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Magnetic Circular Dichroism of Praseodymium Ethyl Sulfate and Praseodymium-Magnesium Double Nitrate

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The magnetic circular dichroism of praseodymium ethyl sulfate and praseodymium–magnesium double nitrate was measured in the visible wave number region at low temperatures down to 17 K. Analysis was carried out for six absorption bands of praseodymium ethyl sulfate and three bands of praseodymium–magnesium double nitrate. With available information on energy levels, the *g* values of the crystal-field levels relevant to absorptions were derived from the MCD parameters obtained. These values are in good agreement with those from other methods.

During the passed ten years the utility of magnetic circular dicroism (MCD) studies has been presented by many authors,[1] especially for clarifying spectroscopic assignments and characterizing the symmetry and angular momentum properties of both ground and excited states of molecules and ions. However, there are only a few evidences to judge the reliability of the results. It was pointed out that MCD provides fairly reliable spectroscopic splitting factors (*g* value) of some rare earth crystals with the aid of well-established energy levels even when no direct Zeeman components of a transition are resolved.[2–4]

We have measured the MCD spectra of praseodymium ethyl sulfate, $Pr(C_2H_5SO_4)_3 \cdot 9H_2O$ (Pr(ES)), and praseodymium–magnesium double nitrate, $Mg_3Pr_2(NO_3)_{12} \cdot 24H_2O$ (Pr(DN)) at low temperatures, and obtained the *g* values for several crystal-field levels of these crystals.

Results and Discussion

The preparation of the Pr(ES) crystal has been reported.[2] Pr(DN) was prepared by the method described by Jantsch.[5] An aqueous solution of stoichiometric amount of $Pr(NO_3)_3 \cdot 6H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ was allowed to evaporate slowly. After a month, a transparent single crystal of double nitrate grew in the form of a thick hexagonal plate $30 \times 30 \times 8$ mm^3, with a well-developed face perpendicular to the principal axis of the crystal. The details of absorption and MCD measurements at low temperatures with use of a metal Dewar vessel have been reported.[2,3] The temperature of crystals cooled by thermal conduction was measured with an Au–Co *versus* chromel thermocouple with one junction pressed directly against the crystal and found to be 80 ± 1 and 17 ± 1 K at liquid nitrogen and helium temperatures, respectively.

The general expression for the MCD of an absorption[6,7] can be applied to a uniaxial crystal such as Pr(ES) and Pr(DN). The ellipticity accompanied by an electronic transition is given by

$$\theta = -\frac{4}{3}\gamma N_a[Af_1/\hbar + (B + C/kT)f_0]H. \tag{1}$$

The explicit expressions for the MCD parameters *A*, *B*, and *C* are given elsewhere.[1,2] The condition assumed in the derivation of Eq. 1 (the Zeeman energy is less than the zero-field state separation, line width and kT) are still satisfied in the present measurements. The ratios of the MCD parameters to the dipole strength D $(=(1/d_a)|\langle a|\boldsymbol{m}|j\rangle|^2)$ are related to the *g* values of the ground a and excited j states in a transition as[8]

$$|A/D| = |g_j - g_a|, \quad |C/D| = |g_a|, \tag{2}$$

where the Zeeman splitting is taken as $2g\beta H$ since there are no multiplets except for the doublet in both Pr(ES) and Pr(DN). We see that term *C* can arise only when the ground state is degenerate, whereas term *A* has the value when the ground and/or excited states are degenerate.

There are 13 ion levels for a trivalent Pr ion with $4f^2$ configuration in the aforementioned crystals, an ion level placed in a crystal-field splitting into several crystal-field levels designated by the crystal quantum number η after Hellwege.[9] From the results of X-ray analyses,[10] the site symmetries around a Pr^{3+} ion in the ethyl sulfate and double nitrate crystals are known to be D_{3h} and C_{3v}, respectively. Thus the crystal-field levels in Pr(ES) and Pr(DN) are classified by $\eta = 0$, ± 1, ± 2, and 3, and $\eta = 0$ and ± 1 respectively, where the levels with double signs are twofold degenerate. The crystal levels in the visible region of Pr(ES)[11,12] and Pr(DN)[13,14] have been determined. The energy level diagrams of these crystals relevant to the present analysis are shown in Fig. 1, in which σ-transitions observed in the present experiments are indicated by lines with arrow. The absorption and MCD spectra

