MAGNETO-MODULATION REFLECTIVITY SPECTRA OF
Bi$_x$Gd$_{3-x}$Fe$_5$O$_{12}$ BETWEEN 4 AND 20 eV

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ABSTRACT

With the synchrotron radiation, a transverse magneto-optical effect in bismuth substituted gadolinium iron garnets was measured by a reflection method. Differences of resonance energy shifts between the lights polarized parallel and perpendicularly to the direction of magnetization of the material were determined on reflectivity peaks in the near ultraviolet and a peak at the photon energy of about 18 eV. This reflectivity peak at about 18 eV was assigned to the 3d-4p transitions of iron ions in the octahedral and tetrahedral sites. A mechanism of the transverse magneto-optical effect in the 3d-4p transitions is discussed.

1. INTRODUCTION

A typical magneto-optical effect other than the Faraday rotation is the Cotton-Mouton effect which is a transverse magnetic field effect. The transverse magnetic field effect is proportional to the magnetic field square, while the Faraday rotation is linear.

We investigated a transverse magneto-optical effect in the vacuum ultraviolet region using the synchrotron radiation from a storage ring. The reason of our investigation is that the synchrotron radiation is linearly polarized to a good extent,[1] and at present, no useful polarizer nor quarter wavelength plate is available in the vacuum ultraviolet region.[2]

The transverse magneto-optical effect is expected to be small, and bismuth substituted gadolinium iron garnet, Bi$_x$Gd$_{3-x}$Fe$_5$O$_{12}$, which is ferrimagnetic and is known to have a very large Faraday rotation in the visible and near infrared region,[3] was chosen as the material to be investigated. The Faraday rotation of this material has been known to originate from optical transitions located in the near ultraviolet.[4] The optical transitions have been assigned to electron transfers from oxygen ions to iron ions, and not to the intra-d crystal field transitions of iron ions. At the photon energy about 18 eV, the 3d-4p transitions of iron ions have been known to be also located.[5]

In the vacuum ultraviolet region, almost all materials are absorbing, and the transverse magneto-optical effect is measured by a reflection method. The principle of measurement is as follows. A linearly polarized light was made incident on a sample set in a rotating external magnetic field. The direction of polarization was kept fixed while the external field caused to rotate the direction of magnetization of the sample in a plane parallel to the reflecting surface. Difference of reflectivities between lights polarized parallel and perpendicularly to the direction of magnetization was measured.

2. EXPERIMENTAL

We adopted a modulation technique to measure the difference of reflectivities. Fig. 1 shows the experimental arrangement. The synchrotron radiation from a 300 MeV storage ring of Synchrotron Radiation Laboratory, Institute for Solid State Physics, The University of Tokyo was made monochromatic with a 1 m Seya-Namioka grating monochromator.[6],[7] The band pass was approximately 1.6 nm. The rotating magnetic field was generated with two identical electromagnets of small size arranged perpendicularly and fed with currents of 90° in phase difference with each other. The sample space between two sets of pole pieces was 8.0 x 8.0 mm. The frequency of rotation was about 173 Hz.

The angle of incidence was 180°. The light reflected from the sample was detected by a photomultiplier coated with sodium salicylate. With a feedback loop of controlling the sensitivity of photomultiplier, the DC component of output which was an averaged reflected light intensity was kept constant. The difference of reflected light intensity which was the AC component of output was detected synchronously with doubled
frequency of the rotation of external field by a lock-in amplifier. The AC component was divided by the DC component, and fractional reflectivity change \( \Delta R/R \) was determined.

Measurements were performed at room temperature which is above the compensation temperature of \( \text{Bi}_1\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12} \), and contributions to the total magnetization from iron ions in the tetrahedral site are larger than and in the opposite direction to those from iron ions in the octahedral site.[8]

In the following experiment, the reflecting surface was the \((-110)\) face of the single crystalline \( \text{Bi}_{1.1}\text{Gd}_{1.9}\text{Fe}_5\text{O}_{12} \), and the external magnetic field rotates in this plane. The axis of easy magnetization of the material was in the \([110]\) direction, in which the polarization direction of incident light was fixed.

### 3. RESULTS

In Fig. 2, a fractional reflectivity change \( \Delta R/R \) at 2.6 eV is plotted against the total magnetization of a sample. The signal \( \Delta R/R \) was measured as a function of the strength of rotating external field, the total magnetization as a function of field strength was separately determined and the field strength was eliminated. The total magnetization was determined from measurements of magnetic moment with integrating an induced electromotive force in a coil wound around the sample with an auxiliary circuit which compensates a flux change due to the rotation of external field.

