

flowers contain the carotenoid pigments in their petals and exhibit a yellow colour. But the intensity of the colour varies from the palest cream to a rich golden hue as determined by the strength of absorption of the blue sector by the pigments. The familiar variations in the colour of the sky from the palest blue to the deepest azure are likewise explicable in terms of the spectral nature of the scattered light in various circumstances. As sunlight is progressively denuded of the components of shorter wavelength in its spectrum by traversing long paths in the atmosphere, a stage is reached when an observer would perceive its colour as yellow. Thus, the colours of the twilight sky can be explained on the same basis as the complementary phenomenon of the blue colour normally exhibited by the sky.

The molecular diffusion of light also plays a highly important role in producing the blue

colour exhibited by the water in deep lakes and by oceanic waters when the turbidity which results in a lack of transparency is at a sufficiently low level. In such cases, it is noticed that the blue colour is much deeper than the colour of the sky. The reason for this difference is to be found in the absorption of sunlight when it traverses long columns of water. This absorption is weak but selective, being confined to the long-wave region in the spectrum. This part of the spectrum would be weakened when the incident light traverses the medium and again after diffusion returns to outer space. As a result of these processes, there would be a large preponderance of the short-wave part of the spectrum in the diffused light emerging from the medium. The highly pronounced blue colour actually exhibited by such waters thus finds a natural explanation.

ON THE ABSORPTION AND FLUORESCENCE SPECTRA OF PRASEODYMIUM DOPED KCl SINGLE CRYSTAL

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INTRODUCTION

THE absorption and fluorescence spectra of Pr^{3+} ion embedded in various solid matrices have been investigated by several workers in the past.¹⁻² Recently some authors³⁻⁵ have reported the fluorescence spectra of certain rare earths doped in NaCl and KCl matrices. The absorption and fluorescence spectra of praseodymium doped in NaCl, KCl and KBr matrices have been the subject of considerable investigation in this laboratory for some time. The results obtained in the spectrum of praseodymium in the KCl matrix are reported in this communication.

EXPERIMENTAL

Single crystals of KCl doped with praseodymium were grown in the following way. Praseodymium oxide was treated with HCl and the chloride solution thus obtained was added to KCl solution so as to obtain 1% concentration of Pr ions in the mixture. The mixture was evaporated to dryness under an infra-red lamp. The dry residue was then transferred to a distillation tube which was attached to a high vacuum line. The tube was heated under vacuum to a temperature of 120–130° C. and

continuously evacuated for 72 hours so as to remove all water of hydration. When this was achieved, the temperature of the tube was further raised to about 900° C. so that its contents could be quickly distilled off. The distillate was collected under vacuum into a vycor crystal-growing tube, which was then filled with dry helium to a pressure of a few cm. of Hg and sealed off from the vacuum line. The crystal-growing tube was then suspended and gradually lowered in the temperature gradient furnace (Stockbarger method), the usual procedure and precautions for growing a crystal as described elsewhere⁶ being adopted.

When the crystal was finally obtained it was found that its upper part was opaque and yellowish-green in colour. This indicates a high concentration of praseodymium in this part of the crystal. The lower part of the crystal was transparent and practically colourless. This portion of the crystal, without removing it from the vycor outer cover, was used to study the absorption and fluorescence spectra of the crystal at liquid nitrogen temperature.

For absorption experiments a tungsten ribbon filament lamp (3 V, 80 A) was used as the source of continuous radiation, while a high

pressure Xenon arc lamp was used with suitable filters for exciting the fluorescence spectrum. The Steinheil 3-prism glass spectrograph with the medium dispersion camera and 3.4 meter Jarrel-Ash grating spectrograph were used to photograph the spectra.

DISCUSSION

Figures 1 and 2 show respectively the absorption and fluorescence spectra of praseodymium recorded in the present investigations. The spectra consist of groups of fairly sharp and in some cases broad and diffuse lines which lie

