Faraday Parameters of the Magnetic Circular Dichroism of Praseodymium Trichloride and Thulium Trichloride in Poly(vinyl alcohol) Film

Yoshifumi KATO and Kyusaku NISHIOKA

Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657

(Received July 16, 1973)

The magnetic circular dichroism and absorption spectra of $PrCl_3$ and $TmCl_3$ in polyvinylalcohol film are measured in the range of 300—700 nm. The absorption bands observed are five for $PrCl_3$, the transitions from the ground state, $^3H_4$, to the excited states, $^1D_2$, $^3P_0$, $^3P_1$, $^1I_6$, and $^3P_2$, of Pr^{3+}, and four for $TmCl_3$, the transitions from the ground state, $^3H_6$, to the excited states, $^3F_3$, $^3F_2$, $^1G_4$, and $^1D_2$, of Tm^{3+}. In order to separate the *C* term of the Faraday parameters, the temperature variation of the spectra is carried out at room temperature to 77 K. The Faraday parameters are derived from the experiment by the use of three methods; the method of moments, the graphical method, and curve fitting. The characteristics of these methods are discussed, and the uncertainty of the parameters obtained is estimated to be 30% or more. A group-theoretical consideration is applied for the interpretation of the results; this consideration fairly well explains the sign of the *C* terms obtained for $PrCl_3$, but not for $TmCl_3$.

Since the general review of Buckingham and Stephens[1] with respect to the magnetic optical activity, there have been published a number of articles[2] on the magnetic circular dichroism (MCD) with the pervasion of instruments and the utilization of a superconducting magnet. From the results obtained, it has been demonstrated that this technique gives valuable information on the electronic structure of molecules, especially the assignments of the absorption spectra and the magnetic properties of the ground and excited states.

In general, since the spin-orbit coupling of rare-earth ions is much stronger than the crystal field, these ions have appreciable orbital magnetic moments and thus strong MCD spectra may be expected, even under a weak magnetic field. Rare-earth salt is, therefore, considered to be a material favorable to the investigation by MCD; even when direct observation of the Zeeman-effect for a transition is prevented by the absorption band-width, MCD measurement makes it possible to study the effect of a magnetic field on a transition. Since the states of rare-earth ions in a salt are a little affected by the surrounding crystal field, the absorption spectra can be easily assigned by comparing these with the results established by the emission spectra of free ions and the absorption, fluorescence, and Zeeman-spectra of single crystals. However, the MCD study is still useful in confirming the spectral assignment obtained incompletely by various other methods.

Several MCD measurements for the compounds involving Pr^{3+} have already been given. Foss and McCarville[3] and Briat *et al.*[4] separately measured the MCD of $PrCl_3$ in an aqueous solution at room temperature. The former estimated the magnitude of the Zeeman-splitting from the experiment. Ferre *et al.*[5] carried out a detailed MCD measurement of Pr^{3+} diluted in an $AlLaO_3$ crystal at 300—100 K. They obtained a number of spectroscopic splitting factors, together with other information, and made a theoretical argument for the results. There have, however, been no studies of the MCD for the salts involving Tm^{3+}.

In this paper, we will present the MCD and absorption spectra of $PrCl_3$ and $TmCl_3$ dispersed into a polyvinyl alcohol (PVA) film measured in the range of room temperature to 77 K. So far as we know, the MCD measurement in a PVA film was first attempted for $Fe(CN)_6^{3-}$ by Kobayashi *et al.*[6] Since the MCD spectra in a PVA film are very similar to those in an aqueous solution, this technique is considered to be appropriate for observing the temperature variation of the MCD for a soluble salt in water. The Faraday parameters of the MCD spectra are derived from the experiment by the use of several methods proposed by previous authors,[7,8] and some discussion is given of the methods used and of the accuracy of the parameters obtained. A group-theoretical consideration is also attempted for the interpretation of the parameters.

Experimental

Materials. A PVA film of samples was obtained by the addition of an aqueous solution of $PrCl_3 \cdot 7H_2O$ or $TmCl_3 \cdot 6H_2O$ into that of PVA and by allowing it to evaporate to dryness on a glass plate. Several PVA films with different concentrations were prepared for the purpose of the measurement with an appropriate absorption strength. The concentration of a sample was determined from the interpolation in the comparison of the absorption strength of a PVA film with that of the corresponding aqueous solution.

Spectral Measurements. All the measurements were carried out by the use of a JASCO model J-10 instrument with a permanent magnet, which had a pole gap of 12 mm and which produced a magnetic field of 4.6 kG on the average. For the measurement at lower temperatures, a sample film about 1 mm thick was directly immersed in liquid nitrogen or in a mixture of liquid and solid methanol placed in a special quartz Dewar vessel which could be closely inserted between magnetic poles. The bubbles produced in the Dewar vessel were removed skilfully not to disturb the measurements. The temperature was determined within an accuracy of ± 1 K by using a copper-constantan thermocouple in contact with a PVA film. The magnitudes of the MCD bands were calibrated with an aqueous solution of *d*-camphor sulfonic acid.