From this magnetic moment measurement, the saturation magnetization of the sample is found to be achieved at the external field of about 250 Oe. Fig. 2 shows that the signal \( \Delta R/R \) is approximately proportional to the square of magnetization. Taking into account the fact that the bulk magnetization determined from the magnetic moment measurement is not the same as the magnetization at the surface seen by the light, it is deduced that the fractional reflectivity change measured in the present experiment is the transverse magneto-optical effect.

In Fig. 3 a), a spectrum of fractional reflectivity change is shown. In Fig. 3 b), a reflectivity spectrum is shown for comparison. A large reflectivity peak with several structures is located at about 4 eV. These structures are the electron transfers from oxygen ions to iron ions. On the high energy side of this peak, superposed are transitions of Bi and Gd ions. These assignments are deduced from comparisons with reflectivity spectra of a group of iron garnets with different constituents such as \( \text{Bi}_{0.5}\text{Y}_{2.5}\text{Fe}_5\text{O}_{12} \).

At about 18 eV, located is a peak which is the 3d-4p transitions of iron ions. The transition energies have been considered to be shifted down from those of the free ion spectrum of Fe IV, because of overlap between orbits of the iron ions and those of ligand oxygen ions.[9] The reflectivity measurement was extended up to about 30 eV, and no distinct reflectivity structure was found, especially at about 23 eV where the 3d-4p transitions of the free ion spectrum of Fe IV are located.

Each structure in the spectrum of fractional reflectivity change is of the dispersion type and has a corresponding structure in the reflectivity spectrum. The structure of the dispersion type indicates that the resonance energy of the light polarized parallel to the magnetization shifts from that of the light polarized perpendicularly.

On an assumption of rigid shift, a reflectivity spectrum, \( R \), near a resonance \( E_0 \) is expressed by a function of energy difference from the resonance \( R(E - E_0) \), where \( E \) is the photon energy. When the resonance of the light polarized parallel shifts from that of the light polarized perpendicularly by \( \Delta E_0 \), the fractional reflectivity change, \( \Delta R/R \), is the following,
provided that $\Delta E_0$ is small.

The fractional reflectivity change shown in Fig. 3 a) is compared with the logarithmic energy derivative of reflectivity $=-1/R(\text{d}R/\text{d}E)$ obtained from Fig. 3 b), and the shift of resonance energy $\Delta E_0$ of each structure is determined. Results are shown in Table I. Every shift is in the order of $10^{-4}$ eV.

A special attention is paid to the peak at about 18 eV. A detailed measurement of reflectivity spectrum reveals four small structures indicated by arrows in Fig. 3 b) and denoted by A to D in the order of increasing energy. The energy differences $E_D - E_A = 1.6$ eV, and $E_C - E_B = 0.7$ eV, coincide with the $10D_q$ values reported on Y$_3$Fe$_5$O$_{12}$ of iron ions in octahedral and tetrahedral sites, respectively.[10], [11] We, therefore, assigned A and D peaks to transitions from $e_g$ and $t_2g$ orbits to the 4p orbits of iron ions in the octahedral site, and B and C peaks to transitions from $e$ and $t_2$ orbits of iron ions in the tetrahedral site.

Table I. Energy shift

<table>
<thead>
<tr>
<th>Location of Structure</th>
<th>Energy Shift $\Delta E_0$ ($\times 10^{-4}$ eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>9.0</td>
</tr>
<tr>
<td>4.5</td>
<td>10.6</td>
</tr>
<tr>
<td>5.6</td>
<td>6.0</td>
</tr>
<tr>
<td>6.3</td>
<td>7.3</td>
</tr>
<tr>
<td>7.6</td>
<td>4.6</td>
</tr>
<tr>
<td>16.8</td>
<td>5.3</td>
</tr>
<tr>
<td>18.4</td>
<td>4.0</td>
</tr>
</tbody>
</table>

where the 4p orbits are denoted as $t_1$. The fractional reflectivity change is large for the transitions A and D, but signs are different.

4. DISCUSSION

Microscopic mechanisms of the Faraday rotation in magnetic materials have been identified with spin conserving transitions from a spin parallel state to an excited state in which a spin orbit interaction is present. For the transverse magneto-optical effect, the presence of a spin dependent interaction with other states such as an off diagonal spin orbit interaction is necessary.

