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Effective Transition Probability for the Faraday Effect of Lanthanide(III) Ion Solutions

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The Faraday effect is the rotation of the plane of polarized light due to magnetic-field-induced circular birefringence in a material, which occurs in the case that the direction of light propagation and that of the magnetic field are parallel.[1,2] As shown in the Supporting Information (SI), the Faraday rotation angle, θ_F, of a lanthanide(III) ion, Ln(III), that has a degenerate ground state is theoretically represented by the Faraday C term:[3]

$$\theta_F = VlB = AK \frac{g}{2J+1} \frac{\lambda_{jn}^2}{\lambda_{jn}^2 - \lambda_0^2} ClB \qquad (1)$$

where V is the Verdet constant, l is the optical path length, B is the magnetic flux density, g is the Landé splitting factor, J is the total angular momentum quantum number, λ_{jn} is the wavelength for the $n \rightarrow j$ transition, λ_0 is the wavelength of the light source, C is the Ln(III) concentration, A is a constant that is equal to 8.09×10^{59} s^2 A^{-2} m^{-3} T^{-1} M^{-1} at 298 K, and K is the effective transition probability defined in the present study, which is given by eq 2:

$$K = - \sum_{M_J=-J}^{J} M_J \text{Im}(\langle n, M_J | \mu_X | j \rangle \langle j | \mu_Y | n, M_J \rangle) \qquad (2)$$

in which M_J ($= -J, -J+1, ..., J-1, J$) is the magnetic quantum number and μ_X and μ_Y are the electric dipole moment operators perpendicular to the magnetic field (see section S1 in the SI). The Faraday effect has been studied mainly for ferromagnetic solids and thin films because the contribution of the magnetic domain to Faraday rotation is very large.[4−7] Only a few measurements have been reported for solutions.[8−13] The Faraday rotation of Ln(III) in phosphate glass has been measured by Berger et al.[14] In their report, the magnitude of the Verdet constant varied periodically with the number of 4f electrons, and they tried to explain their results using the theory of van Vleck and Hebb,[15] in which the Verdet constant is proportional to the magnetic susceptibility. However, the relationship between the Faraday rotation and the magnetic moment of Ln(III) has not yet been clarified. The present study has elucidated the contributions of the magnetic moment and the excited state to the Faraday effect of Ln(III) aqueous solutions by introducing the effective transition probability K.

In the present study, by using a pulsed magnetic field, we measured the Faraday rotation of aqueous solutions of 14 Ln(III) ions having a systematically increasing number of 4f electrons. Figure 1 shows the apparatus for the measurement of the Faraday rotation of a solution under the pulsed magnetic field. A high magnetic field (>15 T) could be applied using a small electric magnet, though the duration was shorter than 1 ms.

Two kinds of semiconductor laser, with wavelengths of 410 and 640 nm, were used as the light source. A light beam passed through a polarizer, the sample solution, and an analyzer, which was rotated 45° with respect to the polarizer, and was then detected with a photodiode. The change in the intensity of the transmitted light was displayed on an oscilloscope. A cylindrical optical cell, 5 mm
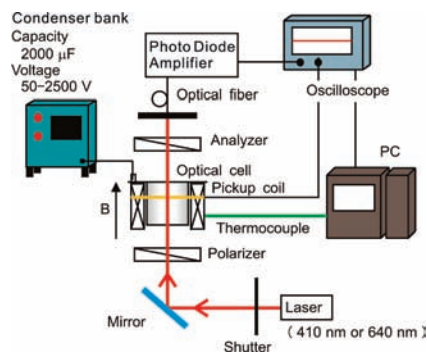

Figure 1. Apparatus for measuring the Faraday rotation.

in diameter and 8 mm long, was filled with an aqueous solution of Ln(III)Cl$_3$, whose concentration was varied over the range 0−1.5 M. A pulsed magnetic field of up to 7 T was applied using a homemade coil (5.3 mm i.d.) with a capacitor bank (2000 μF). The intensity of the pulsed magnetic field was determined from the clockwise Faraday rotation of pure toluene.[17] The Faraday rotation angle was obtained as the maximum of the observed rotation angle, which was determined from the observed intensity change of the transmitted light. The rotation direction of a paramagnetic solution including Ln(III) ion was counterclockwise. The observed Verdet constant was obtained from eq 1 as $V = \theta_F/lB$.

The linear correlation between the V and C predicted by eq 1 was confirmed (section S3). Furthermore, a simple additivity was observed for the Verdet constants of mixed solutions containing different Ln(III) ions (section S4). Therefore, the following empirical equation was obtained:

$$V = V_a + \sum_i v_i^C C_i \qquad (3)$$

where V_a is the Verdet constant of water and v_i^C is the molar Verdet constant of the ith Ln(III) ion.
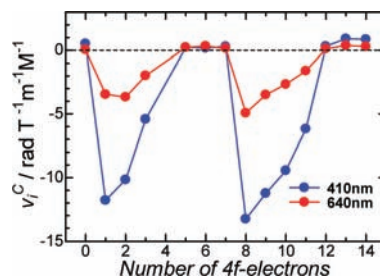

Figure 2. Molar Verdet constant v_i^C vs the number of 4f electrons.