Method of Analysis

Theoretical. The theoretical expression of the MCD for an absorption band has been formulated by Buckingham and Stephens[1] and used to analyze the experiments by most investigators.[2,3] The ellipticity in an isotropic solution accompanied by an electronic transition, $a \rightarrow j$, is given by;[1,9]

$$\theta = -\frac{8\pi^2 H_z N}{3ch}[f_1 A + f_2(B + C/kT)], \quad (1)$$

$$A = \frac{3}{d_a}\sum_{a,j}[\langle j|\mu_z|j\rangle - \langle a|\mu_z|a\rangle]Im\{\langle a|m_x|j\rangle\langle j|m_y|a\rangle\},$$

$$B = \frac{3}{d_a}\sum_{a,j}\mathrm{Im}\{\sum_{k\neq a}[\langle k|\mu_z|a\rangle/\Delta E_{ka}][\langle a|m_x|j\rangle\langle j|m_y|k\rangle - \langle a|m_y|j\rangle\langle j|m_x|k\rangle] + \sum_{k\neq j}[\langle j|\mu_z|k\rangle/\Delta E_{kj}] \times [\langle a|m_x|j\rangle\langle k|m_y|a\rangle - \langle a|m_y|j\rangle\langle k|m_x|a\rangle]\},$$

$$C = \frac{3}{d_a}\sum_{a,j}\langle a|m_z|a\rangle \mathrm{Im}\{\langle a|m_x|j\rangle\langle j|m_y|a\rangle\}. \quad (2)$$

Here, f_1 and f_2 express the frequency functions defining the band shape, N is the total number of absorption centers per unit of volume in the ground state, a, d_a is the degeneracy of this state, and $\boldsymbol{m}=e\sum_i \boldsymbol{r}_i$ and $\boldsymbol{\mu}=-\beta\sum_i(\boldsymbol{l}_i+2\boldsymbol{s}_i)$ are the electric and magnetic dipole-moment operators respectively. The summations are over all the states degenerate with $a \rightarrow j$. In the conventional units used by previous authors,[2a,9] the molar ellipticity, θ_M, per unit of magnetic field is in units of the degree deciliter decimeter^{-1} mol^{-1}, A in D$^2\beta$, and B and C/kT in D$^2\beta$/cm^{-1} (β=Bohr magneton, D=Debye unit). Then, the coefficient of Eq. (1) becomes -21.346. The A, B, and C Faraday parameters arise from the Zeeman-splitting of $a \rightarrow j$, the mixing of a and j with the other states, k, due to a magnetic field, and the change in the population of the Zeeman-components of the a state respectively. As may be seen in Eq. (2), the C term can arise only when the ground state, a, is degenerate, because the expectation value of μ_z must otherwise be zero; similarly, the A term arises when the ground state, a, and/or the excited state, j, are degenerate. On the other hand, the B term, consisting of an infinite summation about the other states, k, can exist always, although the contribution of the B term to the total θ_M may not be sizable for paramagnetic substances. It is apparent that the MCD of $PrCl_3$ and $TmCl_3$ should have the contributions from all the Faraday parameters, since the ground state of Pr^{3+} is a degenerate state, $^3H_4$, and that of Tm^{3+} is $^3H_6$. In Eq. (1), a dielectric correction is ignored, but this problem is avoided by expressing our results as the ratio of the Faraday parameters to the electric dipole strength, $D(D=(3/d_a)\sum|\langle a|m_x|j\rangle|^2)$. In order to obtain valuable information from the measurement, it is first necessary to extract the values of the Faraday parameters. We have applied the following three methods previously proposed; the method of moments,[7] the graphical method[8] and curve fitting.

Method of Moments. This method was first Introduced by Henry, Schnatterly, and Slichter[10] in interpreting the MCD of a color center; later the generalization and application to other types of absorption systems was done by Stephens *et al.*[7,11] The moment of molar extinction coefficient, ε, and of molar ellipticity, θ_M, about the average absorption frequency, ν, are defined as:[7,11a]

$$\langle\varepsilon\rangle_n = \int_{band}(\varepsilon/\nu)(\nu-\bar{\nu})^n d\nu, \quad \langle\theta_M\rangle_n = \int_{band}(\theta_M/\nu)(\nu-\bar{\nu})^n d\nu. \quad (3)$$

With the assumption of the rigid shift model, the zero-th and first-order moments for an isotropic solution of noninteracting molecules are approximated as;

$$\langle\varepsilon\rangle_0 = 108.9D, \ \langle\varepsilon\rangle_1 = 0, \ \text{(definition of } \bar{\nu}) \quad (4)$$

$$\langle\theta_M\rangle_0 = -33.53(B+C/kT), \ \langle\theta_M\rangle_1 = 33.53A. \quad (5)$$

Using these equations, one can evaluate the Faraday parameters from the moments obtained by numerical integrations through the absorption and MCD curves. This method, therefore, does not require any assumption of band shape, position or width, or any model for the vibronic structure of the states.

Graphical Method. This method, proposed by Badoz *et al.*,[8] starts from a special assumption regarding a band shape. If the shape function is taken as a Gaussian form, f_G, the expressions for ε/ν and θ_M/ν are given under the rigid shift model as;

$$\varepsilon/\nu = 108.9Df_G \equiv Y, \quad (6)$$

$$\theta_M/\nu = -33.53[Af_G' + (B+C/kT)f_G] \equiv \Delta Y,$$

where;

$$f_G = 1/(\sqrt{\pi}\delta)\exp[-(\nu-\nu_0)^2/\delta^2]. \quad (7)$$

Now, it can easily be shown from Eq. (6) that;

$$Y'/Y = -(2/\delta^2)(\nu-\nu_0),$$

$$\Delta Y/Y = \theta_M/\varepsilon = 0.3080[(2/\delta^2)(\nu-\nu_0)A/D - (B+C/kT)/D]. \quad (8)$$

Since the values of the left side in Eq. (8) obtained from the experiment are linearly related to the frequency, ν, one can obtain graphically the half-width, δ, at $1/e$ and the frequency, ν_0, of the maximum absorption and the Faraday parameters divided by D. In this procedure, there is no further assumption except for a band-shape function if the derivative of the absorption curve can be obtained accurately.