A possible mechanism for the transition from the $^6A_1$ to $^6T_1$ states is illustrated in Fig. 4 in which an off diagonal spin orbit interaction with the $^4T_1$ state is taken into account. The $^4T_1$ state is assumed to lie above the $^6T_1$ state by an energy $\Delta$. The spin orbit splitting parameters in the $^6T_1$ and $^4T_1$ states are respectively denoted as $\lambda_6$ and $\lambda_4$, and each multiplet splits into three levels which are described by an effective total angular momentum $J$. The off diagonal spin orbit interaction parameters are denoted as $\lambda_{J}'s$ ($J = 5/2, 3/2$).

Owing to a mixing of the $^4T_1$ state which is a forbidden state, relative transition probabilities from the spin parallel state $^6A_1$ ($S = 5/2, M_S = 5/2$) decrease

$$\tan(2\theta_5/2) = (2\lambda_4/2)/(\Delta + 3\lambda_4/2 + \lambda_6), \quad \tan(2\theta_3/2) = (2\lambda_3/2)/(\Delta - \lambda_4 + 7\lambda_6/2).$$

In the figure, $\pi$ is the transition due to the light polarized parallel to the spin, and $\alpha$ and $\gamma$ to the lights which excite angular momentum antiparallel and parallel to the spin, i.e. to the left and right circularly polarized lights.

The average energies weighted by the transition probabilities are the transition energies of those polarized lights, $\langle E(\pi) \rangle$, $\langle E(\alpha) \rangle$, and $\langle E(\gamma) \rangle$.

$$\langle E(\alpha) \rangle = E_0 - (1/2)\Delta + (5/2)\lambda_6,$$
$$\langle E(\pi) \rangle = E_0 - (1/2)\Delta - (5/7)E(4T_1, 5/2)\sin^2(\theta_5/2),$$
$$\langle E(\gamma) \rangle = E_0 - (1/2)\Delta - (5/2)\lambda_6 - (2/7)E(4T_1, 5/2)\sin^2(\theta_5/2) - (2/3)E(4T_1, 3/2)\sin^2(\theta_3/2).$$

The origin of Faraday rotation is the energy difference, $\langle E(\alpha) \rangle - \langle E(\gamma) \rangle$, and when the spin orbit interaction in the $^6T_1$ state is not zero, the Faraday rotation occurs irrespective of the presence.
of off diagonal spin orbit interaction. On the other hand, the transverse magneto-optical effect is determined by the shift \( \Delta \delta_0 \),

\[
\Delta \delta_0 = \langle (1/2)E(C_+) + E(C_-) - E(\pi) \rangle,
\]

and it is not brought about unless the off diagonal spin orbit interaction is present.

In eq. (3), \( E(4T_1,J) \) is the energy of the state with which the \( 6T_1 \) state couples through the off diagonal spin orbit interaction and \( \sin^2(\pi J) \) is in the order of \( (\lambda_0)^2/(E(4T_1,J) - E(6T_1,J))^2 \), the square of the off diagonal spin orbit interaction constant divided by the energy difference between the coupled states.

When the \( 4T_1 \) state is taken to be of the same electron configuration as the \( 6T_1 \) state, and the free ion values of Fe IV \[12\] are used, eq. (4) gives the correct order of magnitude of the present experimental values for the 3d-4p transitions at about 18 eV. It is concluded, therefore, that an off diagonal spin orbit interaction with other state is a possible mechanism of the transverse magneto-optical effect in magnetic materials.

It should be noted that an effect of the same magnitude and of the reversed sign appears in the counter state with which the state being observed couples through off diagonal interactions. Furthermore, when the counter state is not resolved from the state being observed as a result of such effects as that of lattice vibrations, the transverse magneto-optical effect disappears. Those are features of the mechanism due to off diagonal interactions with other states. Many off diagonal spin orbit interactions with states other than the \( 4T_1 \) are actually present. When one takes into account all of them, the situation is described by a \( S^2 \) term in the effective Hamiltonian usually used in the ESR studies.

The free ion values give the transverse magneto-optical effect which is different between the excitation of the \( t_2 \) orbits and that of the \( e \) orbits, but no difference between the excitation of iron ions in the octahedral site and that of iron ions in the tetrahedral site. In order to explain the difference between the octahedral and tetrahedral sites, one should take into account the ligand oxygen orbits which affects the spin orbit interaction constant of the \( t_2 \) orbits differently for iron ions in different sites.

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REFERENCES