

# EPR SPECTRUM OF GADOLINIUM IN HYDRATED PRASEODYMIUM NITRATE

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## ABSTRACT

The paramagnetic resonance spectrum of  $Gd^{3+}$  in  $Pr(NO_3)_3 \cdot 6H_2O$  single crystals, is studied at room temperature. A seven line spectrum for  $H//Z$  as well as for  $H//X$  corresponding to  $\Delta M = \pm 1$  transitions is observed along with a number of low field transitions ( $\Delta M \geq 2$ ). The spin-Hamiltonian analyses is presented.

## INTRODUCTION

RECENTLY we have studied the paramagnetic resonance<sup>1</sup> of  $Gd^{3+}$  doped in  $SmCl_3 \cdot 6H_2O$  single crystals. Earlier Weger and Low<sup>2</sup> have reported the results on  $Gd^{3+}$  doped  $LaCl_3 \cdot 7H_2O$  and Johnston, Wong and Stafsudd<sup>3</sup> on  $Gd^{3+}$  doped  $La_2(SO_4)_3 \cdot 9H_2O$  single crystals. We felt that it would be interesting to extend the study to some of the other hydrated salts. The present paper deals with the paramagnetic resonance of  $Gd^{3+}$  doped  $Pr(NO_3)_3 \cdot 6H_2O$  single crystals.

## THEORY

The resonance field equations for  $H//Z$  corresponding to  $\Delta M = \pm 1$  are given in the earlier paper<sup>1</sup> along with the transformations of  $b_n^m$  needed to get the resonance field equations for  $H//X$ . By making use of the earlier literature<sup>2,4,5</sup> it can be shown that the resonance field equations for  $H//Z$  corresponding to the observed low field transitions ( $\Delta M \geq 2$ ) are as follows:

$$\begin{aligned} -\frac{1}{2} \rightarrow -\frac{5}{2}: \quad g\beta H \\ = \frac{1}{2} \left[ h\nu + 6b_2^0 - 22b_4^0 + E \left\{ \frac{60}{1+F} - \frac{90}{1-3F} \right\} \right]; \end{aligned}$$

$$\begin{aligned} \frac{3}{2} \rightarrow -\frac{3}{2}: \quad g\beta H \\ = \frac{1}{3} \left[ h\nu + E \left\{ \frac{42}{1-25F^2} - \frac{120}{1-F^2} \right\} \right], \end{aligned}$$

$$\frac{1}{2} \rightarrow -\frac{5}{2}: g\beta H$$

$$= \frac{1}{3} \left[ h\nu + 6b_2^0 - 22b_4^0 + E \left\{ \frac{270F}{1-9F^2} - \frac{60}{1-F} \right\} \right],$$

$$-\frac{1}{2} \rightarrow -\frac{7}{2}: g\beta H$$

$$= \frac{1}{3} \left[ h\nu + 12b_2^0 - 2b_4^0 + 6b_6^0 + E \left\{ \frac{60}{1+F} - \frac{21}{1-5F} - \frac{45}{1-3F} \right\} \right],$$

$$\frac{5}{2} \rightarrow -\frac{3}{2}: g\beta H$$

$$= \frac{1}{4} \left[ h\nu - 4b_2^0 + 10b_4^0 + 14b_6^0 + E \left\{ \frac{21}{1-5F} - \frac{60}{1-F} - \frac{45}{1+3F} \right\} \right],$$

$$\frac{5}{2} \rightarrow -\frac{5}{2}: g\beta H = \frac{1}{5} \left[ h\nu - E \left\{ \frac{90}{1-9F^2} \right\} \right],$$

$$\frac{3}{2} \rightarrow -\frac{7}{2}: g\beta H$$

$$= \frac{1}{5} \left[ h\nu + 10b_2^0 + 10b_4^0 - 8b_6^0 - E \left\{ \frac{210F}{1-25F^2} + \frac{60}{1+F} \right\} \right],$$