Curve Fitting. The molar ellipticity, θ_M, is a function involving the Faraday parameters, the frequency of maximum absorption, and the half-width as parameters, P. By assuming a shape function for a band, one can fit an explicit expression of θ_M to an experimental curve. When θ_M is expanded to the first order in terms of these parameters and a least-squares procedure is applied, the final equation to be solved is reduced to be following matrix form;

$$\tilde{\boldsymbol{J}}\boldsymbol{J}\Delta\boldsymbol{P} = \tilde{\boldsymbol{J}}\Delta\boldsymbol{\theta}_M \quad (9)$$

$$\boldsymbol{J} \equiv \partial(\theta_{M1}, \cdots\cdots, \theta_{Mn})/\partial(P_1, \cdots\cdots, P_m), \quad (10)$$

where $\boldsymbol{J}$ and $\tilde{\boldsymbol{J}}$ are the Jacobi and its transposed matrix respectively, n and m being the number of θ_M measured and that of the parameters used respectively. From Eq. (9), the parameter correction, $\Delta\boldsymbol{P}$, to be revised can be evaluated iteratively from the difference, $\Delta\boldsymbol{\theta}_M$, between the measured and calculated ellipticity. This method is already familiar from other spectral analyses.[12]

Throughout all the methods, the separation of the C term has been done by means of the temperature variation of θ_M; the Faraday parameters were derived by means of a FACOM 230-35 computer in Kobe University.

Results and Discussion

Results and the Faraday Parameters. The absorption and MCD spectra observed are given in Fig. 1 for $PrCl_3$ and in Fig. 2 for $TmCl_3$. As may be seen in Figs. 1 and 2, at lower temperatures the widths of the absorption bands generally become more sharp and some bands evidently split into two bands or disappear due to the change in the population of the ground crystal-field levels, while the MCD spectra also exhibit a large temperature dependence.

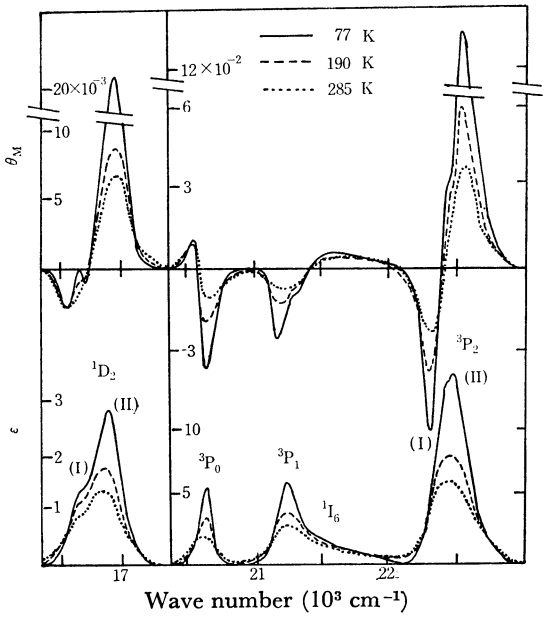

Fig. 1. Temperature variations of the absorption and MCD spectra of $PrCl_3$ in PVA film. θ_M and ε are the MCD in molar ellipticity units (degree deciliter decimeter^{-1} mol^{-1}) per unit Gauss and the molar extinction coefficient, respectively.

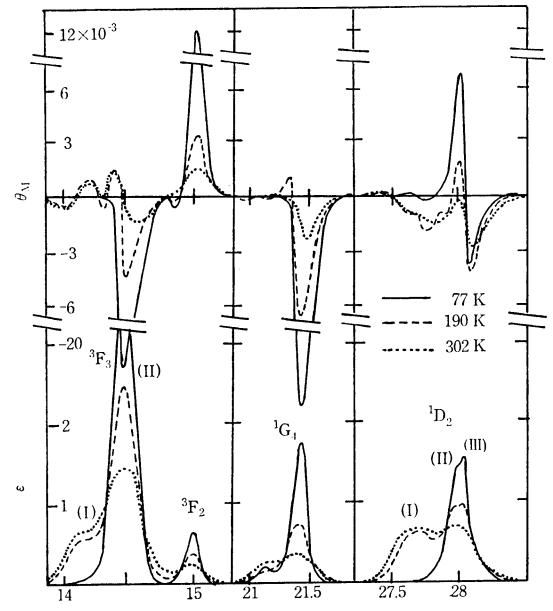

Fig. 2. Temperature variations of the absorption and MCD spectra of $TmCl_3$ in PVA film. Notations and units are the same as Fig. 1.

