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# A theoretical investigation on the strong magneto-optical enhancement in Ce-substituted yttrium iron garnet

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**Abstract.** Calculations of the Faraday rotation and ellipticity spectra at photon energies between 0.98 and 3.50 eV (wavelengths between 1260 and 360 nm) resulting from Ce ions in the Ce-substituted yttrium iron garnets based on the quantum theory are presented. The Faraday effect contributed by the Ce ions is caused mainly by the intra-ionic electrical dipole transitions between the 4f and 5d configurations. The crystal field (CF) and the superexchange interaction are two crucial factors in determining the Faraday effect contributed by the Ce sublattice. The energy differences between the lowest and the second CF-split 5d levels and the lowest CF-split 4f level are 1.36 eV and 3.10 eV, respectively. Therefore there are anomalous rotatory dispersions at about 1.36 eV and 3.10 eV. The difference between the transition intensities for the right- and left-handed circularly polarized light between the lowest CF-split 5d level and the ground state is negative, while the corresponding value for the transition between the second CF-split 5d level and the ground state is positive. So the Faraday rotation is positive over the whole photon energy region between 1.36 and 3.10 eV and is negative outside this region. The calculated spectra are in good agreement with experiment.

## 1. Introduction

Many experimental investigations on the magneto-optic (MO) effect and the magnetic properties of rare-earth (RE)-substituted iron garnets have been carried out. Recently it has been found that Ce-substituted yttrium iron garnet (Ce:YIG) has a very large Faraday rotation (FR) in the visible and near-infrared regions (Leycuras *et al* 1985, Gomi *et al* 1988, 1990, 1991, Kucera *et al* 1989). The factor per $Ce^{3+}$ ion is $2 \times 10^4$ deg cm$^{-1}$ at a wavelength of 633 nm and $-1.3 \times 10^4$ deg cm$^{-1}$ at 1150 nm. This rotation is a factor of 6 larger than that found for $Bi^{3+}$ ions, which gives the best MO enhancement found in the past 20 years. The high specific efficiency of the $Ce^{3+}$ ions in YIG as Faraday rotators allows low RE dopant concentration, resulting in magnetic properties not very different from those of pure YIG, and provides an intense FR. Thus Ce:YIG film is a very promising MO material. It is found that the Ce substitution prominently enhances the Faraday effect not only in the infrared region at $h\nu = 1.4$ eV, but also in the ultraviolet region at $h\nu = 3.1$ eV. Owing to the resonance dispersion effect, the FR varies rapidly, as the frequency is swept over the

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1.4 eV region and the 3.1 eV region, and this is accompanied by a large Faraday ellipticity (Kucera *et al* 1989, Gomi *et al* 1991). However, the FR in Pr:YIG and other RE-substituted YIGs have the same sign at 633 and 1150 nm wavelengths, and the magnitude is much less than in Ce:YIG (Leycuras *et al* 1985, Gomi *et al* 1990, 1991, Guillot *et al* 1990). Therefore it is of scientific and technical significance to carry out a theoretical study on the MO and the magnetic behaviour of the RE-substituted iron garnets. However, to our knowledge, there is still a lack of theoretical study on the MO and the magnetic behaviour of RE:YIG based on the quantum theory. In this paper, the theoretical calculations of the spontaneous electric FR and ellipticity caused by the Ce sublattice in Ce-substituted iron garnets in the wavelength region from 360 to 1260 nm based on the quantum theory are presented.

In one of our previous papers (Xu and Duan 1992), the MO and the magnetic behaviour of paramagnetic Ce, Pr and Nd trifluorides were well explained on the basis of the quantum theory. It is shown that the MO effect of these trifluorides in the visible region is mainly due to the intra-ionic electric dipole (ED) transitions between $4f^n$ and $4f^{n-1}$ 5d configurations. The crystal field (CF) acting on the RE ions has a great effect on the MO effect. The MO behaviours of Kramers and non-Kramers ions are different. In this paper, the model and approach used there are extended to study the MO behaviour of the Ce-substituted garnets.

