

# THE $^1I_6$ STATE OF $Pr^{3+}$ IN $LaCl_3$ AT $77^\circ K$ .

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## ABSTRACT

A single crystal of 5%  $Pr^{3+}$  in  $LaCl_3$  was grown by Stockbarger's method and its absorption spectrum at  $77^\circ K$ . recorded in the region 4200–5400 Å on a grating spectrograph having a dispersion of 5 Å/mm. in the first order. Polarization of the absorption lines has also been obtained. In the group of lines arising from  $^1I_6 \leftarrow ^3H_4$  transition, six more lines in addition to the four previously known have been observed. Satisfactory analysis of all these ten lines is given. One additional Stark level in  $^1I_6$  is established at  $21407\text{ cm.}^{-1}$  with  $\mu = 1$ . For a few lines the polarization results obtained here do not agree with those of previous workers but fit in satisfactorily in the analysis.

## INTRODUCTION

THE absorption spectrum of  $PrCl_3$  was obtained and interpreted by Sayre *et al.*<sup>1</sup> in general agreement with what had been found previously for other  $Pr^{3+}$  salts.<sup>2</sup> Judd<sup>3</sup> calculated the approximate positions of the levels and their stark components and found satisfactory agreement between the simplified theory and the experimental results. Dieke and Sarup<sup>4</sup> observed absorption to the previously unknown  $^1I_6$  state which they confirmed by Zeeman effect studies of the absorption lines. However, only three stark levels of  $^1I_6$  state could be established out of seven normally expected to show up at the temperature of liquid helium that they used. During an investigation of the energy levels of  $Tm^{3+}$  in  $LaCl_3$  matrix, we prepared single crystals of  $Pr^{3+}$  and  $Nd^{3+}$  in  $LaCl_3$ , in order to eliminate possible impurity lines from the observed absorption and fluorescence spectra of  $Tm^{3+}$ . It was thought that the higher concentration used (5%) of  $Pr^{3+}$  in  $LaCl_3$  might bring out some of the other stark levels of  $^1I_6$  which Dieke and Sarup<sup>4</sup> could not observe. It has been indeed possible to obtain six more lines in this transition and locate one more stark level. It is also noticed that for two other stark levels the present observations do not agree with those of Dieke and Sarup.<sup>4</sup>

## EXPERIMENTAL

1. *Preparation of single crystal.*—In order to prepare 5%  $Pr^{3+}$  in  $LaCl_3$ , stoichiometric proportions of spectroscopically pure oxides of lanthanum and praseodymium supplied by Johnson and Matthey were taken and converted into chlorides by digesting with pure distilled hydrochloric acid. The solution of mixed chlorides was evaporated to dryness and the mixture was dehydrated under vacuum. The dehydrated mixture was transferred into a specially designed distilling tube made of vycor (Fig. 1 *b*) and was distilled under high vacuum. The distillate was collected at a portion of the main tube in a small crystal-growing tube also of vycor (7 mm. in diameter and 8–10 cm. in length) the lower end of which was drawn out in the form of a narrow capillary and closed. The tube was filled with dry helium at a pressure of a few mm. of mercury and the small tube sealed off from the main