There are 13 electronic levels for the $4f^2$ configuration of Pr^{3+} as well as for the $4f^{12}$ configuration of Tm^{3+}; the latter being the complementary configuration of the former. Since the energy levels of several single crystals involving Pr^{3+} or Tm^{3+} have been well established,[13] it is easy to assign the absorption bands in PVA by comparison with those of single crystals; the bands of $PrCl_3$ at 16800, 20600, 21400, and 22400 cm^{-1} are identified as transitions from the ground state, $^3H_4$, to the excited states, $^1D_2$, $^3P_0$, $^3P_1$, and $^3P_2$, of Pr^{3+} respectively, the bands of $TmCl_3$ at 14400, 15000, 21300, and 27900 cm^{-1} being the transitions from the ground state, $^3H_6$, to the excited states, $^3F_3$, $^3F_2$, $^1G_4$, and $^1D_2$, of Tm^{3+} respectively. The absorption bands in the ultra-violet region are excluded from present analysis because of the disturbance due to the absorption of PVA itself in this region. (Hereafter, an absorption band will be designated with the relevant excited state.) It is certain that a weak shoulder band on the large-wave number side of the $^3P_1$ band in $PrCl_3$ is the $^1I_6$ band, because of the clear appearance of the small, positive θ_M at the corresponding position of the MCD curve. This assignment is also in agreement with that of Pr^{3+} in $LaCl_3$[14] and of the free ion.[15] Details of the derivation for the Faraday parameters of $PrCl_3$ by the moment analysis and graphical method are given in Tables 1 and 2 respectively. The absorption and MCD curve in PVA and in an aqueous solution for $PrCl_3$ at room temperature are given in Fig. 3, together with the results of the curve fitting. The corresponding tables and figures for $TmCl_3$ are abbreviated. The mean derivation $(\sum_i(\theta_M^{cald})_i/(\theta_M^{obsd})_i \times 100/n)$ for all the curve fittings were within 2%. As may be seen in Fig. 3, in both the absorption and MCD spectra, the spectral wave numbers in PVA commonly shift to a smaller side within 50 cm^{-1} of those

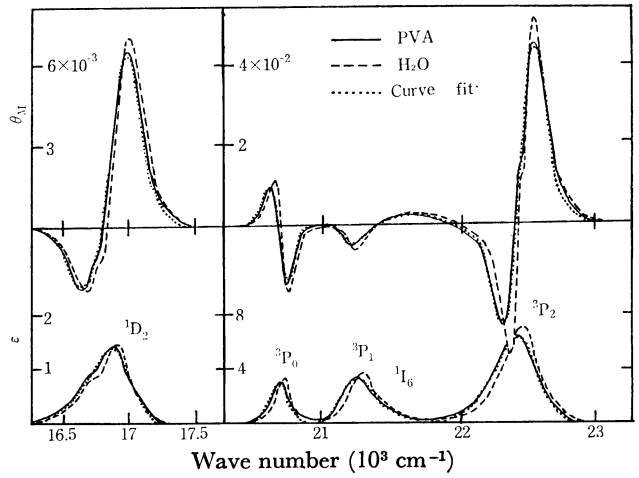

Fig. 3. Absorption and MCD spectra of $PrCl_3$ in PVA film and an aqueous solution at a room temperature, together with the results of the curve fitting. Notations and units are the same as in Fig. 1.

TABLE 1. PARAMETER VALUES FOR $PrCl_3$ IN PVA FILM BY THE MOMENT ANALYSIS

Excited state	T (K)	$\bar{\nu}$ (cm^{-1})	D ($10^{-4}D^2$)	A/D (β)	$(B+C/kT)/D$ ($10^{-3}\beta$/cm^{-1})
$^1D_2$	77	16870	5.241	2.054	−15.432
	188	16840	3.917	2.198	−6.481
	285	16830	3.529	2.262	−4.395
	289[a)]	16870	3.330	2.319	−5.153
$^3P_0$	77	20650	3.184	−0.952	11.852
	190	20640	2.540	−1.073	5.891
	285	20630	2.295	−1.228	3.201
	292[a)]	20680	2.361	−1.084	2.514
$^3P_1(^1I_6)$	77	21420	9.220	2.372	3.905
	190	21380	6.680	1.021	15.527
	285	21370	5.713	0.752	9.188
	292[a)]	21400	6.049	0.824	8.168
$^3P_2$	77	22460	16.64	2.998	−15.071
	191	22440	12.73	2.785	−7.651
	285	22420	11.07	3.078	−6.084
	289[a)]	22470	11.01	2.876	−6.431

a) Data in an aqueous solution.

TABLE 2. PARAMETER VALUES FOR $PrCl_3$ IN PVA FILM BY THE GRAPHICAL METHOD

Excited state	T (K)	ν_0 (cm^{-1})	δ[b)] (cm^{-1})	A/D (β)	$(B+C/kT)/D$ ($10^{-3}\beta$/cm^{-1})
$^1D_2$(I)	77	16700	99.1	1.365	−9.870
	188	16720	164.6	1.386	2.240
	285	16730	181.4	1.143	5.325
	289[a)]	16730	125.6	0.866	6.334
$^1D_2$(II)	77	16890	167.4	2.119	−17.341
	188	16880	202.1	2.518	−9.740
	285	16880	226.7	2.764	−7.468
	289[a)]	16910	161.2	1.813	−8.377
$^3P_0$	77	20650	57.3	−0.960	16.494
	190	20660	60.1	−0.805	9.026
	285	20660	80.8	−1.284	6.429
	292[a)]	20700	72.6	−1.187	3.961
$^3P_1$	77	21220	84.1	−0.385	17.858
	190	21240	115.8	−0.311	11.012
	285	21240	138.2	−0.369	7.503
	292[a)]	21270	111.9	−0.231	7.213
$^3P_2$(I)	77	22400	143.4	5.083	−5.841
	191	22410	146.5	3.202	−2.790
	285	22410	166.8	2.829	1.362
	289[a)]	22460	150.4	3.025	1.655
$^3P_2$(II)	77	22470	151.2	4.254	−2.113
	191	22470	164.2	3.432	−1.272
	285	22460	191.9	4.571	−0.461
	289[a)]	22480	165.9	3.208	−0.755

a) Data in an aqueous solution. b) The half-width at $1/e$ of maximum absorption.

in aqueous solution, but the band shapes in PVA are almost identical with those in an aqueous solution. This fact shows that the electronic environment about a rare-earth ion in PVA is like that in an aqueous solution. Consequently, the site symmetry of a rare-earth ion in PVA could be considered to be C_{3v}.

