

# Communications Research Centre

## SPECTROSCOPIC STUDIES OF Nd<sup>3+</sup> IONS IN POCℓ<sub>3</sub>

by  
A. Watanabe

IC

DEPARTMENT OF COMMUNICATIONS  
MINISTÈRE DES COMMUNICATIONS

OTTAWA, SEPTEMBER 1973

CANADA

CRC TECHNICAL NOTE No. 661

*Display 7/11/73*

LKC  
TK  
5102.5  
.R48e  
#661  
c.2

COMMUNICATIONS RESEARCH CENTRE

DEPARTMENT OF COMMUNICATIONS  
CANADA

Industry Canada  
Library - Queen  
MAR 20 2013  
Industrie Canada  
Bibliothèque - Queen

SPECTROSCOPIC STUDIES OF Nd<sup>3+</sup> IONS IN POLYMER

by

A. Watanabe

*(Informatique Directorate)*

COMMUNICATIONS CANADA  
~~C. R. C.~~  
LIBRARY - BIBLIOTHÈQUE

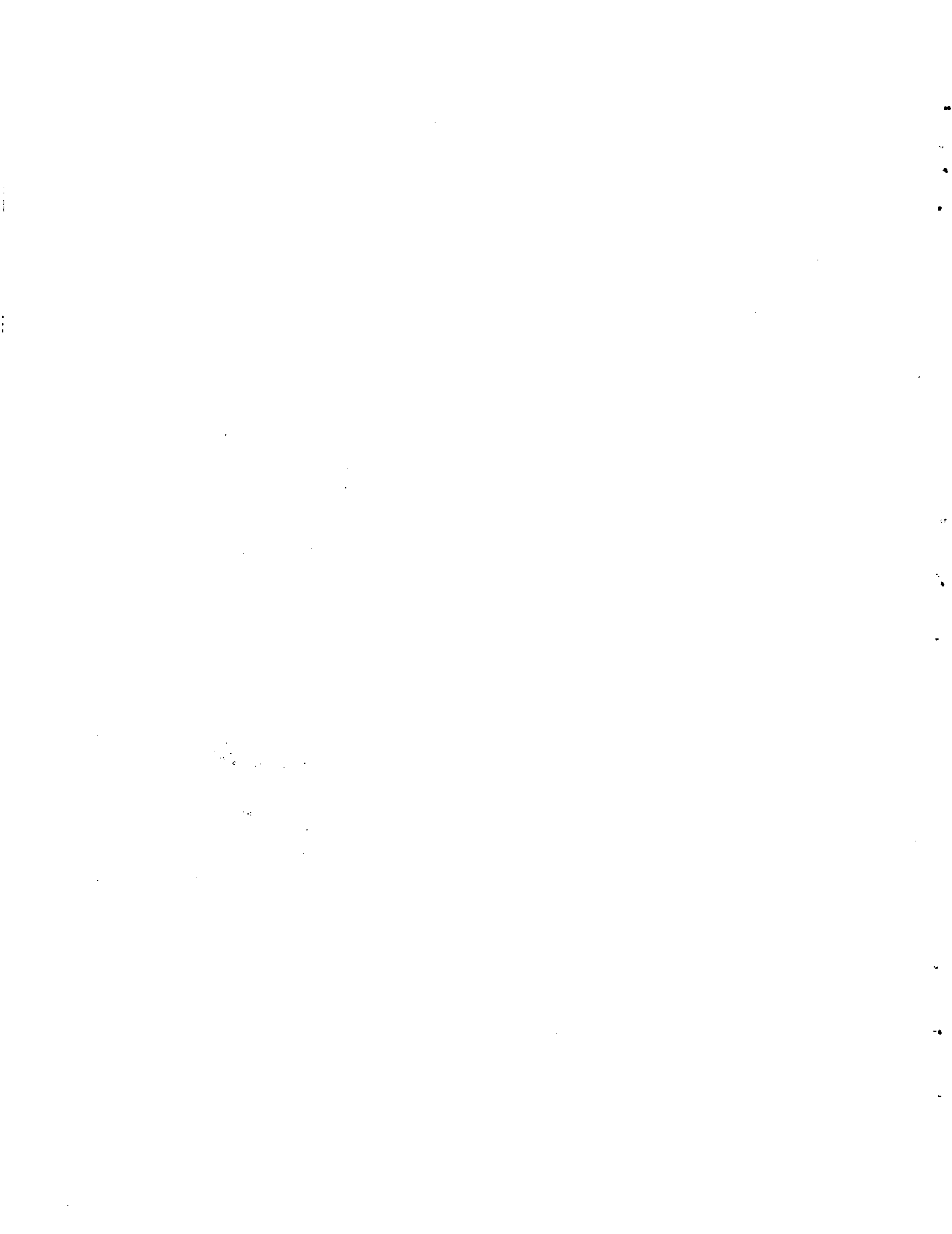
CRC TECHNICAL NOTE NO. 661

September 1973

OTTAWA

**CAUTION**

This information is furnished with the express understanding that:  
Proprietary and patent rights will be protected.