Both the Ce and the iron sublattices provide contributions to the FR in the Ce-substituted iron garnets. The total contribution of two iron sublattices is well represented by the YIG FR and it is much less than the contribution of the Ce sublattice. It has been shown that the single-ion model is valid for the FR caused by the RE sublattice in RE:YIG when the temperature is not very low and the concentration of RE ions is not very high (Gomi *et al* 1990, 1991, Guillot *et al* 1990). Furthermore, the FR due to the RE sublattice in Ce:YIG and Pr:YIG is strongly dependent on the wavelength. Therefore we think that it is caused mainly by the intra-ionic ED transitions between the $4f^n$ and $4f^{n-1}$ 5d configurations of the RE ions which are split by the CF and the superexchange interaction.

## 2. Theoretical calculation of Faraday rotation and ellipticity

The complex FR per unit length caused by the ED transition is (Crossley *et al* 1969)

$$\varphi = F_\theta + \mathrm{i}\psi = \tfrac{1}{9}(\pi\omega/c\bar{n})(\bar{n}^2+2)^2(\chi^- - \chi^+). \tag{1}$$

Here $F_\theta$ is the FR, $\psi$ is the Faraday ellipticity, $\omega$ is the angular frequency of the light wave, $c$ is the velocity of light in vacuum, $\bar{n}$ is the mean refractive index of the material, and $\chi^-$ and $\chi^+$ are the electric susceptibilities for right- and left-hand circularly polarized light. By inserting the quantum-mechanical expressions for AC susceptibility into equation (1), we obtain

$$F_\theta = \frac{N\pi(\bar{n}^2+2)^2}{9\bar{n}c\hbar}\sum_{n,g} A_{ng}\frac{\omega^2(\omega_{ng}^2-\omega^2-\Gamma_{ng}^2)}{(\omega_{ng}^2-\omega^2+\Gamma_{ng}^2)^2+4\omega^2\Gamma_{ng}^2}\rho_g \tag{2}$$

$$\psi = \frac{N\pi(\bar{n}^2+2)^2}{9\bar{n}c\hbar}\sum_{n,g} A_{ng}\frac{\omega\Gamma_{ng}(\omega_{ng}^2+\omega^2+\Gamma_{ng}^2)}{(\omega_{ng}^2-\omega^2+\Gamma_{ng}^2)^2+4\omega^2\Gamma_{ng}^2}\rho_g \tag{3}$$

for each type of ion present in the material, where

$$A_{ng} = |\langle n|V_-|g\rangle|^2 - |\langle n|V_+|g\rangle|^2. \tag{4}$$

**Table 1.** The values of the parameters of CF acting upon the $Ce^{3+}$ ions.

| | $A_{20}$ (cm$^{-1}$) | $A_{2\pm2}$ (cm$^{-1}$) | $A_{40}$ (cm$^{-1}$) | $A_{4\pm2}$ (cm$^{-1}$) | $A_{4\pm4}$ (cm$^{-1}$) | $A_{60}$ (cm$^{-1}$) | $A_{6\pm2}$ (cm$^{-1}$) | $A_{6\pm4}$ (cm$^{-1}$) | $A_{6\pm6}$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 4f | −1363 | 340 | −9889 | 588 | 1520 | 4288 | −310 | 1120 | 153 |
| 5d | −4200 | 1500 | −166 900 | 9250 | 62 730 | | | | |

In equations (2)–(4), $N$ is the number of ions per unit volume. $\Gamma_{ng}$ is the half-width of resonance lines, $|g\rangle$ is a set of ground states with energy $E_g$, $|n\rangle$ are excited states with energy $E_n, \hbar\omega_{ng} = E_n - E_g$, and $V_\pm$ are the electric dipole moment operators for right- and left-handed circularly polarized light:

$$V_\pm = e(x \pm \mathrm{i}y). \tag{5}$$

$\rho_g$ is the occupation probability of the state $|g\rangle$ and is given by

$$\rho_g = \exp\left(-\frac{E_g}{kT}\right) \bigg/ \left[\sum_g \exp\left(-\frac{E_g}{kT}\right)\right] = \rho_0 \exp\left(-\frac{E_g}{kT}\right). \tag{6}$$