The plots of $(B+C/kT)/D$ to $1/kT$ obtained by the moment method, graphical method and curve fitting are given in Figs. 4—6 for $PrCl_3$ and in Figs. 7—9 for $TmCl_3$. In these figures, the linear relations are,

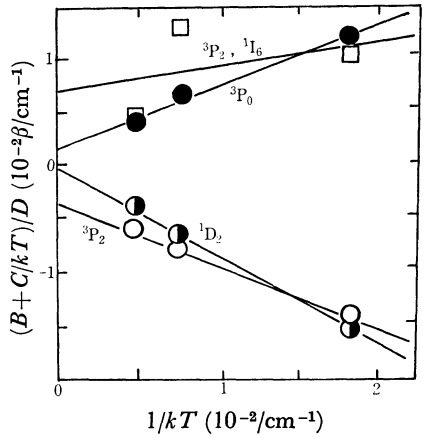

Fig. 4. Temperature dependence of $(B+C/kT)/D$ of $PrCl_3$ by the moment analysis.

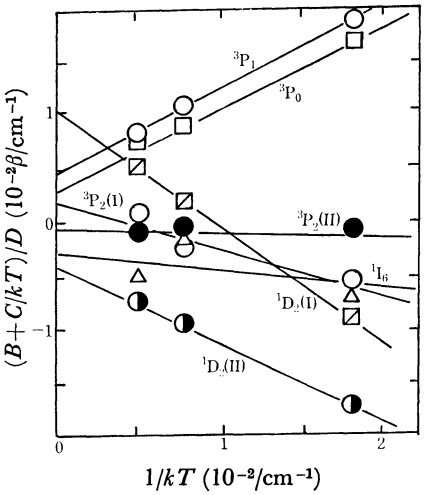

Fig. 5. Temperature dependence of $(B+C/kT)/D$ of $PrCl_3$ by the graphical method.

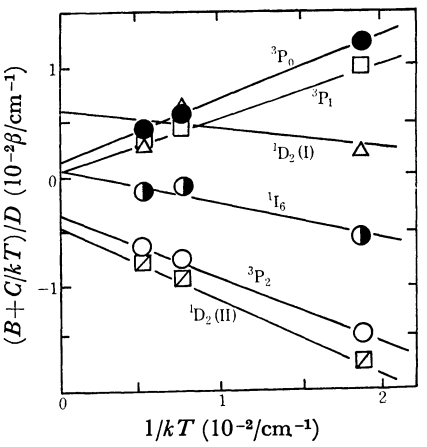

Fig. 6. Temperature dependence of $(B+C/kT)/D$ of $PrCl_3$ by the curve fitting.

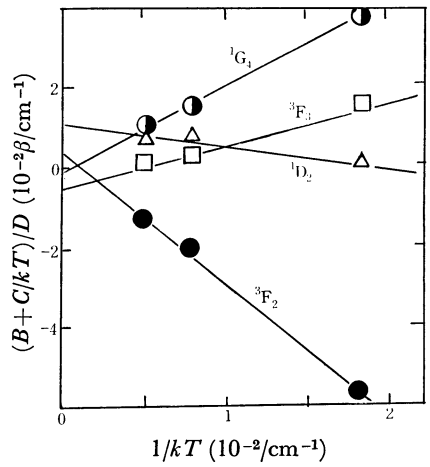

Fig. 7. Temperature dependence of $(B+C/kT)/D$ of $TmCl_3$ by the moment analysis.

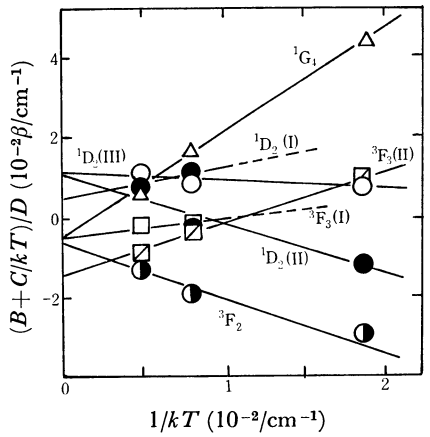

Fig. 8. Temperature dependence of $(B+C/kT)/D$ of $TmCl_3$ by the graphical method.