## TABLE OF CONTENTS

ABSTRACT .....	1
1. INTRODUCTION .....	1
2. APPARATUS AND EXPERIMENTAL METHODS .....	1
3. ABSORPTION AND FLUORESCENCE SPECTRA .....	2
4. CONCENTRATION QUENCHING AND ENERGY TRANSFER .....	7
5. ACKNOWLEDGEMENTS .....	9
6. REFERENCES .....	9

# SPECTROSCOPIC STUDIES OF $\text{Nd}^{3+}$ IONS IN $\text{POCl}_3$

by

A. Watanabe

## ABSTRACT

Experimental results are reported for a spectroscopic study of  $\text{Nd}^{3+}$  ions dissolved in  $\text{POCl}_3$ -based aprotic solvents. The splitting of the  ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$  fluorescence band in local electric fields of cubic and non-cubic symmetries is discussed. Fluorescence excitation spectra which illustrate the transfer of energy from optically pumped  $\text{UO}_2^{2+}$  ions to fluorescent  $\text{Nd}^{3+}$  ions are shown.

## 1. INTRODUCTION

There exists today a wealth of information about the spectroscopy of  $\text{Nd}^{3+}$  ions in crystals and glasses<sup>1,2</sup>. The recent work of Heller<sup>3,4,5,6</sup> and Schimitschek<sup>7</sup> have revealed some of the interested properties of  $\text{Nd}^{3+}$  ions in  $\text{POCl}_3$ -based solvent systems. In this note are presented detailed results of some aspects of these studies: an analysis of fluorescence spectra arising from local electric fields of cubic and non-cubic symmetries, a reinterpretation of a previously published crystal-field spectrum of  $\text{Nd}^{3+}$  ions in  $\text{POCl}_3$ :  $\text{ZrCl}_4$ , a study concentration quenching effects and the observations of energy transfer from  $\text{UO}_2^{2+}$  ions to  $\text{Nd}^{3+}$  ions.

## 2. APPARATUS AND EXPERIMENTAL METHODS

The solutions were prepared from dried neodymium salts and vacuum-distilled liquids, following the preparative techniques described by Heller<sup>8</sup>. Sample preparation procedures were carried out in a nitrogen atmosphere inside an evacuable stainless-steel dry box<sup>9</sup>. The absorption spectra were recorded on a Cary 14 spectrophotometer. Commercially available absorption cells of path length 2 mm were used. The fluorescence spectra were recorded

on a fluorescence spectrometer that has been described previously<sup>10</sup>. The fluorescence cells were made from lengths of thick-wall quartz tubing of 2 mm inner diameter.

### 3. ABSORPTION AND FLUORESCENCE SPECTRA

In rare-earth ions, the partially filled 4f-electron shell lies within some of the completely filled shells; thus the interaction of the 4f electrons with the external environment is weak and the free-ion energy levels of the  $\text{Nd}^{3+}$  ion<sup>11</sup> shown in Figure (1) give a good representation of the energy levels in bulk media. Figure (2) shows examples of absorption spectra obtained for  $\text{Nd}^{3+}$  ions in representative  $\text{POCl}_3$ -based solvents. The top trace shows an absorption spectrum for  $\text{Nd}(\text{ClO}_4)_3$  dissolved in  $\text{POCl}_3:\text{ZrCl}_4$ , the middle trace is for  $\text{Nd}_2\text{O}_3$  in  $\text{POCl}_3:\text{TiCl}_4$ , and the bottom trace is for  $\text{NdCl}_3$  in  $\text{POCl}_3:\text{TiCl}_4$ . The three absorption bands all show the same general features, but the detailed structure of the individual bands is different for the three cases.

