

ULTRA-VIOLET ABSORPTION SPECTRA AND HIGHER EXCITED STATES OF Nd³⁺ IN LaCl₃ AT 77° K.

BY R. M. AGRAWAL, R. K. ASUNDI, F.A.Sc., R. C. NAIK,
D. RAMAKRISHNAN AND SHOBHA SINGH

(Analytical Division, Atomic Energy Establishment, Trombay, Bombay, India)

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INTRODUCTION

THE absorption spectrum of trivalent neodymium in crystals at low temperatures has been investigated by many workers in the past.¹⁻⁴ Recently a rather exhaustive work on the absorption and fluorescence spectra of Nd³⁺ in LaCl₃ was reported by Carlson and Dieke.⁵ However, since the samples were mounted in glass tubes, their absorption data were limited to 30000 cm.⁻¹ only. In the present investigation we have extended the range and explored the region between 30000 and 40000 cm.⁻¹ by growing the experimental crystal in a vycor tube. Neodymium doped LaCl₃ single crystal has been selected for the reason that the lines obtained are sharp and the crystal has a higher symmetry (C_{3h}) for which the theory is rather well established.

EXPERIMENTAL DETAILS

Spectroscopically pure oxides of La and Nd supplied by Johnson and Matthey of England were used for the preparation of the chlorides. The single crystal was grown according to a modified Stockbarger method from the melt of anhydrous chlorides (5% Nd³⁺ in LaCl₃) contained in a sealed and tapering vycor tube filled with dry helium at a few centimetres pressure.⁶ Absorption spectra at 77° K. have been photographed in the second order of the Jarrell Ash 3-metre Ebert grating spectrograph described earlier.⁶ This gives a linear inverse dispersion of 2.5 Å/mm. A high pressure 1,500 watt Xenon-arc lamp provided the necessary continuous spectrum. The intensity of the continuum begins to fall off in the ultra-violet but is sufficiently strong in the region explored. The light beam from this source is condensed by suitable quartz lenses and reflected along the axis of the spectrograph by a highly reflecting aluminised mirror obtained by depositing a fine film of aluminium on a glass plate by vacuum evaporation. Figure 1 shows the optical arrangement used. The tube containing

the crystal was directly immersed in liquid nitrogen contained in a quartz dewar flask similar to one described earlier.⁶ Observations were made with the crystal symmetry axis perpendicular to the light beam. Polarized spectra were obtained with a calcite rhomb kindly supplied by Professor P. K. Kichlu of Delhi University. Suitable filters were used to cut off the first-order spectrum. Kodak III-0 plates were used and the exposure times varied from 15–30 minutes at 3000 Å and 4–5 hours at 2500 Å. Different thicknesses of the crystal could be used and satisfactory results were obtained with thickness of 3–7 mm. Iron arc lines were recorded for standard lines.

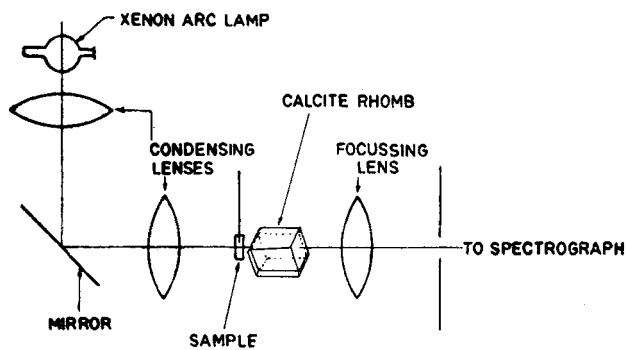


FIG. 1. Optical Arrangement for Absorption Studies

RESULTS AND DISCUSSION

Apart from the already known groups of absorption lines, five new groups of lines have been recorded in the present experiments in the region between 30000 and 40000 cm^{-1} . Table I gives the wavelengths (in air) of absorption lines of these groups as obtained by measurements on several plates, together with the corresponding wave-numbers in vacuum, their observed polarisation and visually estimated intensities. The measurements are correct to $\pm 0.02 \text{ \AA}$ for the sharp lines, the accuracy being slightly lower for diffuse and/or broad lines. These lines are arranged in groups designated by letters N, O, P, Q and T, the groups R, S, A, B \dots , etc., up to M being already reported by Carlson and Dieke.⁵ Wybourne⁷ has calculated the free ion energy values of the various states of Nd^{3+} . C. R. Sharma has also calculated* these values using Wong's method⁸ of a Taylor series expansion of eigen-values. The correspondence between the calculated and observed positions of the levels is sufficiently close to allow the assignment of the newly observed groups as transitions from the ground state $^4I_{9/2}$ to the excited states $^2H_{9/2}$, $^2D_{3/2}$, ($^3H_{11/2}$ and $^2D_{5/2}$), $^2F_{5/2}$ and $^2F_{7/2}$ respectively.