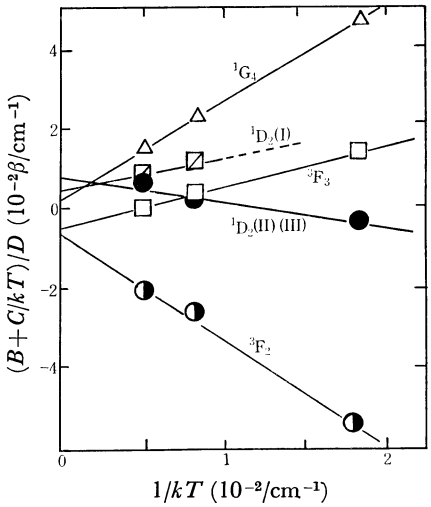

Fig. 9. Temperature dependence of $(B+C/kT)/D$ of $TmCl_3$ by the curve fitting.

in general, well retained except for a few cases. The summaries of the Faraday parameters obtained are shown in Table 3 for $PrCl_3$ and in Table 4 for $TmCl_3$, where the values in parentheses are considered to be less reliable. The values of the B terms for all the bands are considerably smaller than those of the C terms. The ratio of C to B is approximately $\Delta E: kT$, as estimated by others.[1,9] Since ΔE, the order of magnitude of the energy difference between electronic states, is assumed to be $\sim 5000\ cm^{-1}$, and since kT is $\sim 200\ cm^{-1}$ at room temperature, this ratio becomes larger than 25; thus, the B term can be neglected at lower temperatures. The Faraday parameters obtained by means of the three methods are in fairly good agreement with one another in reliable cases.

The three methods used have some individual characteristics. The moment method may be the most powerful and general technique. In actual application, there is, however, an arbitrariness in the separation of an overlapping band; furthermore, the inclusion of higher-order moments complicates the analysis. The graphical method makes it possible to separate an overlapping band straightforwardly, as has already been pointed out by Badoz *et al.*,[8] but we could not always place trust in the numerical evaluation of the derivative of an absorption band. In the curve fitting, there is no assurance of any definite convergence by an iterative procedure using an assumed formula; in fact, some parameters may be very sensitive to the intial trial values used.

As to the accuracy of the Faraday parameters, it is possible to estimate for the transition to the non-degenerate excited state, $^3P_0$, of $PrCl_3$. In this case, the magnitude of the A/D should be, in principle, equal in absolute value and reverse in sign to that of the C/D, as may be seen in Eq. (2). This fact is not fully satisfied in any of the methods. As may be seen

Table 3. Values of the Faraday parameters of $PrCl_3$ by various methods
Units of A/D and C/D are in β, and those of B/D in $10^{-2}\ \beta/cm^{-1}$.
Values in parentheses are less reliable.

Excited state	Moment analysis			Graphical method			Curve fitting			Theor. estimate of C/D
	A/D	B/D	C/D	A/D	B/D	C/D	A/D	B/D	C/D	
$^1D_2$(I)	2.17	−0.03	−0.81	1.30	1.08	−1.11	1.32	(0.60)	(−0.17)	negative
$^1D_2$(II)				2.47	−0.40	−0.71	1.75	−0.31	−0.73	
$^3P_0$	−0.98	0.06	0.63	−1.02	0.31	0.74	−0.89	0.17	0.56	positive
$^3P_1$	(1.72)	(0.71)	(0.29)	0.36	0.44	0.76	0.14	0.09	0.46	negative
$^1I_6$				(0.98)	(−0.21)	(−0.22)	(1.57)	(0.08)	(−0.35)	negative
$^3P_2$(I)	2.95	−0.32	−0.68	(3.70)	(0.27)	(−0.53)	2.65	−0.24	−0.62	negative
$^3P_2$(II)				(4.08)	(−0.02)	(−0.10)				

TABLE 4. VALUES OF THE FARADAY PARAMETERS OF $TmCl_3$ BY VARIOUS METHODS
Units of A/D and C/D are in β, and those of B/D in $10^{-2}\ \beta/cm^{-1}$.
Values in parentheses are less reliable.

Excited state	Moment analysis			Graphical method			Curve fitting			Theor. estimate of C/D
	A/D	B/D	C/D	A/D	B/D	C/D	A/D	B/D	C/D	
$^3F_3$(I)	−0.51	−0.50	1.08	(1.28)	(−0.48)	(0.44)	−0.45	−0.48	1.06	positive
$^3F_3$(II)				−1.15	−1.16	1.34				
$^3F_2$	1.86	0.41	−3.18	2.09	−0.60	−1.22	1.93	−0.60	−2.67	positive
$^1G_4$	−2.66	−0.13	1.97	−1.91	−0.42	2.55	−1.70	0.18	2.43	positive
$^1D_2$(I)				(−1.36)	(0.45)	(0.70)	(0.12)	(0.33)	(0.93)	
$^1D_2$(II)	−0.94	1.24	−0.62	(1.56)	(0.81)	(−1.32)	(−0.53)	(0.70)	(−1.07)	positive
$^1D_2$(III)				(−1.74)	(0.85)	(−0.10)				

in Table 3, the ratios of the absolute value of the A/D to that of the C/D are 0.6—0.7. Thus, the uncertainty in the parameters obtained is estimated to be 30% or more. It seems plausible, as Stephens[7a] has deduced, that 30% is the limit of the uncertainty of the parameters by the moment analysis. It is hazardous to conclude simply which method is superior to the others without a further detailed study of a favorable case. It may be pointed out that a careful consideration is necessary to obtain quantitative information on the basis of the experimental Faraday parameters.