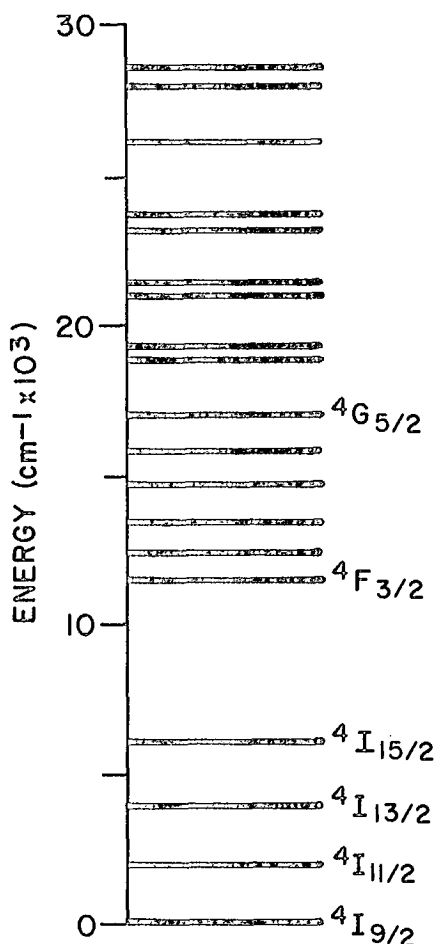


Fig. 1. The free-ion energy levels of the  $\text{Nd}^{3+}$  ion.

The fluorescence of the  $\text{Nd}^{3+}$  ions was excited by optically pumping the  ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{5/2}$  transition at approximately 586 nm with the wavelength-selected output of a 1000-watt Xe lamp. Fluorescence spectra of the  ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$  transition are shown in Figure (3) for three samples whose absorption spectra were given in Figure (2). These spectra also show some common characteristic features, but there are some obvious differences in the three traces. The prominent feature at approximately 870 nm appears as a single component in the top trace, while in the middle trace there are two smaller features appearing on either side of the single components. In the bottom trace, the central component is not present and only the components at the sides remain. As well, there are some differences in broad components on the longer wavelength region of the band. In addition to these features, we also detected in the sample with non-cubic symmetry (bottom trace) a very weak feature displaced approximately  $935\text{ cm}^{-1}$  from the sharp feature at approximately 875 nm. This feature would appear off the right-hand side of the graph at a wavelength of approximately 952 nm.

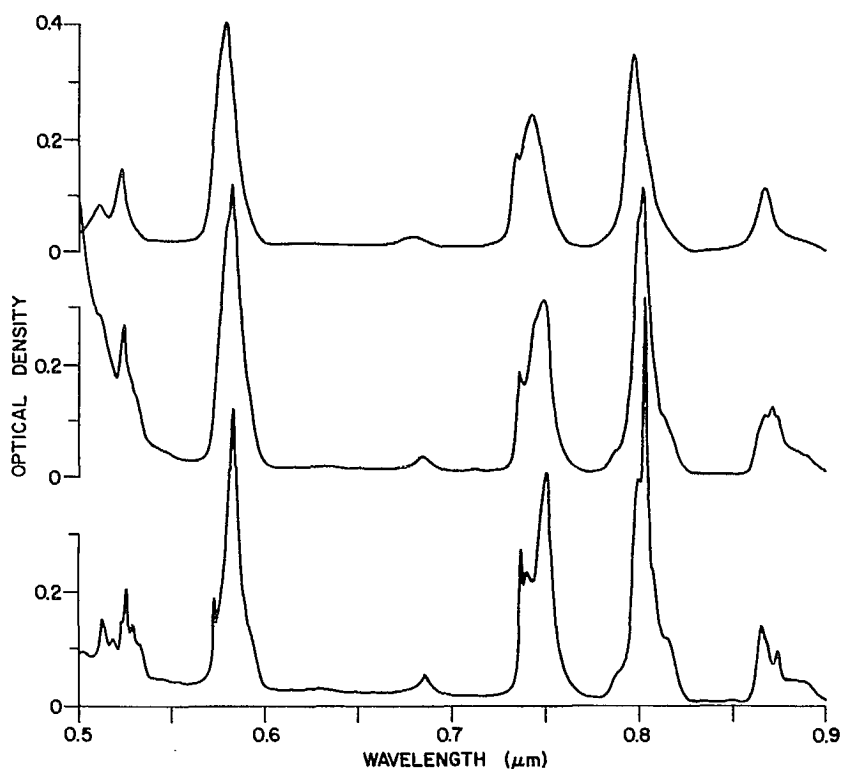


Fig. 2. Representative absorption spectra for the  $\text{Nd}^{3+}$  ion dissolved in  $\text{POCl}_3$ -based solvents. The top trace shows a typical spectrum for  $\text{Nd}^{3+}$  ions occupying cubic sites [ $\text{Nd}(\text{ClO}_4)_3$  in  $\text{POCl}_3:\text{ZrCl}_4$ ], the middle trace for a mixture of cubic and non-cubic sites [ $\text{Nd}_2\text{O}_3$  in  $\text{POCl}_3:\text{TiCl}_4$ ] and the bottom trace for non-cubic sites [ $\text{NdCl}_3$  in  $\text{POCl}_3:\text{TiCl}_4$ ].