$$\frac{7}{2} \rightarrow -\frac{7}{2}: g\beta H = \frac{1}{7} \left[ h\nu - E \left\{ \frac{42}{1-25F^2} \right\} \right]$$

where

$$F = \frac{b_2^0}{g\beta H}; \quad E = \frac{(b_2^0)^2}{18g\beta H}.$$

## EXPERIMENTAL RESULTS AND DISCUSSIONS

The experimental procedure and method of growing  $\text{Gd}^{3+}$  doped  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  single crystals are the same as reported in the earlier paper.<sup>1</sup>  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  is a triclinic crystal for which no crystallographic structure seems to be available. The EPR of  $\text{Gd}^{3+}$  doped in this crystal shows a seven line spectrum for  $\text{H} // \text{Z}$  as well as for  $\text{H} // \text{X}$  corresponding to the  $\Delta M = \pm 1$  transitions. The spectra obtained are given in Figs. 1 and 2, respectively.

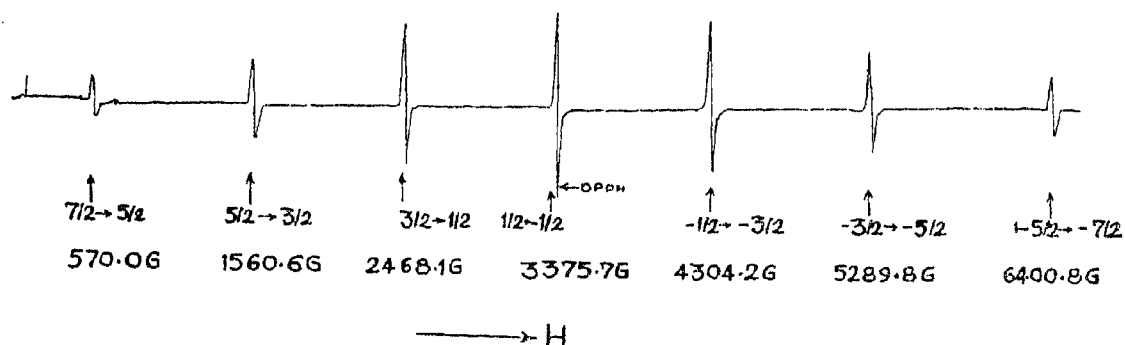


FIG. 1. EPR spectrum of  $\text{Gd}^{3+}$  in single crystals of  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  at  $\text{H} // \text{Z}$  direction.

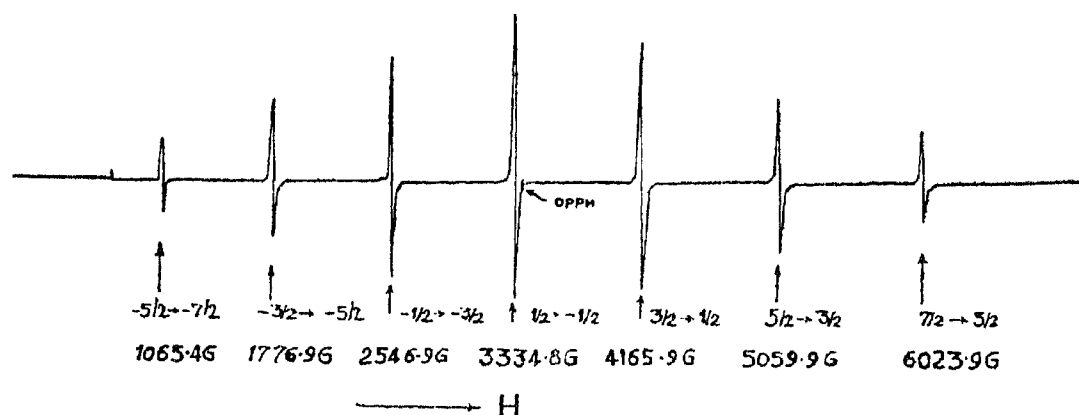


FIG. 2. EPR spectrum of  $\text{Gd}^{3+}$  in single crystals of  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  at  $\text{H} // \text{X}$  direction.