Figure 2 shows the observed molar Verdet constant at the two laser wavelengths as a function of the number of 4f electrons, n_{4f}, in the ground state. The molar Verdet constants changed periodically

as a function of n_{4f} and could be grouped into the first half-series from La(III) to Gd(III), whose 4f orbital is half-filled, and the second half-series from Tb(III) to Lu(III). The pattern of variation is similar to that observed in glasses.[14,16] The similar profiles observed at the different wavelengths of 410 and 640 nm in Figure 2 indicate that the electron transition mainly contributing to the Faraday rotation of Ln(III) ions is $4f^n \rightarrow 4f^{n-1}5d$ in the ultraviolet region rather than $4f \rightarrow 4f$ in the visible region, because several $4f \rightarrow 4f$ transitions can be observed in the absorption spectra of Ln(III) solutions between 410 and 640 nm. In order to obtain K, the effective transition probability of the Faraday rotation, the contribution of the wavelength dispersion, the degeneracy factor, and the Landé splitting factor were eliminated by dividing υ_i^C by $\lambda_{jn}^2/(\lambda_{jn}^2 - \lambda_0^2)$ and $g/(2J + 1)$. The reported wavelengths for the lowest $4f^n \rightarrow 4f^{n-1}5d$ transitions of the Ln(III) ions[18] were used in this calculation, and the results are plotted in Figure 3.
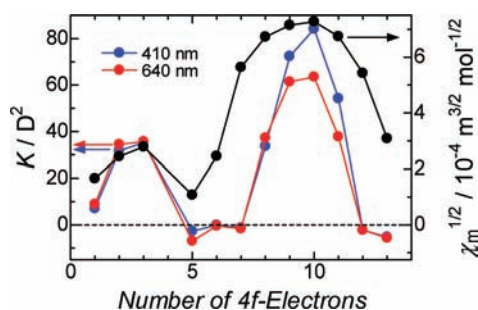

Figure 3. Values of K (red and blue) and $\chi_m^{1/2}$ (black) vs the number of 4f electrons.

The K values in Figure 3 also showed two groups, as noted for υ_i^C in Figure 2, though the magnitudes differed between the two groups. There was no correlation between the effective transition probability and the integral absorption coefficient of the lowest $4f^n \rightarrow 4f^{n-1}5d$ transition of Ln(III)[18] (section S6) Hence, it was concluded that the effective transition probability was different from the normal transition probability, suggesting that the former contained the magnetic quantum number and the transition moment perpendicular to the magnetic field. Values of the square root of the molar magnetic susceptibility for the Ln(III) solutions, which were measured using a magnetic balance in the present study, are also shown in Figure 3. The value of $\chi_m^{1/2}$ is known to be directly proportional to the magnetic moment for Ln(III) ions.
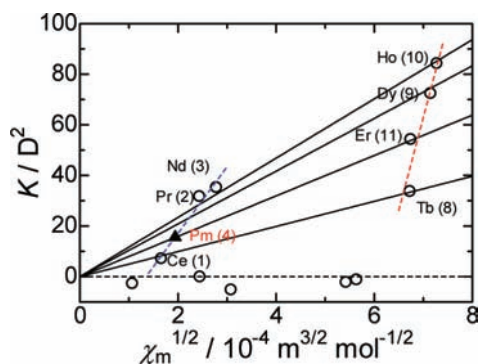

Figure 4. Linear correlations between K and $\chi_m^{1/2}$. Values of n_{4f} are given in parentheses.

In the plots of Figure 4, Ln(III) ions can be divided into three groups: (1) $n_{4f} = 1-3$; (2) $n_{4f} = 5-7$, 12, and 13, whose values of

K were nearly equal to zero; and (3) $n_{4f} = 8-11$. The $K \approx 0$ value for the second group means that their $4f^n \rightarrow 4f^{n-1}5d$ optical transition probability is almost zero. Interestingly, linear relationships between the first and third groups were found, as indicated by the solid lines in Figure 4. The K values of Ln(III) ions with $n_{4f} = i$ ($i = 1, 2, 3$) and $i + 7$ (half-occupied 4f subshell) were directly proportional to $\chi_m^{1/2}$, with different slopes for different i (the values of slopes are shown in section S5). The linear relationship suggests that the optical transition probability perpendicular to the magnetic field is similar for Ln(III) ions with $n_{4f} = i$ and $i + 7$. The larger slope for the Ln(III) ions with larger $\chi_m^{1/2}$, as denoted by the two dotted lines in Figure 4 (see Table S5 in the SI), means that the optical transition probability in the two groups $n_{4f} = 1-3$ and $n_{4f} = 8-11$ depends on the magnetic moment. It was possible to predict the values of $\chi_m^{1/2}$ and K for Pm(III), whose stable isotope does not exist, from the intersection of the solid line passing through K of Er(III) and the blue dotted line in Figure 4. The predicted value of χ_m (3.77×10^{-8} m^3 mol^{-1}) is in good agreement with the value 3.79×10^{-8} m^3 mol^{-1} calculated from the J value of the ground state of Pm(III); K for Pm(III) was predicted to be 15.6 D^2.

In conclusion, a new regularity was discovered in the Faraday effect of Ln(III) solutions. The contributions of the $4f^n \rightarrow 4f^{n-1}5d$ transition and the magnetic moment to the molar Verdet constant of Ln(III) ions were experimentally clarified by determining the effective transition probability of the Faraday effect, K. The relationship between K and $\chi_m^{1/2}$, which depends on the electron configuration of the 4f subshell, was found for the first time.

Supporting Information Available: Derivation of eq 1, the procedure for determining the Verdet constant, the observed data that provided the linear relationships with the concentration, the additivity of the Verdet constant, and the values of the slopes in Figure 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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