The general features of these spectra were interpreted in terms of the symmetry of the local electric field about the fluorescing neodymium ions. Figure (4) is a schematic diagram of the  ${}^4\text{F}_{3/2}$  and  ${}^4\text{I}_{9/2}$  manifolds in fields of various symmetries. In a cubic field the upper manifold is unsplit and the lower consists of one doubly degenerate and two quadruply degenerate components<sup>1,2</sup>. Three transitions are possible and all three are allowed on the basis of symmetry by electric-dipole selection rules. In all fields of symmetry lower than cubic, apart from the Kramers degeneracy, the degeneracy of both manifolds is completely removed. Thus 10 transitions are possible and all 10 are allowed by electric-dipole selection rules.

The spectrum shown at the top of Figure (3) has only three discernible features. They evidently arise from the fluorescence of ions occupying cubic sites. The fluorescence spectrum for  $\text{NdCl}_3$  dissolved in  $\text{POCl}_3:\text{TiCl}_4$  is shown at the bottom of the figure. The intense component seen at approximately 870 nm in the top trace is split into two components in the bottom trace. This splitting evidently arises from a splitting of the  ${}^4\text{F}_{3/2}$  level into two Kramers-degenerate components in a non-cubic field. Some changes are also evident in the broader features in the long-wavelength portion of the spectra. The spectrum shown in the centre of Figure (3) shows a prominent feature at 870 nm with two smaller bumps, one on either side of the main peak. These features indicate that both cubic and non-cubic sites can occur in  $\text{POCl}_3$ -based solutions at the same time.

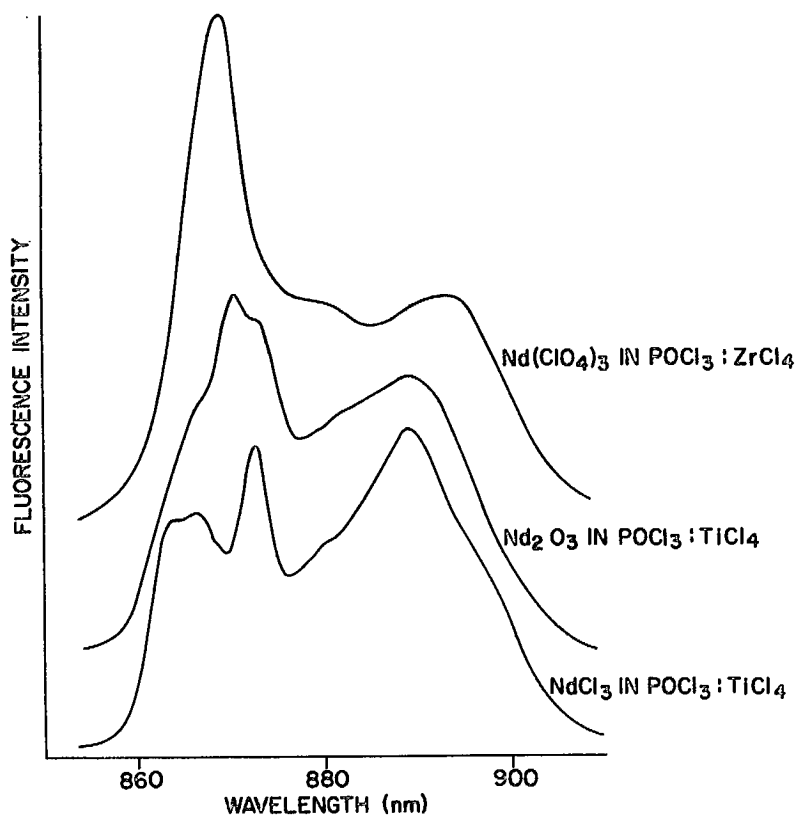


Fig. 3. The fluorescence spectra of the  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$  transition for the same samples as in Figure (2).