The peak to peak derivative width of  $\Delta M = \pm 1$  transitions is about 14–17 gauss which is much less than that reported earlier in the case of  $\text{Gd}^{3+}$  doped  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  single crystals. Apart from the  $\Delta M = \pm 1$  transitions a number of low field transitions are also observed in the present case. These varied in position and intensity as the magnetic field is rotated with respect to the Z-axis. A careful study of these lines is made for  $\text{H} // \text{Z}$  direction and the observed transitions are shown in Fig. 3 along with  $\Delta M = \pm 1$  transitions. The parameters of the spin-Hamiltonian have been obtained in the manner described in the earlier paper<sup>1</sup> and are given in Table I, where the parameters obtained earlier<sup>1</sup> in the case of  $\text{Gd}^{3+}$  doped  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  are also included for the sake of comparison. The absolute sign of  $b_2^0$  could not be

determined in the present experiment since the measurements made here are at room temperature. We assumed  $b_2^0$  to be positive and found the relative signs of the different  $b$  parameters.

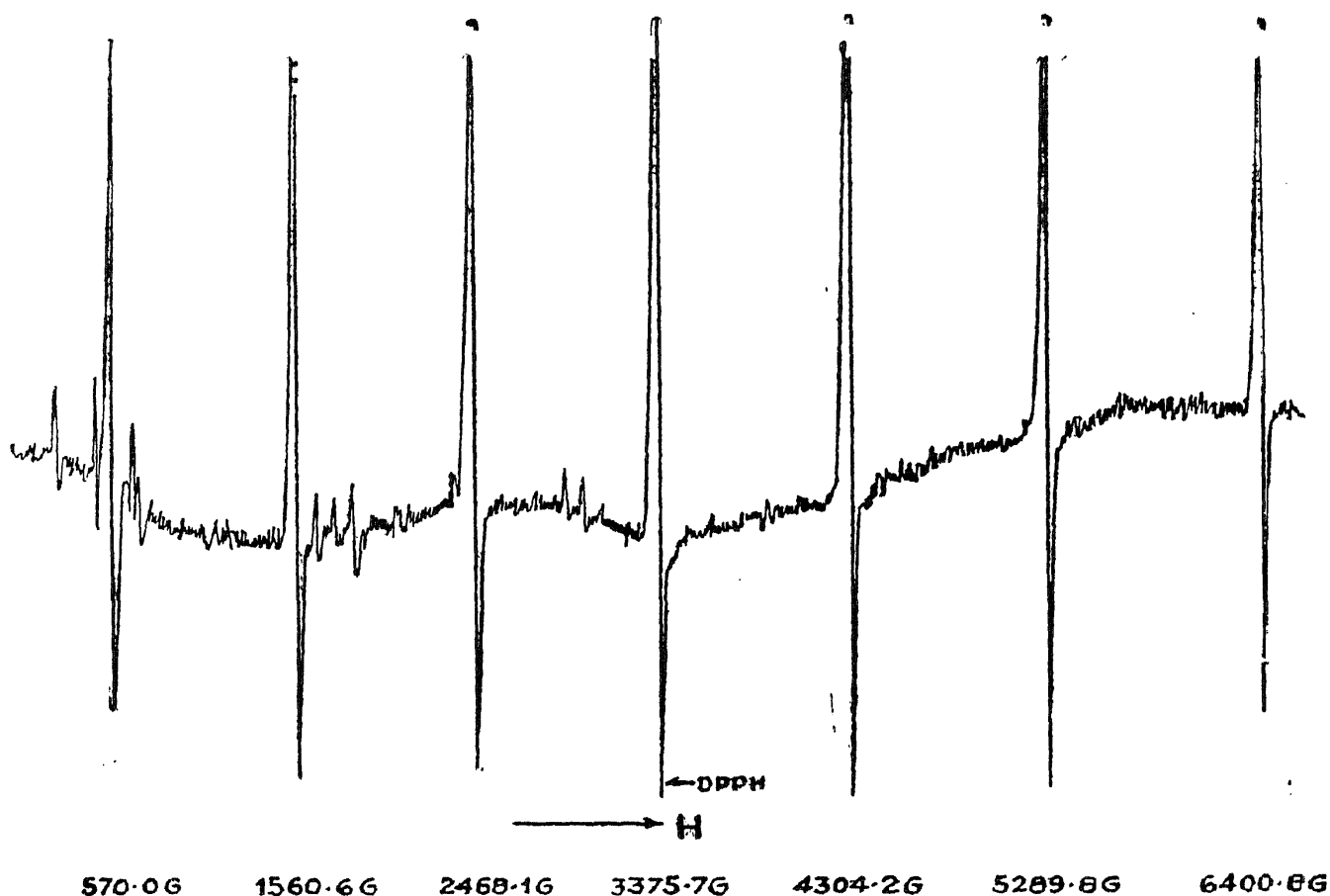


FIG. 3. Low field transitions ( $\Delta M \geq 2$ ) of  $Gd^{3+}$  in single crystals of  $Pr(NO_3)_3 \cdot 6H_2O$  along with seven  $\Delta M = \pm 1$  transitions at  $H//Z$  direction.

TABLE I

*The spin-Hamiltonian parameters of  $Gd^{3+}$  doped  $Pr(NO_3)_3 \cdot 6H_2O$  and  $SmCl_3 \cdot 6H_2O$  single crystals*