It is necessary to calculate the energy levels split by the CF and superexchange interaction and the corresponding wavefunctions. The Hamiltonian of a $Ce^{3+}$ ion in the crystal can be written as

$$H = H_0 + H_{\mathrm{so}} + H_{\mathrm{c}} + H_{\mathrm{ex}} \tag{7}$$

where

$$H_0 = -(\hbar^2/2m)\nabla^2 - Z^* e^2/4\pi\epsilon_0 r \tag{8}$$

$$H_{\mathrm{so}} = \xi(r)\boldsymbol{l} \cdot \boldsymbol{s} \tag{9}$$

$$H_{\mathrm{c}} = \sum_{\lambda,k} A_{\lambda k} Y_{\lambda k}(\theta, \varphi) \tag{10}$$

$$H_{\mathrm{ex}} = 2\mu_0\mu_{\mathrm{B}}\boldsymbol{H}_{\mathrm{m}} \cdot \boldsymbol{s}. \tag{11}$$

Here $r$ is the distance from the nuclear core of charge $|Z^* e|$ to the electron with mass $m$, charge $e$ and momentum $p$. $-\mathrm{i}\hbar\boldsymbol{\nabla}$ is the operator of the momentum $p$. The term $H_0$ contains the kinetic energy and the potential energy of the electrons in the field of the nuclear core. $H_{\mathrm{so}}$ represents the spin–orbit interaction. $\boldsymbol{l}$ is the orbital angular momentum operator, $\boldsymbol{s}$ is the spin angular momentum operator, $\xi(r)$ is the spin–orbit coupling parameter, $H_{\mathrm{c}}$ is the CF Hamiltonian, $H_{\mathrm{ex}}$ is the superexchange interaction upon the $Ce^{3+}$ ion and $H_{\mathrm{m}}$ is the molecular field.

Because the superexchange interaction is less than the spin–orbit interaction and the CF effect, we carried out the perturbation calculation in the following order of priorities: $H_{\mathrm{so}} + H_{\mathrm{o}}$ and $H_{\mathrm{ex}}$. The CF-split energy levels and the corresponding wavefunctions have been obtained by solving the following secular equation:

$$\| \langle \varphi_i | H_{\mathrm{so}} + H_{\mathrm{c}} | \varphi_j \rangle - E\delta_{ij} \| = 0. \tag{12}$$

In calculating the splitting of the 4f states, both $^2F_{5/2}$ and $^2F_{7/2}$ multiplets have been included. As for the 5d states, the $^2D_{3/2}$ and $^2D_{5/2}$ multiplets have been included.

The choice of the proper set of the parameters of the CF acting upon the $\mathrm{Ce}^{3+}$ ions is a crucial step. The values obtained with a point charge model are too small to obtain correct results. A similar situation was also found when studying the magnetic properties of the RE-substituted garnets. Nekvasil *et al* (1985) determined a set of parameters for the CF acting upon the $\mathrm{Sm}^{3+}$ ions in SmIG by fitting the experimental results about the magnetic phase transition in SmIG. It is expected that the parameters of the CF upon the RE ions in different RE:YIGs change gradually with the atomic number of the RE ions. So we determined the parameters of the CF upon the $\mathrm{Ce}^{3+}$ ions according to the values of the CF parameters obtained by Nekvasil *et al* for the $\mathrm{Sm}^{3+}$ ions in SmIG and the ratio of the values of $\langle r^2\rangle$, $\langle r^4\rangle$ and $\langle r^6\rangle$ of the RE ions and then made a small change to fit to the measured values of the FR. The non-zero parameters are shown in table 1. The values of $\xi$ for the 4f and 5d configurations and the difference between the mean energies of these two configurations have been taken from the paper by Starostin (1976). The energies of the CF-split levels are shown in table 2. Because the environment of the $\mathrm{Ce}^{3+}$ ions has $D_2$ symmetry, every energy level is doubly degenerate. The wavefunctions of the lowest three levels of the 4f configuration are given in table 3. The Zeeman splitting of the states of the 4f configuration caused by the superexchange interaction was obtained by solving the following secular equation:

$$\|\langle\psi_i|H_{\mathrm{so}}+H_{\mathrm{c}}+2\mu_0\mu_{\mathrm{B}}\boldsymbol{H}_{\mathrm{m}}\cdot\boldsymbol{s}|\psi_j\rangle-E\delta_{ij}\|=0. \qquad (13)$$