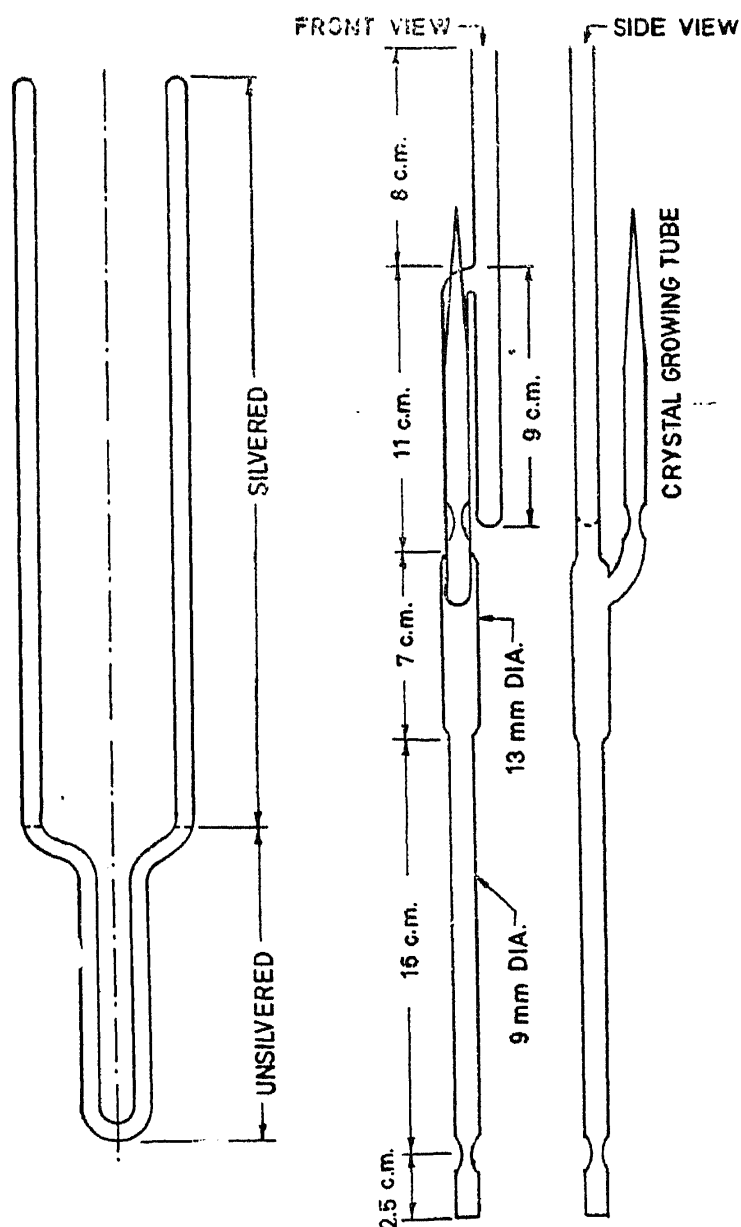


FIG. 1. (a) Pyrex dewar; (b) Distillation tube,

tube. A single crystal was grown by lowering the small tube containing the sample in a temperature gradient furnace at the rate of one inch per day. A good transparent crystal was obtained by this well-known Stockbarger's method.

2. *Observation of the spectra.*—Absorption spectra of this single crystal were photographed at 77° K. in the region 4200–5400 Å on a three-metre Jarrel Ash-grating spectrograph. The grating is 4-inch wide, has 15,000 lines/inch and a dispersion of 5 Å/mm. in the first order. A tungsten ribbon filament lamp operating at 6 volts and 18 amps. provided the necessary continuous spectrum. The tube containing the crystal was kept at the closed unsilvered end of the dewar flask (Fig. 1 *a*) directly immersed in liquid nitrogen. Different parts of the crystal having different thicknesses were used. Spectra were recorded with light incident in a direction perpendicular to the crystal axis. The  $\pi$  and  $\sigma$  components of the polarized spectra denoting electric vector parallel and perpendicular with respect to the  $\bar{C}$ -axis of the crystal,

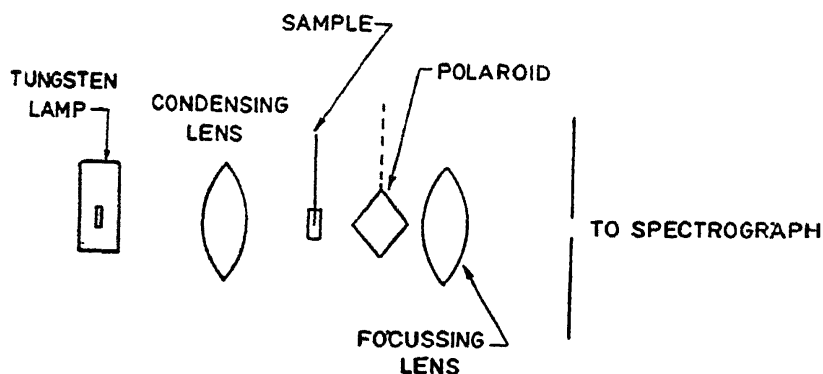


FIG. 2. Optical arrangement for absorption studies.

were separated by a polaroid and recorded. Figure 2 gives the optical arrangement used. Kodak 103 aF and Ilford R-40 plates were used to record the spectra. Times of exposure varied from 10 minutes to 1½ hours. Longer exposures were necessary in order to reduce the width of the broad lines for better measurements. Iron arc spectrum was recorded for standard lines.

### RESULTS AND DISCUSSION

Table I gives the average wavelengths and wave-numbers in vacuum of the expected group of absorption lines as obtained by measurements on several plates, together with their polarizations and visually estimated intensities. Table II is reproduced from the paper of Dieke and Sarup<sup>4</sup> for this group for comparison. The agreement between the four common lines as far as the wave-numbers are concerned is deemed satisfactory. The polarization data for two of the lines, however, do not agree. Figure 3 is an enlarged

TABLE I

*Absorption spectrum of a single crystal of 5%  $Pr^{3+}$  in  $LaCl_3$  at  $77^\circ K$ .*

	$\text{\AA}$	I	$\text{cm.}^{-1}$	Pol
	4670.1	8	21407	$\pi$
	72.4	9 bbd	397	$\sigma$
	79.8	7 bd	362	$\pi$
	85.9	1 d	335	$\sigma$
	90.6	1 d	313	$\pi$
$^1I_6$	94.0	8 bd	298	$\sigma$
	4701.0	6 bbdd	266	$\pi$
	09.2	1 dd	229	$\sigma$
	15.2	4 d	202	$\sigma$
	22.4	2 dd	170	$\pi$

d=diffuse; bb=very broad; b=broad; dd=very diffuse.