* Private communication.

TABLE I
Absorption lines of Nd³⁺ at 77° K.

Group	State	Calculated free ion energy cm. ⁻¹	λ in air Å	ν vac. cm. ⁻¹	Visual inten- sity	Polarisa- tion
N	² H _{9/2}	32729	3069.49	32569.2	3	π
		(32495)	3068.02	32584.8	2	σ
			3067.30	32592.5	4d	π
			3058.80	32683.1	1d	π
			3056.00	32713.0	0	π
			3052.13	32754.5	7	σ
			3049.35	32784.3	10b	π
O	² D _{3/2}	33771	3022.34	33077.3	4	π
		(33265)	3021.61	33085.3	4	σ
			3021.09	33091.0	1	σ
			3011.13	33200.5	7	σ
			3009.93	33213.7	10b	$\sigma\pi$
P	² H _{11/2} and	34119	2951.89	33866.7	2	$\sigma\pi$
		(33839)	2940.93	33992.9	1	π
	² D _{5/2}	34970	2936.65	34042.5	8	$\sigma\pi$
		(34693)	2936.22	34047.4	4	σ
			2929.42	34126.5	8	$\sigma\pi$
			2920.25	34233.6	3	$\sigma\pi$
Q	² F _{5/2}	39665	2624.38	38092.9	3	π
		(39405)	2623.87	38100.3	3	$\sigma\pi$
			2615.88	38216.7	5	σ or $\sigma\pi$
			2612.66	38263.7	3	$\pi\sigma$
T	² F _{7/2}	41114	2536.66	39410.1	1	..
		(40812)	2533.05	39466.2	4	..
			2530.03	39513.4	1	..
			2529.02	39529.1	4	..
			2528.36	39539.4	2	..
			2522.20	39636.0	3	..
			2520.54	39662.1	1	..

Note.—Values in brackets in column 3 are calculated by C. R. Sharma by Wong's method.⁸ Those not in brackets are from Wybourne.⁷

The relevant data are given in Table I. Group T is recorded with low intensity and it has not been possible to decide definitely about the polarisation of the lines of this group.

TABLE II

Selection rules for electric dipole transitions for an ion of configuration f^{2n+1} in a crystal field of C_{3h} symmetry

μ	$\pm 1/2$	$\pm 3/2$	$\pm 5/2$
$\pm 1/2$..	σ	$\sigma\pi$
$\pm 3/2$	σ	π	σ
$\pm 5/2$	$\sigma\pi$	σ	..

As is seen from data in Table I, the groups appear more or less at expected positions, but it is not found possible to propose any analysis for all of them. It has been possible, however, to analyse group O completely, employing the selection rules for transitions treated as electric dipoles given in Table II, and assuming the μ -values and positions of the various stark levels of the ground state $^4I_{9/2}$ as given by Carlson and Dieke.⁵ The excited state $^2D_{3/2}$ can have but two stark components with μ -values 1/2 and 3/2. From the lowest stark component of the ground state with $\mu = 5/2$, transitions to both these components are expected and observed. These lie at 33200.5 and 33213.7 cm^{-1} . From the other stark components of the ground level at 115 cm^{-1} ($\mu = 1/2$) and 123 cm^{-1} ($\mu = 3/2$) which may be expected to be appreciably populated at 77° K., one and two lines respectively are expected to be observed in absorption to the levels in $^2D_{3/2}$. These are also observed. Other stark components of ground state lie too high (above 240 cm^{-1}) and hence are not appreciably populated at 77° K. to give rise to any absorption lines. Thus five lines in all are expected to show up in absorption as a result of transitions from such of the stark components of the ground state as may be expected to be appreciably populated, to the stark components of $^2D_{3/2}$ and all these are observed in this group. The polarisation and intensity data support the proposed analysis. Plate XXV is a reproduction of the lines in the various groups and contains also the energy level diagram (analysis) of the transition $^2D_{3/2} \leftarrow ^4I_{9/2}$, giving rise to the lines of the O group and their polarisation characteristics.