Because the superexchange interaction upon the $\mathrm{Ce}^{3+}$ ions is not very small compared with the energy differences between the lowest three CF levels, the admixing of these three levels by superexchange interaction is not negligible. Therefore the bras and kets in equation (13) include the six wavefunctions of these three levels. The matrix elements $\langle\psi_i|H_{\mathrm{so}}+H_{\mathrm{c}}|\psi_j\rangle\delta_{ij}$ in equation (13) are the energies of these levels. From table 2, it is seen that the energy differences between the higher CF levels of the 4f configuration and these three levels are large enough that the error caused by the neglecting of the higher levels is small. The effect of the exchange interaction on the splitting of 5d states has been neglected, because this leads to only a very small error (about 100 $\mathrm{cm}^{-1}$) of resonance energy $\hbar\omega_{ng}$. As mentioned above, the degenerate 4f levels are split into sublevels owing to the superexchange interaction. When a plane-polarized electromagnetic wave propagates through the crystal, the transition probabilities for the right- and left-handed circularly polarized light between these sublevels and the 5d levels are the same. Hence, there will be no Faraday effect if there is no superexchange interaction, but the Zeeman splitting makes the occupation probabilities of these sublevels different. This results in a Faraday effect.

**Table 2.** The values of the CF-split energy levels of the 4f and 5d configurations taking the average energy of the 4f shell as zero.

| | CF-split energy levels ($\mathrm{cm}^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| 4f | −2321 | −1655 | −1236 | 47.35 | 448.5 | 1574 | 3142 |
| 5d | 8670 | 22702 | 65065 | 73689 | 79148 | | |

The value of the molecular field $H_{\mathrm{m}}$ is determined by comparison with similar values for SmIG (White 1967) and TbIG (Guillot *et al* 1979) and by fitting the measured values of the FR. The value used is 40.6 MA $\mathrm{m}^{-1}$. In order to fit the measured values of the FR, the value of $\langle r\rangle_{4\mathrm{f}5\mathrm{d}}$ of the $\mathrm{Ce}^{3+}$ ion is taken to be 1.01 Å. It is larger than the value obtained

**Table 3.** The wavefunctions of the lowest three CF split levels of the 4f configuration. Here the representation $\vert J, J_z\rangle$ is used; so, for example, $\vert\frac{5}{2},\frac{3}{2}\rangle$ represents the following wavefunction: $\vert J=\frac{5}{2}, M_J=\frac{3}{2}\rangle$.