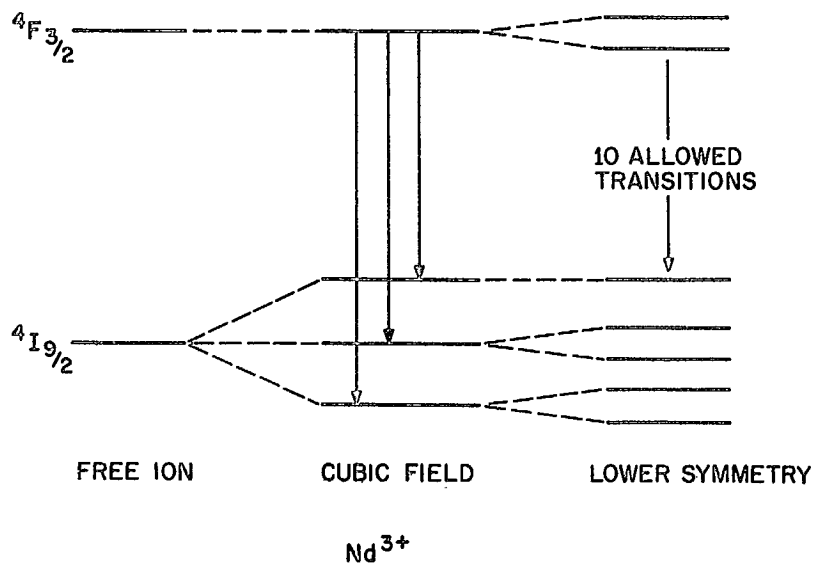


Fig. 4. The splitting of the  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$  states of  $Nd^{3+}$  in a cubic field and in fields of lower symmetry. The number of possible electric-dipole transitions is indicated for the two types of fields.



The values of the wavelengths were read at the peak of each of the features of the spectrum shown at the bottom of Figure (3), and these values were then used to deduce the energy separations for the components of the  ${}^4I_{9/2}$  state. The 'crystal-field' splittings that we obtained are shown in Table 1 for  $Nd^{3+}$  ions in non-cubic sites. The probable error of estimation in our values is approximately  $\pm 10 \text{ cm}^{-1}$ . For comparison the values obtained by Tolstoi *et al.* in  $Nd^{3+}$ -doped  $POCl_3:SnCl_4$  in the solid state<sup>13</sup> at  $4.2^\circ \text{ K}$  are also shown. The similarity of the magnitudes of the splittings is an indication that the local structure of aprotic solvent molecules was not greatly affected by the freezing process. The symmetry that existed in the liquid state evidently was frozen in when the material was frozen, and the freezing process simply led to an ordering of the coordination spheres.

In Tolstoi's  $4.2^\circ \text{ K}$  spectra, five components were clearly visible. These components were identified with the transitions from the lower level of the  ${}^4F_{3/2}$  manifold to the five levels into which the  ${}^4I_{9/2}$  manifold is split when the ion is located in a non-cubic site. As well as these five components, there were two other components which were about two orders of magnitude weaker. These components were identified by Tolstoi as transitions from the very weakly populated upper level of the  ${}^4F_{3/2}$  manifold. The frequencies of these lines indicated that two types of sites were present. In the experiments of Heller<sup>5</sup> on acid solution of  $Nd^{3+}$  in  $SeOCl_2:SnCl_4$  and  $SeOCl_2:SbCl_5$ , only one type of site could be detected spectroscopically. However, it is clear from Tolstoi's well-resolved low-temperature spectra that at least two types of coordination geometries were present around the  $Nd^{3+}$  ions in his samples.

Brecher and French<sup>14</sup> analyzed the fluorescence spectrum of  $Nd^{3+}$  in  $POCl_3:ZrCl_4$  in solid samples at  $100^\circ \text{ K}$ . They analyzed their spectra in terms of only one type of site, and deduced splittings that did not agree with the results of Tolstoi *et al.*<sup>13</sup>. Their spectra were recorded at  $100^\circ \text{ K}$ , where the population of the upper level of the  ${}^4F_{3/2}$  manifold was still appreciable. Nevertheless, there was some intensity variation in the various components that they have identified and even at  $100^\circ \text{ K}$  the relative intensities appear to be more consistent with the interpretation of Tolstoi than with the one that they postulated. A re-assignment of their observed transitions in terms of two types of non-cubic sites gives an energy-level scheme (*see Table I*) for the  ${}^4I_{9/2}$  level which is completely consistent with that of Tolstoi. Thus it would appear that the local structure around  $Nd^{3+}$  ions in  $POCl_3:ZrCl_4$  is very similar to the local structure in  $POCl_3:SnCl_4$ .