TABLE II

 $^1I_6$  Level at  $4.2^\circ K$ . according to Dieke and Sarup<sup>4</sup>

	$\mu'$	$\text{cm.}^{-1}$	Pol	$E''$
	0	21267.5	$\pi$	33
	0	300.0	$\sigma$	0
	0	367.4	$\sigma$	0
$^1I_6$	1	395.6	$\pi$	0

print of the polarized spectrum recording the  $\pi$  and  $\sigma$  components in juxtaposition. It is seen that the lines at 21367 and 21396  $\text{cm.}^{-1}$  of Dieke and Sarup do not agree in polarization with the corresponding lines at 21362 and 21397  $\text{cm.}^{-1}$  in the recorded spectrum.

It may be mentioned that the polarizations of the lines of group  $^3P_1 \leftarrow ^3H_4$  recorded on our plates were checked and found to agree com-

pletely with those reported by Dieke and Sarup<sup>4</sup> and Sayre *et al.*<sup>1</sup> Dieke and Sarup<sup>4</sup> pointed out that  $\text{NdCl}_3$  absorption lines might be mixed up with the  $\text{Pr}^{3+}$  lines in this region which can be resolved only at high resolution and dispersion if  $\text{Nd}^{3+}$  is present as an impurity. Such are  $\text{Nd}^{3+}$  lines at  $21369.56$  and  $21393.35 \text{ cm}^{-1}$  having intensities  $8d$  and  $2d$  and polarizations  $\sigma\pi$  and  $\sigma$  respectively.<sup>5</sup> It is not possible to decide the question of impurity on the basis of the line at  $21397 \text{ cm}^{-1}$  for which the expected polarization is the same for  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$ . But if the line at  $21362 \text{ cm}^{-1}$  for which the observed polarization does not agree with that reported by Dieke and Sarup<sup>4</sup> corresponds to or is mixed up with the  $\text{Nd}^{3+}$  line at  $21369.56 \text{ cm}^{-1}$ , it would have appeared with some intensity also in  $\sigma$  polarization spectrum. It is seen (Fig. 3), however, that this line appears only in the  $\pi$ -polarization. The absence of  $\text{Nd}^{3+}$  as an impurity seems to be further confirmed by the fact that none of the strong lines of  $\text{Nd}^{3+}$  in the region  $4200$  to  $5400 \text{ \AA}$  have been