| Energy (cm$^{-1}$) | Wavefunction |
|---|---|
| −2321 | $-0.089\,13\vert\frac{5}{2},\frac{5}{2}\rangle + 0.9855\vert\frac{5}{2},\frac{1}{2}\rangle + 0.086\,34\vert\frac{5}{2},-\frac{3}{2}\rangle - 0.031\,95\vert\frac{7}{2},\frac{5}{2}\rangle + 0.096\,69\vert\frac{7}{2},\frac{1}{2}\rangle + 0.049\,36\vert\frac{7}{2},-\frac{3}{2}\rangle - 0.022\,21\vert\frac{7}{2},-\frac{7}{2}\rangle$ |
| −2321 | $0.086\,34\vert\frac{5}{2},\frac{3}{2}\rangle + 0.9855\vert\frac{5}{2},-\frac{1}{2}\rangle - 0.089\,13\vert\frac{5}{2},-\frac{5}{2}\rangle + 0.022\,21\vert\frac{7}{2},\frac{7}{2}\rangle - 0.049\,36\vert\frac{7}{2},\frac{3}{2}\rangle - 0.096\,69\vert\frac{7}{2},-\frac{1}{2}\rangle + 0.031\,95\vert\frac{7}{2},-\frac{5}{2}\rangle$ |
| −1655 | $0.9506\vert\frac{5}{2},\frac{5}{2}\rangle + 0.1173\vert\frac{5}{2},\frac{1}{2}\rangle - 0.1850\vert\frac{5}{2},-\frac{3}{2}\rangle + 0.1848\vert\frac{7}{2},\frac{5}{2}\rangle - 0.029\,04\vert\frac{7}{2},\frac{1}{2}\rangle - 0.1113\vert\frac{7}{2},-\frac{3}{2}\rangle + 0.0308\vert\frac{7}{2},-\frac{7}{2}\rangle$ |
| −1655 | $-0.1850\vert\frac{5}{2},\frac{3}{2}\rangle + 0.1173\vert\frac{5}{2},-\frac{1}{2}\rangle + 0.9506\vert\frac{5}{2},-\frac{5}{2}\rangle - 0.0308\vert\frac{7}{2},\frac{7}{2}\rangle + 0.1113\vert\frac{7}{2},\frac{3}{2}\rangle + 0.029\,04\vert\frac{7}{2},-\frac{1}{2}\rangle - 0.1848\vert\frac{7}{2},-\frac{5}{2}\rangle$ |
| −1236 | $0.2104\vert\frac{5}{2},\frac{5}{2}\rangle - 0.074\,83\vert\frac{5}{2},\frac{1}{2}\rangle + 0.7758\vert\frac{5}{2},-\frac{3}{2}\rangle + 0.096\,56\vert\frac{7}{2},\frac{5}{2}\rangle - 0.009\,11\vert\frac{7}{2},\frac{1}{2}\rangle + 0.5810\vert\frac{7}{2},-\frac{3}{2}\rangle - 0.036\,08\vert\frac{7}{2},-\frac{7}{2}\rangle$ |
| −1236 | $0.7758\vert\frac{5}{2},\frac{3}{2}\rangle - 0.074\,83\vert\frac{5}{2},-\frac{1}{2}\rangle + 0.2104\vert\frac{5}{2},-\frac{5}{2}\rangle + 0.036\,08\vert\frac{7}{2},\frac{7}{2}\rangle - 0.5810\vert\frac{7}{2},\frac{3}{2}\rangle + 0.009\,11\vert\frac{7}{2},-\frac{1}{2}\rangle - 0.096\,56\vert\frac{7}{2},-\frac{5}{2}\rangle$ |

by Starostin (1976), but the values of $\langle r^2\rangle$, $\langle r^4\rangle$ and $\langle r^6\rangle$ of the 4f shell given by him are smaller than those given by Freeman and Watson (1962). Furthermore, the extension of the radial wavefunction of the $Ce^{3+}$ ion in the garnets may be one reason for the actual CF being very much larger than that calculated with the point charge model. Kucera (1991) and Jacobs *et al* (1978) argued that the covalency of 5d states with the neighbouring ions might be large. Therefore we think that this value is reasonable.

It is seen from table 2 that, below 4 eV, there are two resonance frequencies (at 1.36 and 3.10 eV). They correspond to the transitions from the lowest and the second CF levels of the 5d configuration to the ground state. The value of $A_{ng}$ is negative for the transition from the lowest 5d CF level to the ground state, while it is positive for the transition from the second 5d CF level to the ground state. Therefore the FR is positive over the whole region between these two resonance frequencies and is negative outside this region. It is assumed that the transitions from the lowest 5d CF level to various 4f levels have the same half-width $\Gamma_1$. The corresponding value for the second 5d CF levels is assumed to be $\Gamma_2$. The values of $\Gamma_1$ and $\Gamma_2$ are determined by fitting the measured FR and ellipticity spectra. The selected values of $\hbar\Gamma_1$ and $\hbar\Gamma_2$ are 0.15 eV and 0.187 eV, respectively. These values are between the values obtained by Gomi *et al* (1991) and those obtained by Kucera *et al* (1989). The energy differences between the higher 5d CF levels and the ground state are larger than 4.0 eV; so the values of the half-width for the transitions from these levels to the 4f states are assumed to be zero.

