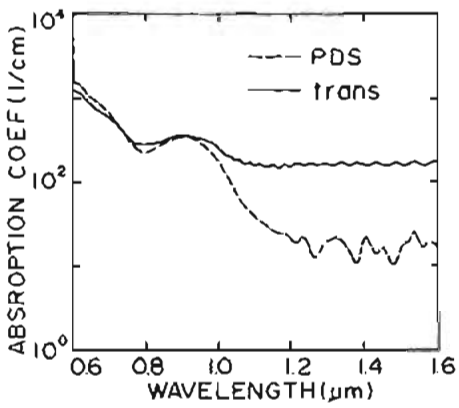

Fig. 1. The optical absorption spectra in an undoped YIG film, measured by means of PDS (dashed curve) and conventional transmission spectroscopy (solid curve). Note that the vertical axis is scaled in logarithmic way.

Figure 2 shows absorption spectra in Co^{2+}-substituted and Co^{3+}-substituted films. Absorption bands are observed in the window region of the host crystals. The energy positions and line shapes are very close to those reported for Co^{2+} and Co^{3+} in YAG.[5] In addition, the absorption structures appear just at the energy positions where the structures in Faraday and Cotton-Mouton spectra were observed.[9] In order to know the net contribution of cobalt ions, we substracted the absorption of the unsubstituted YIG film from the observed absorption spectra of cobalt-substituted films. The results are shown by dashed lines in Figs. 3(a) and 3(b).

Taking into account the absorption in YAG:Co,[5] observed absorption bands can be assigned to the ligand-field transitions, $^4A_2 \rightarrow {}^4T_1(^4P)$ for Co^{2+} and $^5E \rightarrow {}^5T_2$ for Co^{3+}. In the previous studies we have successfully explained the spectra of Faraday effect and Cotton-Mouton effect in cobalt-substituted magnetic garnets in terms of these ligand-field transitions considering the molecular field and the spin-orbit interaction.[4,9]

We calculated the absorption spectra based on the same theoretical procedure as in the analysis of the magneto-optical spectra, using the same fitting parameters adopted in the previous study.

Absorption spectra $\alpha(\omega)$ of Co ion in YIG can be calculated by the following formula:

$$\alpha(\omega) = C \sum_{i=1}^{5} \frac{\omega_i \omega^2 P_i^2 \gamma_i}{(\omega_i^2 - \omega^2 + \gamma_i^2)^2 + (2\omega\gamma_i)^2}. \tag{3}$$

Here, C is a constant, P_i^2, ω_i and γ_i are a transition

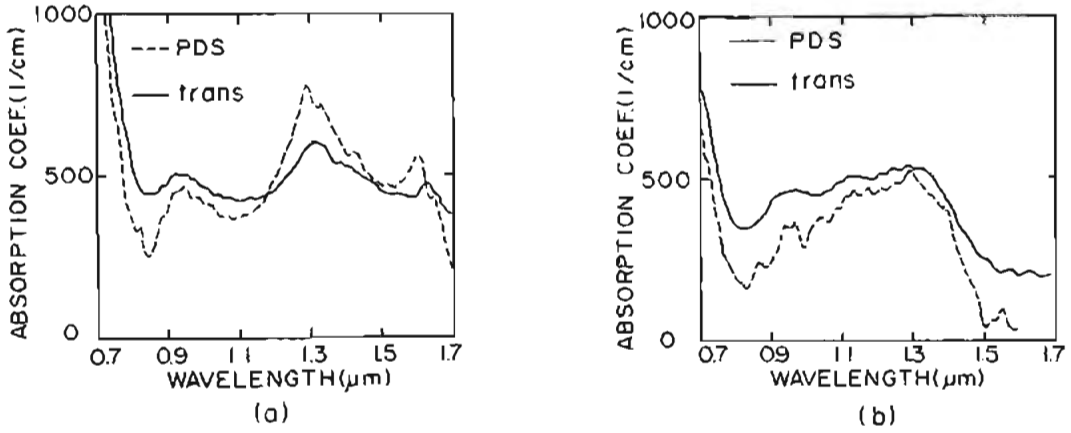

Fig. 2. The optical absorption spectra in (a) Co^{2+}-substituted and (b) Co^{3+}-substituted YIG films, measured by means of PDS (dashed curve) and conventional transmission spectroscopy (solid curve).