$Gd^{3+}$ doped $Pr(NO_3)_3 \cdot 6H_2O$			$Gd^{3+}$ doped $SmCl_3 \cdot 6H_2O$	
$g_{  }$	..	...	$1.993 \pm .002$	$1.990 \pm .002$
$g_{\perp}$	..	..	$1.987 \pm .002$	$1.990 \pm .002$
$b_2^0$	..	..	488.5 (G)	667.7 (G)
$b_4^0$	...	..	1.6	-12.0
$b_6^0$	..	..	0.11	-0.87
$b_2^2$	..	..	-377.5	-426.3
$b_4^4 - b_4^2$	...	...	11.2	48.64
$b_6^6 - b_6^4 + b_6^2$	...	...	5.83	-11.39

The resonance fields corresponding to  $\Delta M = \pm 1$  transitions for H//Z, calculated using the parameters listed in Table I, are given in Table II along with the observed resonance fields for H//Z in the case of  $Gd^{3+}$  doped  $Pr(NO_3)_3 \cdot 6H_2O$  single crystals. The corresponding observed values for H//X are also included in Table II. The relative separations between the four doublets pertaining to the zero-field energy levels, are calculated and are given in Table III along with the relative separations reported earlier<sup>1</sup> in the case of  $Gd^{3+}$  doped  $SmCl_3 \cdot 6H_2O$  single crystals.

TABLE II

*Observed and calculated  $\Delta M = \pm 1$  transitions of  $Gd^{3+}$  in  $Pr(NO_3)_3 \cdot 6H_2O$  single crystals*

Transition	H parallel to the Z-axis		H parallel to the X-axis
	Observed	Calculated	Observed
$5/2 \rightarrow 7/2$	570.0 (G)	563.8 (G)	6023.9 (G)
$3/2 \rightarrow 5/2$	1560.6	1544.3	5059.9
$1/2 \rightarrow 3/2$	2468.1	2470.3	4165.9
$-1/2 \rightarrow 1/2$	3375.7	3379.8	3334.8
$-3/2 \rightarrow -1/2$	4304.2	4305.0	2546.9
$-5/2 \rightarrow -3/2$	5289.8	5291.1	1776.9
$-7/2 \rightarrow -5/2$	6400.8	6401.0	1065.4
DPPH marker	...	3385.8 (G)	...