TABLE 1  
Crystal-Field Split Energy Levels ( $\text{cm}^{-1}$ ) of the  
 ${}^4I_{9/2}$  Manifold of  $\text{Nd}^{3+}$  in Non-Cubic Sites

(a) Present Work $\text{POCl}_3:\text{ZrCl}_4$	(b) Tolstoi <i>et al.</i> <sup>13</sup> $\text{POCl}_3:\text{SnCl}_4$	(c) Brecher and French <sup>14</sup> $\text{POCl}_3:\text{ZrCl}_4$	(d) Reinterpretation of (c) $\text{POCl}_3:\text{ZrCl}_4$
(925)			
$315 \pm 10$	315	428	309
	259	272	
$215 \pm 10$	221	165	221
$100 \pm 10$	110	118	114
0	0	0	0

An examination of the temperature dependence of the  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  fluorescence band over a temperature range from  $-27^\circ\text{C}$  to  $+62^\circ\text{C}$  showed only a small change in the line shape (*see Figure (5)*). At the lower temperatures the shoulder on the shorter-wavelength side of the band becomes somewhat more pronounced, since the linewidths of the individual components decreases with decreasing temperature. However the general features of the band did not change significantly. This temperature range covers the freezing point of the solution, which is approximately  $10^\circ\text{C}$ .

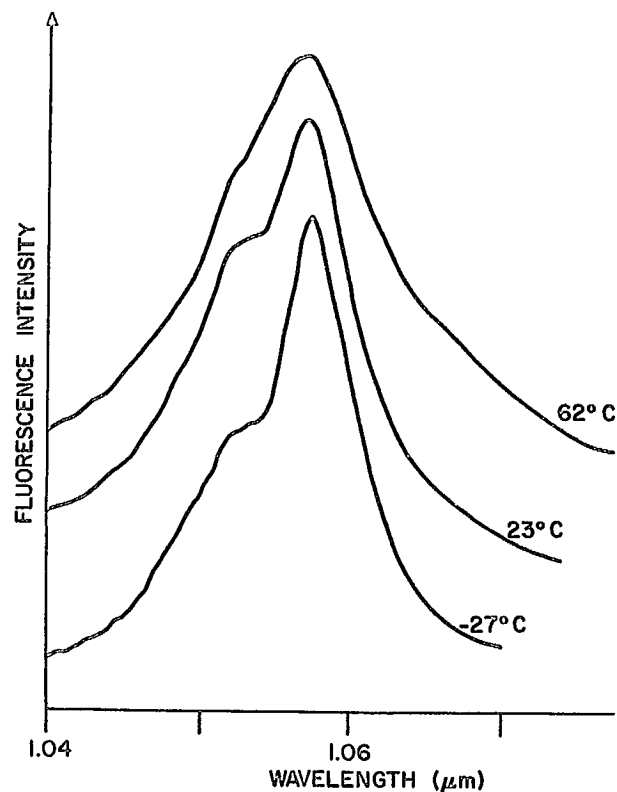
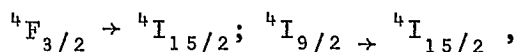


Fig. 5. The  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  fluorescence band for three temperatures.

## 4. CONCENTRATION QUENCHING AND ENERGY TRANSFER

The effect of the concentration on the fluorescence lifetime of the  $\text{Nd}^{3+}$ -doped samples was studied. Figure (6) shows the effect of concentration on the lifetime of the  ${}^4\text{F}_{3/2}$  level for dry samples (upper curve) and somewhat wet samples (lower curve). It is seen that the lifetime of the  ${}^4\text{F}_{3/2}$  level has a constant value for low concentrations up to about 0.1 N and then decreases for higher concentrations. This decrease in lifetime is manifested at lower concentrations for the wet samples than for the dry samples. The decrease in the lifetime of the  ${}^4\text{F}_{3/2}$  level results from a non-radiative energy transfer from an excited ion to a neighbouring ion by means of multipolar transfer<sup>15,16</sup>. The transitions that occur during this process<sup>17</sup> are as follows:



with the first transition taking place in the excited ion and the second in an unexcited ion. The coordination of solvent molecules around the ion makes this process relatively ineffective until fairly high concentrations are reached. Evidently the presence of water in the coordination sphere enhances the probability of multipolar transfer.