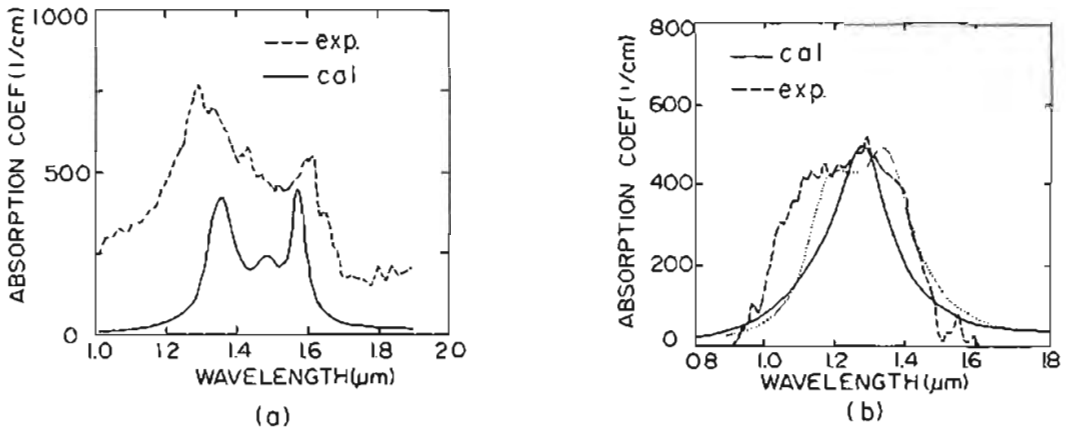

Fig. 3. Comparison between the calculated spectrum (solid curve) and the experimental one (dashed curve) in (a) Co^{2+}-substituted and (b) Co^{3+}-substituted YIG films. The dotted line in (b) illustrates the calculated curve with the spin-orbit parameter $-220\,cm^{-1}$ and the line-width $500\,cm^{-1}$.

Table II. Parameters used for the calculation of absorption spectrum: P_i is a transition strength, ω_i a transition energy and γ_i a damping constant in the i-th transition.

(a) Co^{2+}-substituted films
Transition: $^4A_2(J=3/2) \rightarrow {}^4T_1(J'=5/2, 3/2, 1/2)$

i	J'	ω_i (cm^{-1})	P_i^2	γ_i (cm^{-1})
1	5/2	7382.5	11/20	250
2	3/2	6745	1/5	200
3	1/2	6362.5	1/4	100

(b) Co^{3+}-substituted films.
Transition: $^5E \rightarrow {}^5T_2(J'=1, 2, 3)$

i	J'	ω_i (cm^{-1})	P_i^2	γ_i (cm^{-1})
1	1	8330	3/10	1200
2	2	8110	1/6	1000
3	3	7780	8/15	500

strength, a transition energy and a damping constant for i-th transition, respectively. Table II shows the parameters for eq. (3) which have been determined for Co^{2+} and Co^{3+} to explain spectra of Faraday rotation and Cotton-Mouton effect. Here, the spin-orbit parameters are taken as $255\,cm^{-1}$ and $-110\,cm^{-1}$ for Co^{2+} and Co^{3+}, respectively. In Fig. 3 the calculated spectra are illustrated by solid curves for (a) Co^{2+}-substituted and (b) Co^{3+}-substituted films. Experimental spectra are plotted by dashed lines. In Co^{2+}-substituted film, the agreement between the calculated and experimental spectrum is satisfactory. Thus we got a consistent theoretical explanation for absorption, Faraday and Cotton-Mouton spectra in Co^{2+}-substituted YIG.

As regards the Co^{3+}-substituted film, the agreement between dashed and solid curves was rather poor. We calculated the absorption spectrum taking somewhat different values of parameter from those listed in Table II: we adopted $-220\,cm^{-1}$ for a spin-orbit parameter and $500\,cm^{-1}$ for each line-width. As plotted by a dotted line in Fig. 3(b) the calculated spectrum showed a much improved agreement. However, these parameters could not provide a good fit to the magneto-optical spectra. This may be due to neglect of a low symmetry crystal field, which has been pointed out to be essential for Co^{3+} in T_d symmetry.[10]

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