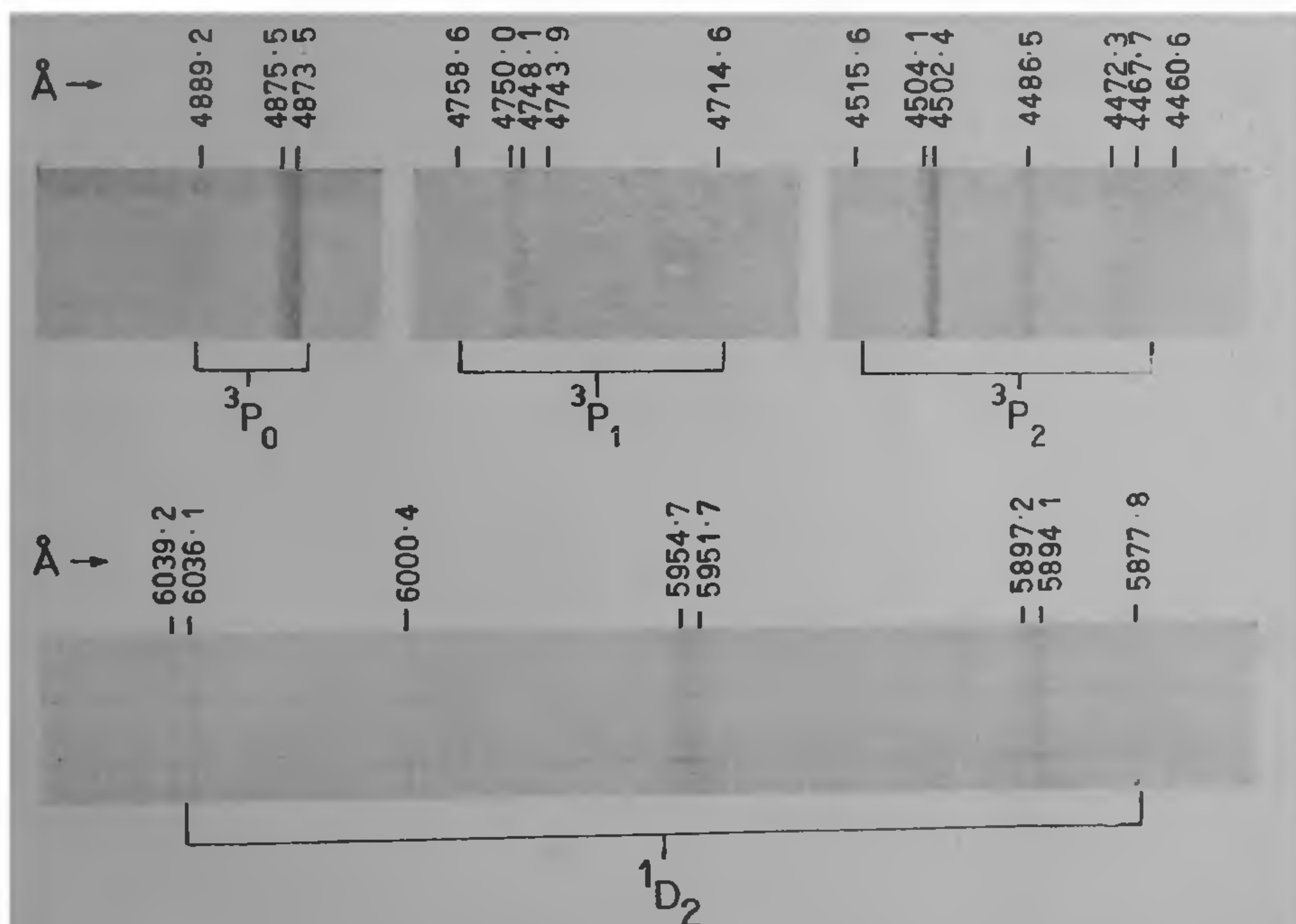


FIG. 1. Absorption spectrum of Pr³⁺ in KCl matrix.
(All transitions are from 3H_1 ground state)