Group-Theoretical Consideration. MCD results could be interpreted by considering the split in energy levels due to C_{3v} crystal symmetry. We will treat the A and C terms in terms of group theory, because the B term is considerably smaller than the others and there is difficulty in arriving of an infinite sum. A free-ion level including spin-orbit interaction splits into the sum of several irreducible representations of C_{3v} symmetry, as is shown in Table 5.[16] Since the species of μ_z and that of m_x and m_y in this symmetry are A_2 and E respectively, we can reduce the values of C/D and A/D according to the Wigner-Eckart theorem.[17] The expressions C/D and A/D for the transitions among crystal levels are given in Table 6, where μ_g and μ_e are a reduced matrix element $\langle E||\mu||E\rangle$ of the E species in the ground and excited states respectively.

TABLE 5. IRREDUCIBLE REPRESENTATIONS OF ION LEVELS UNDER C_{3v} SYMMETRY

Ion level	C_{3v} symmetry
$^3P_0$	A_1
$^3P_1$	A_2+E
$^1D_2$, $^3F_2$, $^3P_2$	A_1+2E
$^3F_3$	$2A_1+A_2+2E$
$^1G_4$, $^3H_4$	$2A_1+A_2+3E$
$^1I_6$, $^3H_6$	$3A_1+2A+4E$

TABLE 6. THEORETICAL REDUCTION OF THE VALUES OF C/D AND A/D FOR THE TRANSITIONS AMONG EACH SPECIES OF C_{3v} SYMMETRY

Transition	$C/D(\beta)$	$A/D(\beta)$
$E\rightarrow A_1$	$(i/\sqrt{2})\mu_g$	$-(i/\sqrt{2})\mu_g$
$E\rightarrow A_2$	$-(i/\sqrt{2})\mu_g$	$(i/\sqrt{2})\mu_g$
$E\rightarrow E$	$-(i/\sqrt{2})\mu_g$	$-(i/\sqrt{2})(\mu_e-\mu_g)$
$A_1\rightarrow E$	0	$(i/\sqrt{2})\mu_e$
$A_2\rightarrow E$	0	$-(i/\sqrt{2})\mu_e$

If we assume that the E species of the ground state consist of only f electrons, the value of μ_g comes to be $-\sqrt{2}\,i$ for Pr^{3+} and $i/\sqrt{2}$ for Tm^{3+} (see Appendix). The absorption bands observed are not due to the transitions between crystal levels, but to overall transitions. However, by assuming that the populations of all the E species in ground state are equal, we can estimate the signs of C/D, which are given in the last column in Tables 3 and 4. As may be seen in these tables, the experimental signs of the C/D for $PrCl_3$ are fairly well explained by such a simple consideration, but those for $TmCl_3$, not so well. This seems to arise from the fact that the assumption of equal populations for the four ground E species of $TmCl_3$ is not adequate, because the total splitting due to the crystal field in $TmCl_3\cdot 6H_2O$ crystal is 460 cm^{-1} (Olsen *et al.*);[18] this is twice or more as large as that of $PrCl_3\cdot 7H_2O$.[14] The further application of such a simplified treatment to the estimate of A/D is not appropriate because it involves several approximations.

Although the values of C/D and $(A+C)/D$ obtained are closely related to a weighted sum of the g-factors of the crystal levels in the ground and excited states concerned respectively, it is difficult to compare these values directly with the results obtained by other experiments because of the lack of accurate knowledge of the splitting crystal levels. From this point of view, it will be desirable to investigate the MCD of single crystals involving a rare-earth ion in order to advance further in the field of quantitative treatment.[19]

This work has been supported in part by the Ministry of Education of Japan.

Appendix

It is well known that the $4f^N$ configurations of rare-earth ions can be described satisfactorily in terms of intermediate coupling. In this case, only J and M_J become good quantum numbers and the wavefunction is a linear combination of LS functions with a constant J. If 305.4, 51.88, 5.321, and 729.5 cm^{-1}, values obtained by Margolis from the energy calculation of $PrCl_3$,[20] are taken as the values of the Slater parameters, F_2, F_4, and F_6, and the spin-orbit coupling constant, ζ, the ground state wavefunction, $\psi(J,M_J)$, of Pr^{3+} is given as;

$$\psi(J,M_J) = 0.9873\psi(^3H_4) + 0.1564\psi(^1G_4) - 0.0288\psi(^3F_4). \quad \text{(A1)}$$

Since the mixing among the LS functions is quite small, we

assume that the ground-state wavefunction of Pr^{3+} consists of only the $^3H_4$ state. When this state is put into the crystal field of C_{3v} symmetry, the eigenfunctions $\phi(L,S,J,M_J)$ for the species of C_{3v} become as follows:[16]

$$\begin{aligned} &A_1 \text{ species} && \phi(5,1,4,0),\\ &&& 1/\sqrt{2}\,[\phi(5,1,4,3)-\phi(5,1,4,-3)],\\ &A_2 \text{ species} && 1/\sqrt{2}\,[\phi(5,1,4,3)+\phi(5,1,4,-3)],\\ &E \text{ species} && \phi(5,1,4,\pm4),\ \phi(5,1,4,\pm1),\\ &&& \phi(5,1,4,\mp2). \end{aligned} \tag{A2}$$

The expectation value of the magnetic dipole-moment operator, $\mu_z=-\beta(L_z+2S_z)$, with respect to a wavefunction, $\phi(L,S,J,M_J)$, is given as;

$$\langle\phi(L,S,J,M_J)|\mu_z|\phi(L,S,J,M_J)\rangle = -M_J g, \quad \text{(in units of } \beta) \tag{A3}$$

where g is a Landć g-factor. Although the value of g varies with the quantum numbers, J, L, and S, we assume it to be ~ 1 for the sake of simplicity, because the order of magnitude of g is about one. This approximation is equivalent to neglecting the contribution from the spin part of μ_z in Eq. (A3). Thus, the expectation values of μ_z for the three E species of the $^3H_4$ state are ∓4, ∓1, and ±2 respectively.