The calculated spectra of the FR and ellipticity contributed by the $Ce^{3+}$ ions for $Y_2CeFe_5O_{12}$ at room temperature are shown in figure 1 and figure 2, respectively. The measured spectra obtained by Gomi *et al* (1991) are given in these figures as well. It is seen that the calculated curves are in good agreement with the measured curves. It should be noted that both the FR and the Faraday ellipticity of about 1.3 eV obtained by Kucera *et al* (1989) are larger than these values. This difference may be caused by the measurement errors of the cerium concentration, because the values are very low in the samples used by Kucera *et al.*

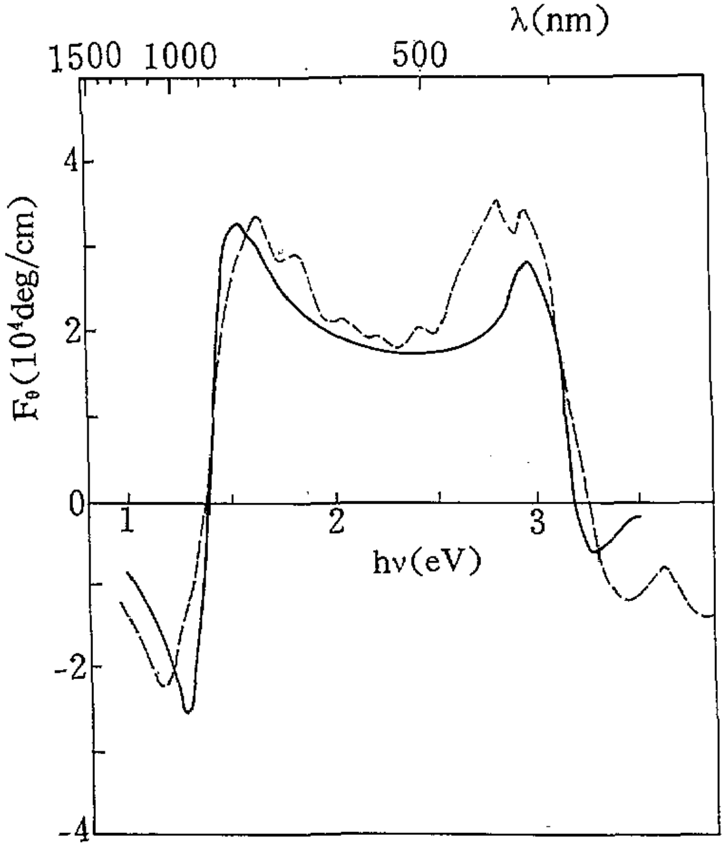

**Figure 1.** The FR spectrum contributed by the $Ce^{3+}$ sublattice of $Y_2CeFe_5O_{12}$ at 294 K: ——, calculated; – – –, curve measured by Gomi *et al* (1991).

## 3. Conclusions and discussion

From the calculated results, it is seen that the MO behaviour of $Ce^{3+}$ ions in Ce:YIG is well explained by the model used in this paper. The CF and the superexchange interaction are two very important factors in determining the FR in the garnets. The selection of the values of the CF parameters is crucial. The values obtained with the point charge model are too small to explain the experimental results. However, as mentioned above, a similar situation was also found when studying the magnetic properties of the RE-substituted garnets. We think that it is reasonable to determine the values of the CF parameters according to the values obtained by Nekvasil *et al* (1985) for the $Sm^{3+}$ ion in SmIG and the ratio of the radii of the RE ions.