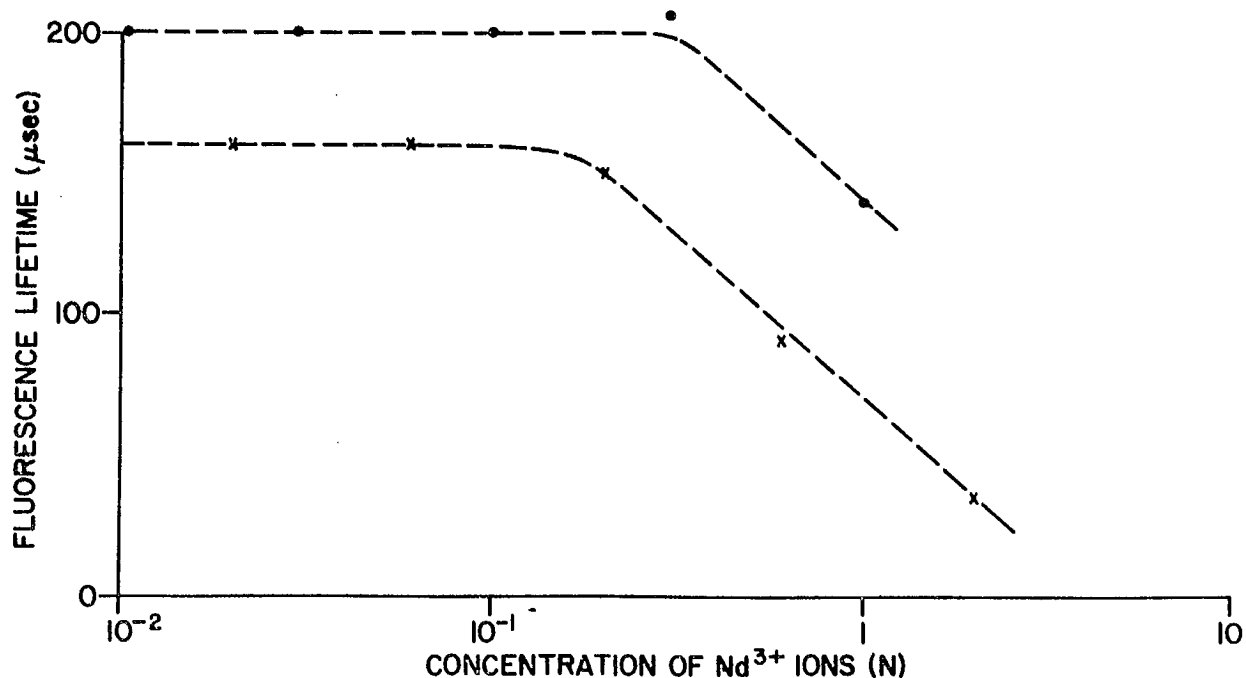


Fig. 6. The concentration dependence of the fluorescence lifetime of the  ${}^4\text{F}_{3/2}$  level of  $\text{Nd}^{3+}$  in  $\text{SeOCl}_2:\text{SnCl}_4$  for wet and dry samples, shown by the X and •, respectively.

Energy transfer to  $\text{Nd}^{3+}$  ions from dissimilar ions was also studied in  $\text{POCl}_3$ -based solvents. The experiments showed no transfer to  $\text{Nd}^{3+}$  ions with the addition of the following salts to the solution:  $\text{DyCl}_3$ ,  $\text{HoCl}_3$ ,  $\text{SmCl}_3$ ,  $\text{PrCl}_3$ ,  $\text{ErCl}_3$ ,  $\text{MnCl}_2$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{UO}_2\text{Cl}_2$ . A very small amount of energy transfer was observed from  $\text{Eu}^{3+}$  to  $\text{Nd}^{3+}$ , and a significant amount of energy transfer

was observed from  $\text{UO}_2^{2+}$  ions to  $\text{Nd}^{3+}$  ions. In Figure (7) the excitation spectrum is shown for  $\text{Nd}^{3+}$  ions in the solvent with  $\text{UO}_2^{2+}$  ions (dashed line) and without  $\text{UO}_2^{2+}$  ions (solid line). A comparison of the two spectra shows that the  $\text{Nd}^{3+}$  fluorescence is excited by pumping in the regions around  $0.3 \mu\text{m}$  and  $0.45 \mu\text{m}$  where neodymium normally does not have excitation bands. The excitation in these regions occurs by absorption by the  $\text{UO}_2^{2+}$  ions followed by multipolar energy transfer to the  $\text{Nd}^{3+}$  ions. The absorption band of the doubly doped solution is shown in Figure (8). The sharp absorption lines of  $\text{Nd}^{3+}$  at  $0.35 \mu\text{m}$  are clearly seen to overlap the much broader absorption band of  $\text{UO}_2^{2+}$  which covers the whole region for wavelengths shorter than  $0.45 \mu\text{m}$ . Energy transfer from  $\text{UO}_2^{2+}$  ions to  $\text{Nd}^{3+}$  ions has previously been observed in a coactivated glass host<sup>18</sup>. No significant amount of energy transfer was observed in previous experiments in a liquid host material<sup>6</sup>.