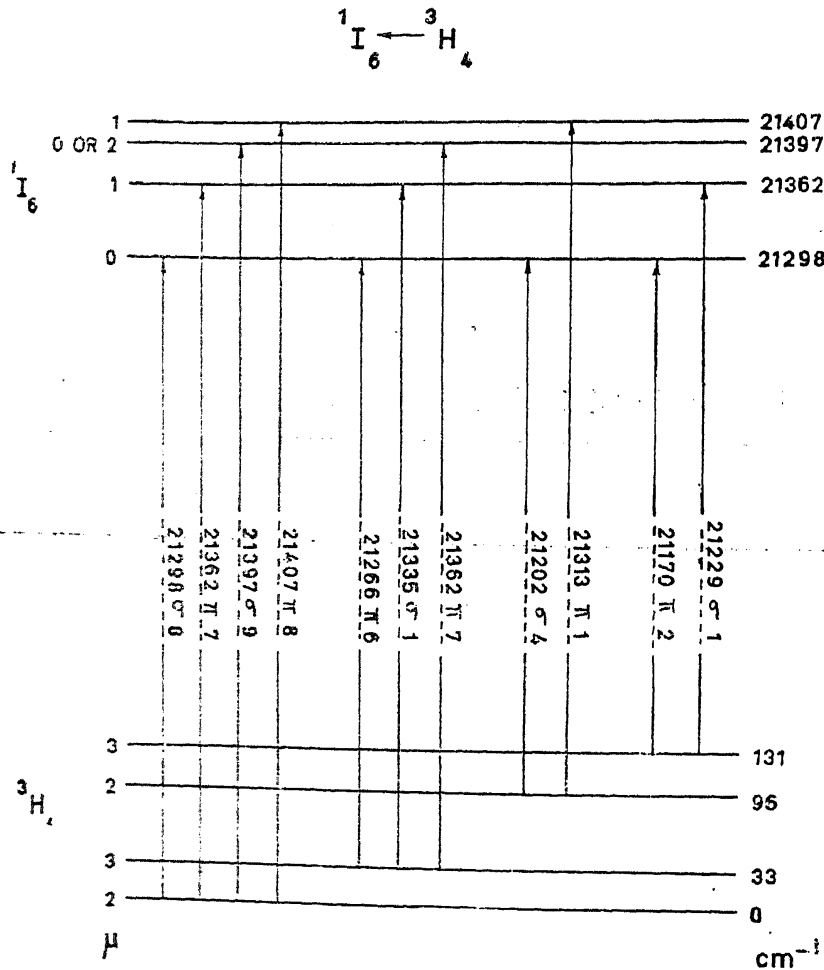


FIG. 4.  $\text{Pr}^{3+}$  in  $\text{LaCl}_3$

observed on the plates. Figure 4 gives the energy level diagram which satisfactorily explains the various lines and their polarizations observed in

the present experiment. The selection rules for electric dipole transitions for an ion of even number of electrons in 4 f shell in a crystal field of  $C_{3h}$  symmetry (shown in Table III) are employed. In this diagram the structure

TABLE III

*Selection rules for electric dipole transitions for  $4f^2$  configuration in a crystal field of  $C_{3h}$  symmetry*

$\mu$	0	$\pm 1$	$\pm 2$	3
0			$\sigma$	$\pi$
$\pm 1$		$\sigma$	$\pi$	$\sigma$
$\pm 2$	$\sigma$	$\pi$	$\sigma$	
3	$\pi$	$\sigma$		

of the ground level  $^3H_4$  as established by Sayre *et al.*<sup>1</sup> and Dieke and Sarup<sup>4</sup> is adopted. For the stark levels of the upper level  $^1I_6$  the energy values reported by Dieke and Sarup<sup>4</sup> with slight modification are adopted but different  $\mu$  values are assigned to them so as to account for the polarizations observed. A new stark level is located at  $21407 \text{ cm.}^{-1}$  in order to explain the prominent absorption lines at  $21407$  and  $21313 \text{ cm.}^{-1}$ . There are a few very faint lines which may be due to superimposed coupled crystal vibrations and are therefore left out of consideration. The line at  $21170 \text{ cm.}^{-1}$  is not easily accounted for. Its low intensity suggests that it may be arising from some upper stark level in the ground state. A transition from  $131 \text{ cm.}^{-1}$  to  $21298 \text{ cm.}^{-1}$  numerically fits this line. Such a transition, however, is forbidden unless the assigned  $\mu$  values are wrong. The  $\mu$  value of level at  $21298 \text{ cm.}^{-1}$  is not likely to be wrong since the Zeeman splitting<sup>4</sup> favours  $\mu = 0$ . But it may not be quite unlikely that the ground level component at  $131 \text{ cm.}^{-1}$  has  $\mu = 3$  in which case the suggested transition will be allowed. Another probability is that the line arises in a transition from some new level in the ground state near  $131 \text{ cm.}^{-1}$  having  $\mu = 3$  to the level at  $21298 \text{ cm.}^{-1}$ .

Two possible transitions are shown for the line at  $21362 \text{ cm.}^{-1}$ . This is because the separations of the concerned levels in the two states is nearly the same. The line being broad it is possible that there is superposition and because both transitions will have identical polarization, it will not be possible to test the possibility of superposition except by employing higher resolution

and dispersion. If the line does involve the transition from  $\mu = 3$  at  $33 \text{ cm.}^{-1}$  in the ground state, the  $\mu$  of the level at  $21397 \text{ cm.}^{-1}$  in the upper state will be definitely determined as 0.

*Note added in Proof*

In a recent paper Margolis (*J. Chem. Phys.*, 1961, **35**, 1367) has reported calculations of energy levels of  $\text{Pr}^{3+}$ . He finds theoretical support to the large Zeeman splitting observed for the lowest level in the  $^1I_6$  state at  $\sim 21298 \text{ cm.}^{-1}$  with  $\mu = 0$ . There is also complete agreement between the calculated and observed facts regarding the next level at  $\sim 21362 \text{ cm.}^{-1}$  with  $\mu = 1$ . For the other two levels observed at  $\sim 21397 \text{ cm.}^{-1}$  with  $\mu = 0$  or 2 and  $\sim 21407 \text{ cm.}^{-1}$  with  $\mu = 1$ , however, the agreement is poor. In a private communication, Professor Dieke agrees with our observations on all the strong lines and the main points of interpretation given in the present paper.

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