On the other hand, when Griffith's coupling coefficient[17] are used, the matrix elements of μ_z with respect to the $E_{\pm1}$ species are reduced to;

$$\begin{aligned} \langle E_{\pm1}|\mu_z|E_{\pm1}\rangle &= V\begin{pmatrix} E & E & A_2 \\ \mp1 & \pm1 & \alpha \end{pmatrix}\langle E\|\mu\|E\rangle \\ &= \pm i/\sqrt{2}\,\langle E\|\mu\|E\rangle. \end{aligned} \tag{A4}$$

Noticing that the E_{+1} state corresponds to the $\phi(5,1,4,-4)$, $\phi(5,1,4,-1)$ or $\phi(5,1,4,+2)$ function from their transformations under the symmetry operations of C_{3v}, and that the value of Eq. (A4) should be equal to the mean value of the three direct estimates by Eq. (A3) because the transitions from these three E species of the $^3H_4$ state can not be separated in our observations, we obtain $\langle E||\mu||E\rangle=-\sqrt{2}\,i$ for the $^3H_4$ state of Pr^{3+}; then, $\langle E||\mu||E\rangle=i/\sqrt{2}$ is obtained for the $^3H_6$ state of Tm^{3+} from similar considerations.

References

1) A. D. Buckingham and P. J. Stephens, *Ann. Rev. Phys. Chem.*, **17**, 399 (1966).

2) For references up to 1970, see the tables cited in: (a) P. N. Schatz and A. J. McCaffery, *Quart. Rev.*, **23**, 552 (1969); *ibid.*, **24**, 329 (1970); (b) D. Caldwell, J. M. Thorne, and H. Eyring, *Ann. Rev. Phys. Chem.*, **22**, 259 (1971).

3) J. G. Foss and M. E. McCarville, *J. Amer. Chem. Soc.*, **87**, 228 (1965).

4) B. Briat, *C. R. Acad. Sci. Paris*, **260**, 853 (1965); B. Briat, M. Billardon, J. Badoz, and J. Lorier, *Anal. Chim. Acta*, **34**, 465 (1966).

5) J. Ferre, A. C. Boccara, and B. Briat, *J. Phys.*, **31**, 631 (1970).

6) H. Kobayashi, M. Shimizu, and Y. Kaizu, This Bulletin, **43**, 2321 (1970).

7) (a) P. J. Stephens, *Chem. Phys. Lett.*, **2**, 241 (1968); (b) P. J. Stephens, *J. Chem. Phys.*, **52**, 3489 (1970).

8) J. Badoz, M. Billardon, A. C. Boccara, and B. Briat, *Symp. Faraday Soc.*, **3**, 27 (1969).

9) P. N. Schatz, A. J. McCaffery, W. Suetaka, G. N. Henning, A. B. Ritchie, and P. J. Stephens, *J. Chem. Phys.*, **45**, 722 (1966).

10) C. H. Henry, S. E. Schnatterly, and C. P. Slichter, *Phys. Rev.*, **137**, A583 (1965).

11) (a) P. J. Stephens, R. L. Mowery, and P. N. Schatz, *J. Chem. Phys.*, **55**, 224 (1971); (b) G. A. Osborne and P. J. Stephens, *ibid.*, **56**, 609 (1972).

12) (a) D. E. Mann, T. Shimanouchi, J. H. Meal, and L. Fano, *J. Chem. Phys.*, **27**, 43 (1957); (b) R. A. Hoffman, *ibid.*, **33**, 1256 (1960); S. Castellano and A. A. Bothner-By, *ibid.*, **41**, 3863 (1964); Y. Kato and A. Saika, *ibid.*, **44**, 2824 (1966).

13) G. H. Dieke, "Spectra and Energy Levels of Rare Earth Ion in Crystals," Interscience Publishers, New York (1968), p. 193.

14) R. Sarup and M. H. Crozier, *J. Chem. Phys.*, **42**, 371 (1965); G. H. Dieke and R. Sarup, *ibid.*, **29**, 741 (1958).

15) J. Sugar, *Phys. Rev. Lett.*, **14**, 731 (1965); J. Sugar, *J. Opt. Soc. Amer.*, **55**, 1058 (1965); H. M. Crosswhite, G. H. Dieke, and W. J. Carter, *J. Chem. Phys.*, **43**, 2047 (1965).

16) B. G. Wybourne, "Spectroscopic Properties of Rare Earths," John Wiley & Sons, Inc., New York (1965), chap. 6.

17) J. S. Griffith, "The Irreducible Tensor Method for Molecular Symmetry Group," Prentice-Hall, Inc., Englewood Cliffs, New Jersey (1962), p. 112.

18) D. N. Olsen and J. B. Gruber, *J. Chem. Phys.*, **54**, 2077 (1971).

19) Recently, we have measured the MCD spectra of rare-earth ethylsulfate crystals, $R(C_2H_5SO_4)_3\cdot9H_2O$ (R=Pr, Nd, Er, and Tm), at liquid helium temperature. The results will be presented in the near future.

20) J. S. Margolis, *J. Chem. Phys.*, **35**, 1367 (1961).