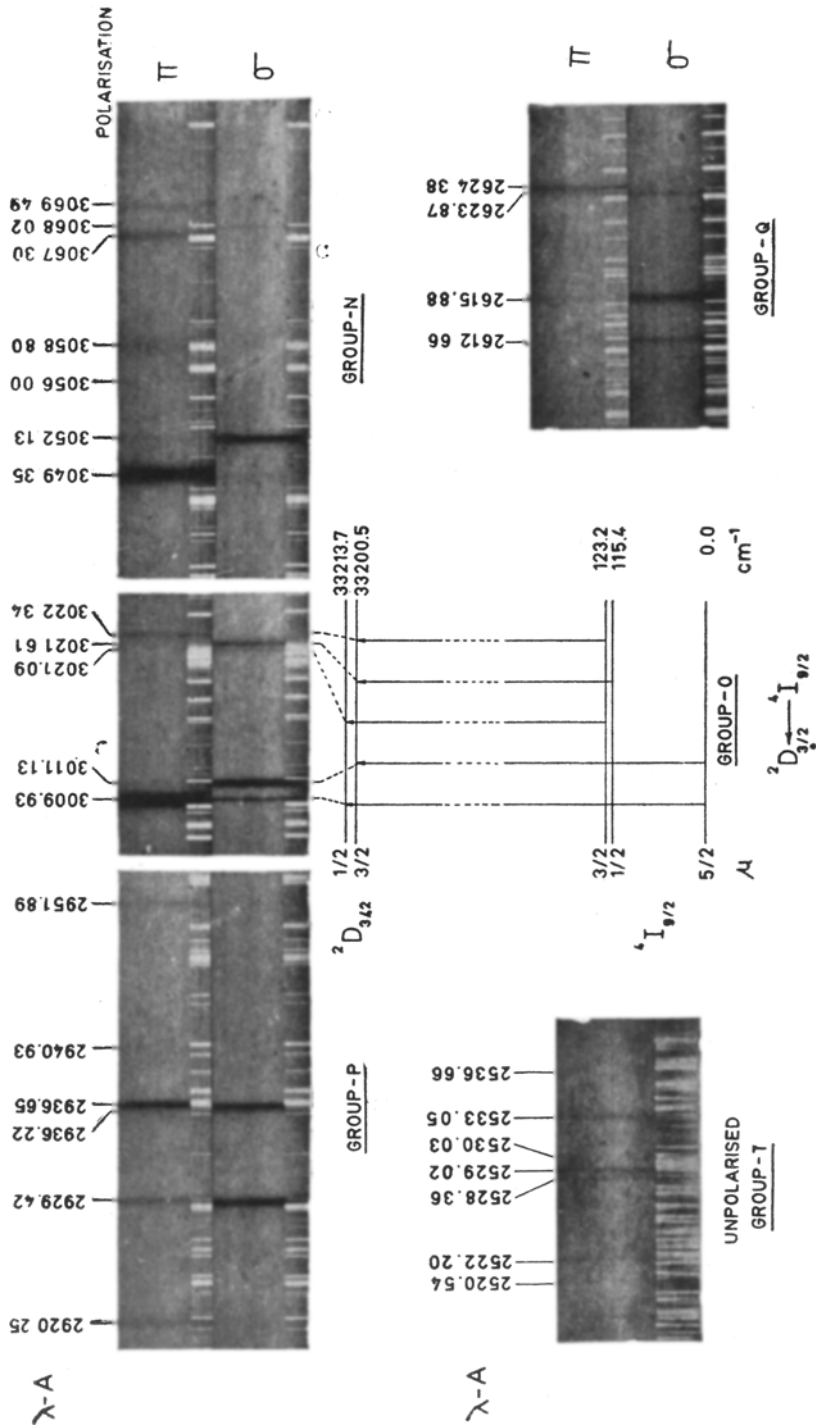
More elaborate experiments at liquid helium temperature and Zeeman splitting data are necessary and may provide sufficient information to analyse the other groups recorded here.

SUMMARY

The paper deals with an extension towards shorter wavelengths of the absorption spectrum of Nd³⁺ employing a 5% Nd³⁺ doped LaCl₃ crystal. Five new groups of lines have been recorded and the analysis and interpretation of one of these groups, viz., group O between 3010 and 3023 Å are given. The lines observed in this group are shown to be due to transitions from the ground level (⁴I_{9/2}) stark components ($\mu = 5/2, 1/2$ and $3/2$) to the two stark components ($\mu = 3/2, 1/2$) of ²D_{3/2} level at about 33200 cm.⁻¹

REFERENCES

1. Spedding, F. H. and Hamlin, H. F. *J. Chem. Phys.*, 1937, **5**, 191 and 429.
2. Ewald, H. .. *Ann. Phys.*, 1939, **34**, 209.
3. Satten, R. A. .. *J. Chem. Phys.*, 1953, **21**, 637.
4. Dieke, G. H. and Heroux, L. *Phys. Rev.*, 1956, **103**, 1227.
5. Carlson, E. H. and Dieke, G. H. *J. Chem. Phys.*, 1961, **34**, 1602.
6. Agrawal, R. M., *et al.* .. *Proc. Ind. Acad. Sci.*, 1962, **55**, 106.
7. Wybourne, B. G. .. *J. Chem. Phys.*, 1960, **32**, 639.
8. Wong, E. Y. .. *Ibid.*, 1961, **35**, 544.



Ultra-violet A¹ absorption Spectra of 5% Nd³⁺ in LaCl₃ at 77° K