The environment of the RE ions in the RE:YIG has $D_2$ symmetry. Therefore, in the case of non-Kramers ions, all CF-split levels are non-degenerate. It is known that the non-degenerate states barely contribute to the Faraday effect. Hence, for non-Kramers RE ions in RE:YIG, the Faraday effect is caused by the admixing of different CF states due to the superexchange interaction. This is another reason for the difference between the MO

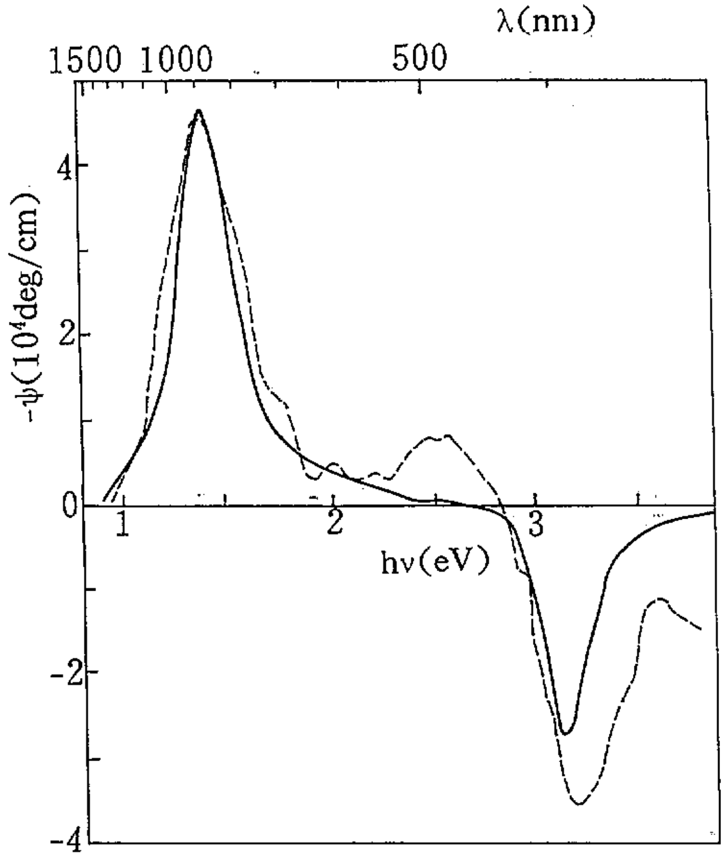

**Figure 2.** Same as figure 1, but for the Faraday ellipticity spectrum.

behaviours of the $Ce^{3+}$ ion and $Pr^{3+}$ ion in YIG being so large, although Pr is next to Ce in the periodic table.

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## References

Crossley W A, Cooper R W and Page J L 1969 *Phys. Rev.* **181** 896
Freeman A J and Watson R E 1962 *Phys. Rev.* **127** 2058
Gomi M, Furuyama H and Abe M 1990 *IEEE Trans. Magn., Japan* **5** 294
—— 1991 *J. Appl. Phys.* **70** 7065
Gomi M, Satoh K and Abe M 1988 *Japan. J. Appl. Phys.* **27** L1536

Guillot M, Feldmann P, LeGall H and Minella D 1979 *J. Physique* **40** 883
Guillot M, LeGall H, Marchand A, Desvignes J M and Artinian M 1990 *J. Magn. Magn. Mater.* **83** 25
Jacobs R R, Krupke W F and Weber M J 1978 *Appl. Phys. Lett.* **35** 410
Kucera M 1991 *J. Magn. Magn. Mater.* **101** 242
Kucera M, Bok J and Nitsch K 1989 *Solid State Commun.* **69** 1117
Leycuras C, LeGall H, Desvignes J M, Guillot M and Marchand A 1985 *IEEE Trans. Magn.* **MAG-21** 1660
Nekvasil V, Guillot M, Marchand A and Tcheou F 1985 *J. Phys. C: Solid State Phys.* **18** 3551
Starostin N V 1976 *Crystal Spectroscopy* ed A D Kaminski, Z P Molgensitle and D T Civilidov (Moscow: Nauka)
White J A 1967 *Proc. Phys. Soc.* **90** 1095
Xu Y and Duan M Q 1992 *Phys. Rev.* B **46** 11 636