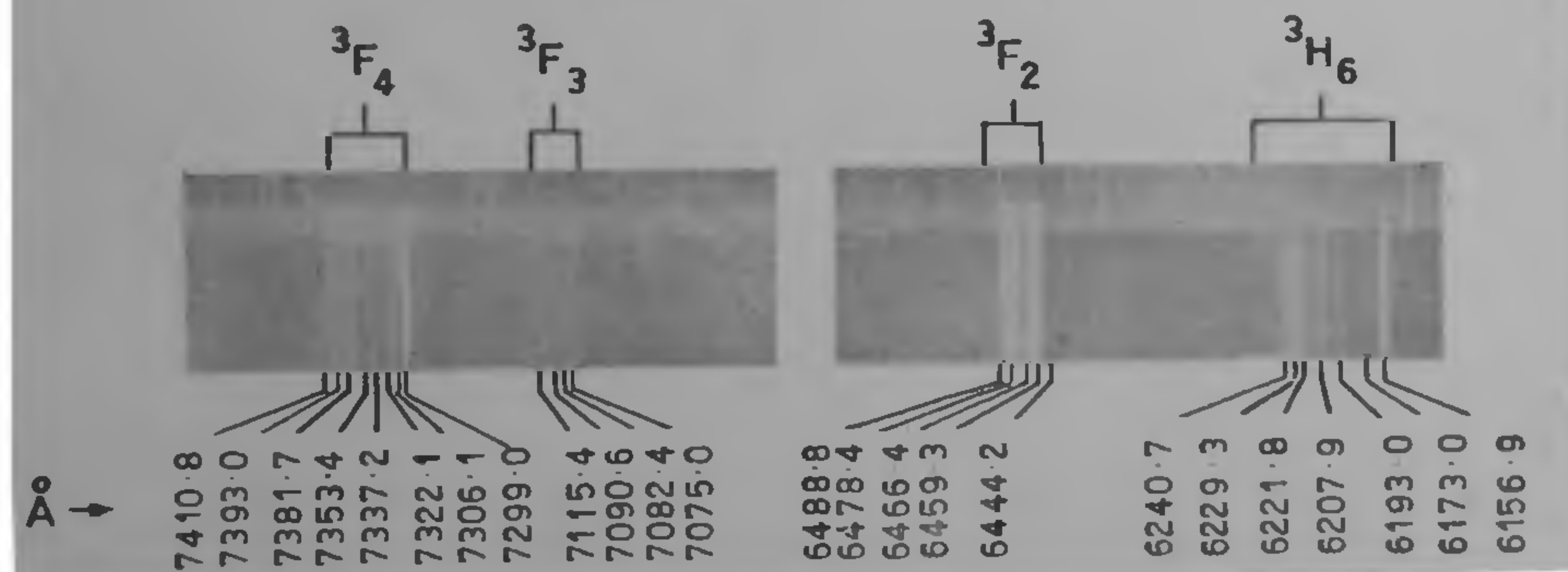


FIG. 2. Fluorescence spectrum of Pr³⁺ in KCl matrix.
(All transitions are from 3P_0 excited state)

near about the same positions as in the corresponding spectra of the Pr^{3+} ion in PrCl_3 , $(\text{Pr} + \text{La})\text{Cl}_3$, etc., crystals.⁷ The wavelengths of the spectral lines have been measured and the relative intensities estimated. A comparison of these data with those already known in the literature for the Pr^{3+} ion shows beyond doubt that praseodymium is in the triply ionized state in the KCl matrix. A tentative analysis of the observed absorption and fluorescence spectra has been made and the energy levels obtained are given in Table I. The first column in Table I gives the terms and the observed

TABLE I

Energy levels of Pr^{3+} ion in KCl matrix

Term	Term value in cm^{-1}
$^3\text{H}_4$ { a ..	0 (13)
{ b ..	8.6 (6)
{ c ..	65.5 (3)
$^3\text{H}_6$ { a ..	4276.1 (1)
{ b ..	4318.5 (1)
{ c ..	4370.3 (1)
{ d ..	4409.5 (1)
{ e ..	4445.5 (1)
{ f ..	4464.9 (1)
{ g ..	4494.2 (1)
$^3\text{F}_2$ { a ..	5000.1 (1)
{ b ..	5036.3 (1)
{ c ..	5053.3 (1)
{ d ..	5081.9 (1)
{ e ..	5105.7 (1)
$^3\text{F}_3$ { a ..	6387.2 (1)
{ b ..	6398.0 (1)
{ c ..	6414.3 (1)
{ d ..	6463.4 (1)
$^3\text{F}_4$ { a ..	6816.9 (1)
{ b ..	6830.2 (1)
{ c ..	6860.4 (1)
{ d ..	6888.2 (1)
{ e ..	6918.2 (1)
{ f ..	6970.3 (1)
{ g ..	6991.0 (1)
{ h ..	7023.5 (1)
$^1\text{D}_2$ { a ..	16562.4 (2)
{ b ..	16660.9 (1)
{ c ..	16797.3 (2)
{ d ..	16961.4 (2)
{ e ..	17008.5 (1)
$^3\text{P}_0$ a ..	20513.6 (3)
$^3\text{P}_1$ { a ..	21055.2 (2)
{ b ..	21074.0 (2)
{ c ..	21204.6 (1)
$^3\text{P}_2$ { a ..	22204.4 (3)
{ b ..	22282.8 (1)
{ c ..	22353.8 (1)
{ d ..	22376.6 (1)
{ e ..	22412.4 (1)

Stark components, which are designated a, b, c, etc., in the order of increasing energy. The figures inside the brackets, in column 2, represent the number of observed transitions involving that level.

The absorption spectrum seems to have revealed all the expected transitions in the region investigated. In absorption spectrograms of multicrystals of Pr^{3+} in KCl matrix, some weak lines are found near about 4650 Å which most likely involve absorption to the $^1\text{I}_6$ state. Further experiments will make the situation clear. The fluorescence spectrum shows only four groups of lines all arising from the $^3\text{P}_0$ state. This shows that in the KCl matrix, the $^3\text{P}_1$ and $^1\text{D}_2$ states, which give rise to fluorescence transitions in the anhydrous $(\text{Pr} + \text{La})\text{Cl}_3$, etc., matrices, are not fluorescent. On the other hand it may be noted that transitions from the $^3\text{P}_0$ level to the $^3\text{F}_3$ level, which have not so far been observed in the fluorescence spectra of the Pr^{3+} ion in other matrices, seem to occur in the KCl matrix.

From Table I it may be observed that in some terms, viz., $^3\text{F}_2$, $^3\text{F}_3$, $^1\text{D}_2$, and $^3\text{P}_2$ the degeneracy is either completely or almost completely removed. This indicates that the Pr^{3+} ion has only a low site symmetry in the KCl matrix.

Single crystals of NaCl and KBr doped with Pr are also grown by the same method. The absorption and fluorescence spectra of Pr in the KBr matrix are similar in their structure to those in the KCl matrix; the line groups are in general displaced to the longer wavelength side. The spectra of Pr in the NaCl matrix are very diffuse. These and other details of the Pr^{3+} spectra in the different matrices will be communicated separately.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. P. Ramakoteswara Rao for help in preparing the manuscript and checking the results and Dr. N. A. Narasimham for his interest in the work.

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