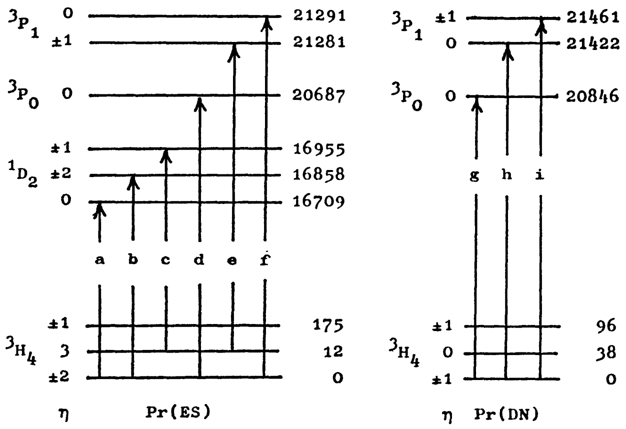

Fig. 1. Energy level diagrams of Pr(ES) and Pr(DN). The units of energy are in cm^{-1}. Allowed σ-transitions are indicated by arrows.

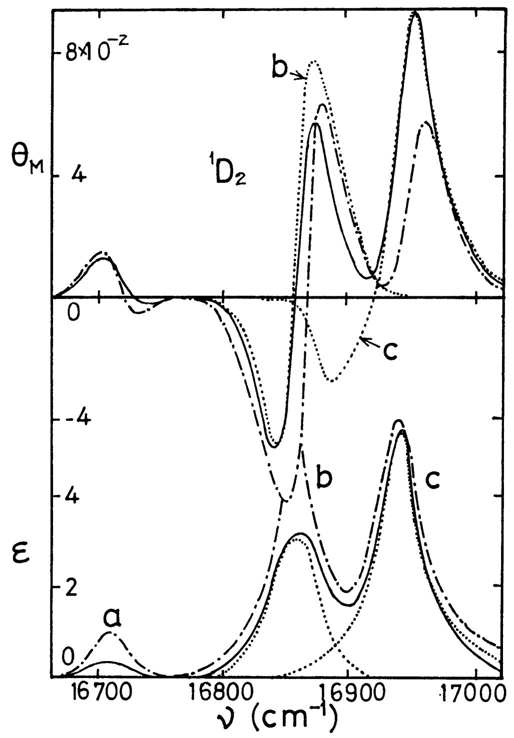

Fig. 2. Absorption and MCD spectra for the $^3H_4 \rightarrow {}^1D_2$ transition of Pr(ES) at 17 (solid line) and 80 K (chain line). The curves shown by dotted lines are those resolved into the constituent curves at 17 K. θ_M and ε are the MCD in molar ellipticity units (K dl dm^{-1} mol^{-1}) per unit gauss and molar extinction coefficient respectively.

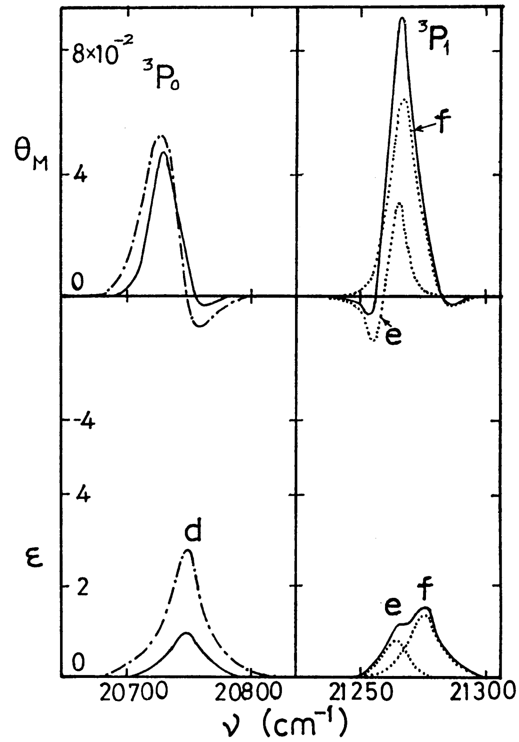

Fig. 3. Absorption and MCD spectra for the $^3H_4 \rightarrow {}^3P_0$, $^3P_1$ transitions of Pr(ES) at 17 (solid line) and 80 K (chain line). See the note in Fig. 2.

observed are shown in Figs. 2—4, where molar extiction coefficient ε and molar ellipticity θ_M in terms of K dl dm^{-1} mol^{-1} G^{-1} are used for the sake of convenience. The lowest crystal-field level of the $^3H_4$ state of Pr(ES) is doubly degenerate ($\eta = \pm 2$), and the population of the next level ($\eta = 3$), which is 12 cm^{-1} higher than the lowest level, is 36% that of the latter at 17 K. Thus it is necessary to take account of σ-transitions from these two levels for Pr(ES) (Fig. 1). On the other hand, all the absorption bands of Pr(DN) at 17 K might arise from only the lowest crystal-field level $^3H_4$ ($\eta = \pm 1$), since the population of the next level ($\eta = 0$), 38 cm^{-1} higher than the lowest level, is 4% that of the latter at 17 K.