It may be noted here that Drumheller<sup>6</sup> has reported earlier low field transitions up to  $\Delta M = \pm 1$  in the case of  $BaF_2 : Gd^{3+}$  and Low and Shaltiel<sup>7</sup> reported transitions up to  $\Delta M = \pm 5$  in case of  $ThO_2 : Gd^{3+}$ . An attempt is made to identify the low field transitions in the present experiments by comparing the observed transitions with the theoretically expected positions. The resonance fields corresponding to these lines are listed in Table IV along with the assigned transitions and the theoretically expected resonance fields. The assignments are to be taken as tentative as these are involving very large values of  $\Delta M$ . These assignments, if correct, indicate the presence of a large amount of mixing of the different states at low field values.

TABLE III

*Relative separations between the zero-field energy levels of  
Gd<sup>3+</sup> doped Pr (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and SmCl<sub>3</sub>·6H<sub>2</sub>O*

	Gd <sup>3+</sup> doped Pr (NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O kmc.	Gd <sup>3+</sup> doped SmCl <sub>3</sub> ·6H <sub>2</sub> O kmc.
$\pm 7/2 \leftarrow \rightarrow \pm 5/2$	7.74	10.0
$\pm 5/2 \leftarrow \rightarrow \pm 3/2$	4.93	7.1
$\pm 3/2 \leftarrow \rightarrow \pm 1/2$	6.01	7.4

TABLE IV

*Low field transitions of Gd<sup>3+</sup> doped Pr (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O*

Transition	Relative intensity (measured to within 20%)	Observed	Expected
$-1/2 - 5/2$	5	3026 (G)	3036 (G)
$3/2 - 3/2$	16	728	$719 \pm 7$
$1/2 - 5/2$	5	1777	1753
$(-1/2 - 7/2)^+$	5	2937	2985
$(5/2 - 3/2)^+$	16	350	$416 \pm 3$
$5/2 - 5/2$	10	753	748
$3/2 - 7/2$	9	1669	1668
$(7/2 - 7/2)^+$	24	530	491
Unassigned*	15	1861	...

+ The transitions indicated in parentheses show larger deviations between observed and calculated values than others. They are therefore to be taken as doubtful assignments.

\* The origin of this line is not well understood. It might be due to some impurity.

There are two isotopes of Gd<sup>3+</sup> (155, 157) that have a nuclear spin 3/2 with relative abundance 14.7 and 15.7 per cent, respectively. The Gd<sup>156</sup>, Gd<sup>158</sup>, Gd<sup>160</sup> and others which total about 70% will have no hyperfine interaction while Gd<sup>155</sup> and Gd<sup>157</sup> will have. The absence of the hyperfine structure

in the present experiments could be explained probably due to the large width of the lines. It may be noted that the hyperfine structure<sup>6-8</sup> reported so far for  $Gd^{3+}$  is either in the case of samples enriched<sup>8</sup> with  $Gd^{155, 157}$  or in the cases where the transitions are sufficiently narrow<sup>7, 9-11</sup> for the hyperfine structure to be clearly visible.

The presence of only one set of spectrum corresponding to  $\Delta M \pm 1$  transitions in the case of  $Gd^{3+}$  doped  $Pr(NO_3)_3 \cdot 6H_2O$  shows that gadolinium ion occupies only one kind of observable site in  $Pr(NO_3)_3 \cdot 6H_2O$ . The fact that the zero-field splitting ( $\pm 7/2 \leftrightarrow \pm 1/2$ ) is approximately 18.68 kmc. in the case of  $Gd^{3+}$  doped  $Pr(NO_3)_3 \cdot 6H_2O$  as against 24.5 kmc. in the case of  $Gd^{3+}$  doped  $SmCl_3 \cdot 6H_2O$  indicates that the crystalline electric field experienced by  $Gd^{3+}$  ion due to the ligands is much weaker in the case of  $Pr(NO_3)_3 \cdot 6H_2O$  than in the case of  $SmCl_3 \cdot 6H_2O$ .

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