A summary of the MCD parameters derived from the method of moments[7,15] is given in Table 1. Separation of term C from term B can be performed by means of the temperature dependence of θ_M as shown in Fig. 5. The A/D value for a transition should be independent

Table 1. MCD parameters divided by dipole strength D, central frequency ν_0 and half-width Γ at $1/e$ of the maximum absorption in Pr(ES) and Pr(DN). Values in parentheses are assumed ones

Transition	T (K)	ν_0 (cm^{-1})	Γ (cm^{-1})	D (10^{-4}D^2)	A/D (β)	$(B+C/kT)/D$ (β/cm^{-1})	B/D (β/cm^{-1})	C/D (β)
Pr(ES)								
(a) $^3H_4(\pm 2) \longrightarrow {}^1D_2(0)$	80	16708	24	0.225	−0.751	−0.0360	−0.0225	−0.75
	17	16709	20	0.080	−0.801	−0.0861		
(b) $^3H_4(\pm 2) \longrightarrow {}^1D_2(\pm 2)$	80	16858	26	1.401	2.02	0.0128	0.0262	(−0.77)
	17	16858	31	0.905	2.09	−0.0371		
(c) $^3H_4(3) \longrightarrow {}^1D_2(\pm 1)$	80	16941	26	1.470	1.04	−0.0209	−0.0244	0
	17	16942	26	1.599	1.13	−0.0278		
(d) $^3H_4(\pm 2) \longrightarrow {}^3P_0(0)$	80	20686	21	0.508	−0.796	−0.0419	−0.0286	−0.74
	17	20687	21	0.173	−0.771	−0.0913		
(e) $^3H_4(3) \longrightarrow {}^3P_1(\pm 1)$	17	21269	14	0.092	1.61	−0.0527	−0.0527	0
(f) $^3H_4(\pm 2) \longrightarrow {}^3P_1(0)$	17	21291	19	0.219	−0.791	−0.112	−0.0477	(−0.77)
Pr(DN)								
(g) $^3H_4(\pm 1) \longrightarrow {}^3P_0(0)$	80	20847	43	0.055	−0.775	−0.0165	−0.0017	−0.82
	17	20845	43	0.087	−0.791	−0.0719		
(h) $^3H_4(\pm 1) \longrightarrow {}^3P_1(0)$	17	21421	24	0.256	0.800	−0.0780	−0.0120	(−0.79)
(i) $^3H_4(\pm 1) \longrightarrow {}^3P_1(\pm 1)$	17	21461	29	0.197	2.05	−0.0666	−0.0016	(0.79)

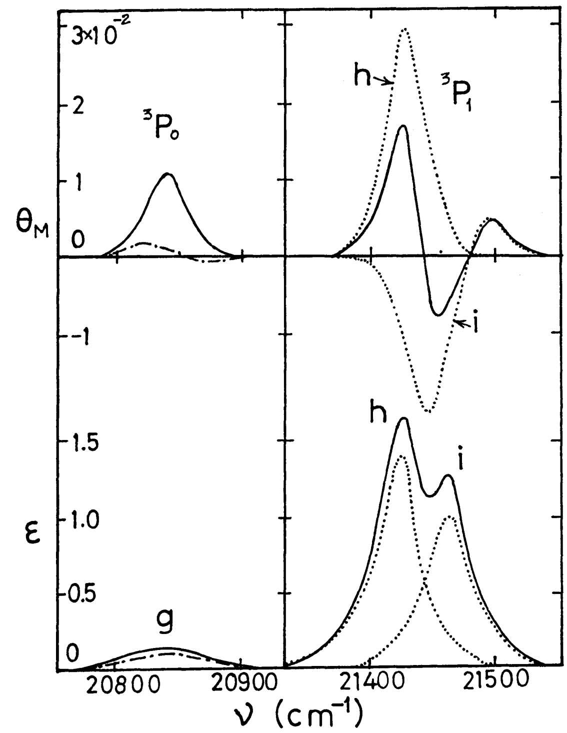

Fig. 4. Absorption and MCD spectra of Pr(DN) at 17 (solid line) and 80 K (chain line). See the note in Fig. 2.

of temperature. This is satisfied for both Pr(ES) and Pr(DN) (Table 1). Absolute C/D values for various transitions from the same lower level should be identical, indicating the $|g|$ value of this level. Although the absorption bands (b) and (c) in Pr(ES) overlap each other (Fig. 2), separation of the experimental MCD into the MCD's corresponding to these absorption bands is possible when we take the $|C/D|$ values of the $\eta=\pm 2$ and 3 levels of the $^3H_4$ state to be 0.77 β and 0 β, respectively. The former is the average value obtained from the band (a) and (d), for which all the $|A/D|$ and $|C/D|$ values should be equal since both bands correspond to the transitions from the lowest crystal-field level $^3H_4$ ($\eta=\pm 2$) to non-degenerate excited levels. The latter value should, in principle, be zero since the lower level $^3H_4(\eta=3)$ is non-degenerate. The absorption and MCD curves for each of the bands (b) and (c) (dotted lines, Fig. 2) originate from a curve fitting by using the values given in Table 1 for central frequencies, half-widths and dipole strengths, and by adopting the above values for $|C/D|$ values, the Gaussian form for the shape function f_0 and then the rigid shift model[7] ($f_1=\mathrm{d}f_0/\mathrm{d}\nu$) in Eq. 1. For both absorption and MCD, the sum of two constituent curves reproduces satisfactorily the experimental curve. A similar treatment is applied to the separation of other overlapping absorption and MCD curves into the constituent curves; *i.e.*, the (e) and (f) bands in Pr(ES), and the (h) and (i) bands in Pr(DN). Thus all the MCD parameters for observed bands can be determined. As expected, B terms due to higher-order perturbation are small as compared to the other terms, the contribution of B terms to θ_M not being sizable for paramagnetic salts. Ultimately the absolute g value of the ground state of Pr(ES) and that of Pr(DN) are estimated to be 0.77 β and 0.79 β, respectively. The g values for excited crystal-field levels can be evaluated by using Eq. 2. The absolute g values thus obtained are compared with other experimental values by the Zeeman splittings[13,14] and paramagnetic resonances,[16,17] and theoretical values[18] in Table 2. The g values from MCD are in good agreement with the other experimental ones within the experimental error (*ca.* 15%). The theoretical values also agree with the experimental ones except for the g value of the $^1D_2(\eta=\pm 2)$ level in Pr(ES), which is 1.6 times larger than the experimental value. For theoretical g values of rare earth crystals by the wavefunctions determined so as to get the best agreement of calculated energies

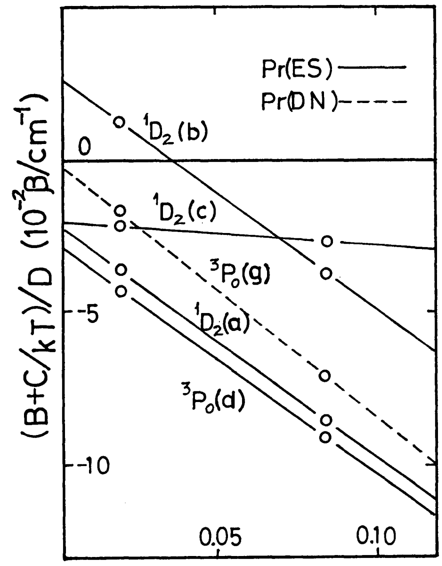

Fig. 5. Temperature dependence of $(B+C/kT)/D$ of Pr(ES) (solid line) and Pr(DN) (broken line) obtained by the moment analysis.

TABLE 2. COMPARISON OF THE g VALUES IN Pr(ES) AND Pr(DN)

Level	Energy (cm⁻¹)	Absolute value of g		
		MCD[a]	Zeeman[b]	Calcd[c]
Pr(ES)				
$^3H_4(\pm 2)$	0	0.77	0.85(0.775)	0.86
$^1D_2(\pm 2)$	16858	1.30	1.30	2.07
(± 1)	16955	1.09		1.03
$^3P_1(\pm 1)$	21281	1.61	1.39	1.50
Pr(DN)				
$^3H_4(\pm 1)$	0	0.79	0.72(0.725)	0.67
$^3P_1(\pm 1)$	21461	1.24	1.17	1.50

a) As the g value of an excited level, two kinds of values are derived from Eq. 2, the value close to those by the other methods being adopted. b) The values from Refs. 13 and 14 for Pr(ES) and Pr(DN), respectively. The values by paramagnetic resonances are given in parentheses. See Refs. 16 and 17 for Pr(ES) and Pr(DN), respectively. c) The values from Ref. 18.

with the observed values obtained from crystal spectra, it frequently occurs that only for few specific crystal-field levels the calculated g values differ considerably from the observed ones, although there is good agreement between both values for most crystal-field levels.[19,20] This problem is further discussed elsewhere.[18] The present analysis has confirmed previous results,[2-4] *viz.*, with available information on energy levels, the g values obtained from the MCD measurement of Pr crystals as well as those from the Zeeman effects and paramagnetic resonances are reliable.

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