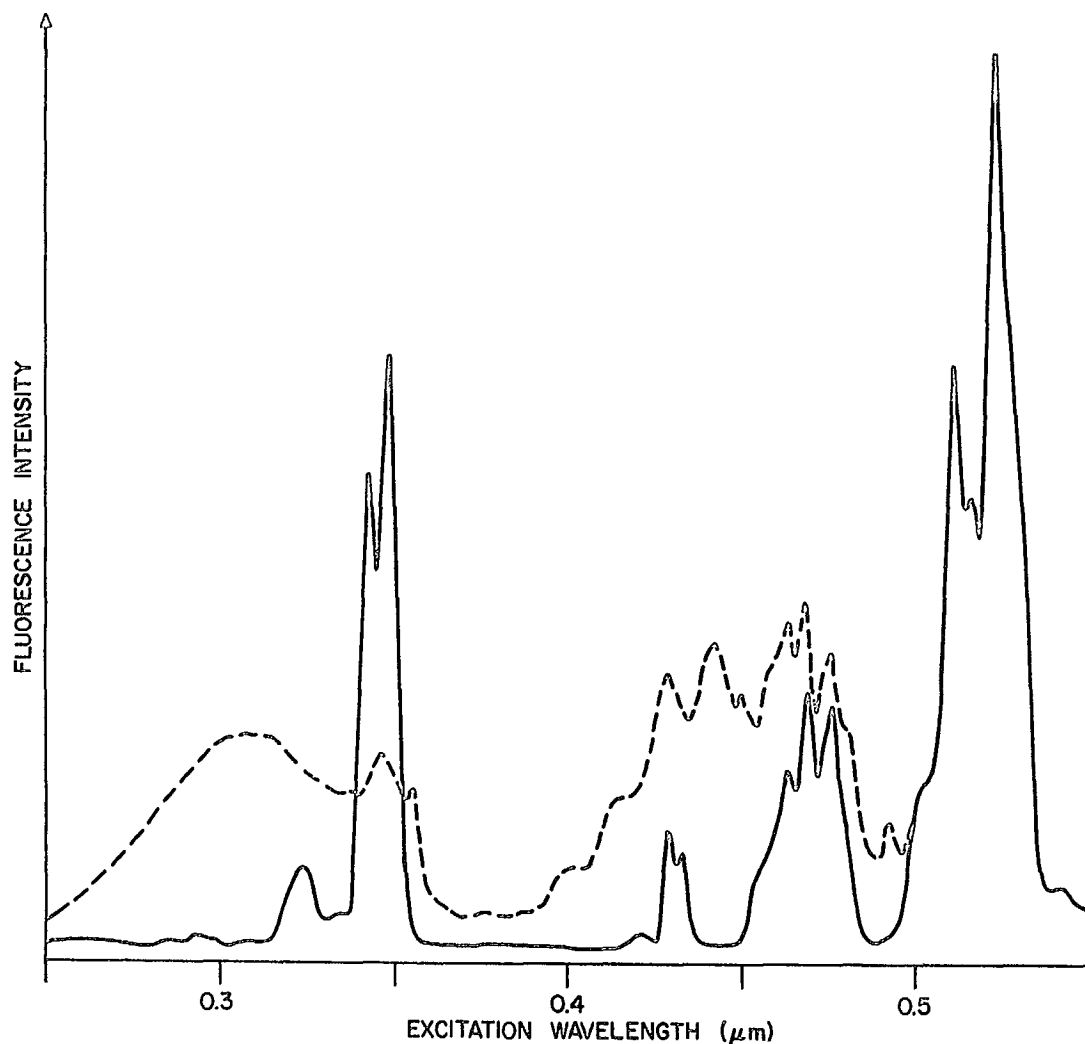


Fig. 7. The excitation spectrum of  $\text{Nd}^{3+}$  ions dissolved alone in  $\text{POCl}_3$ :  
 $\text{ZrCl}_4$  (solid line) and codoped with  $\text{UO}_2^{2+}$  (dashed line).

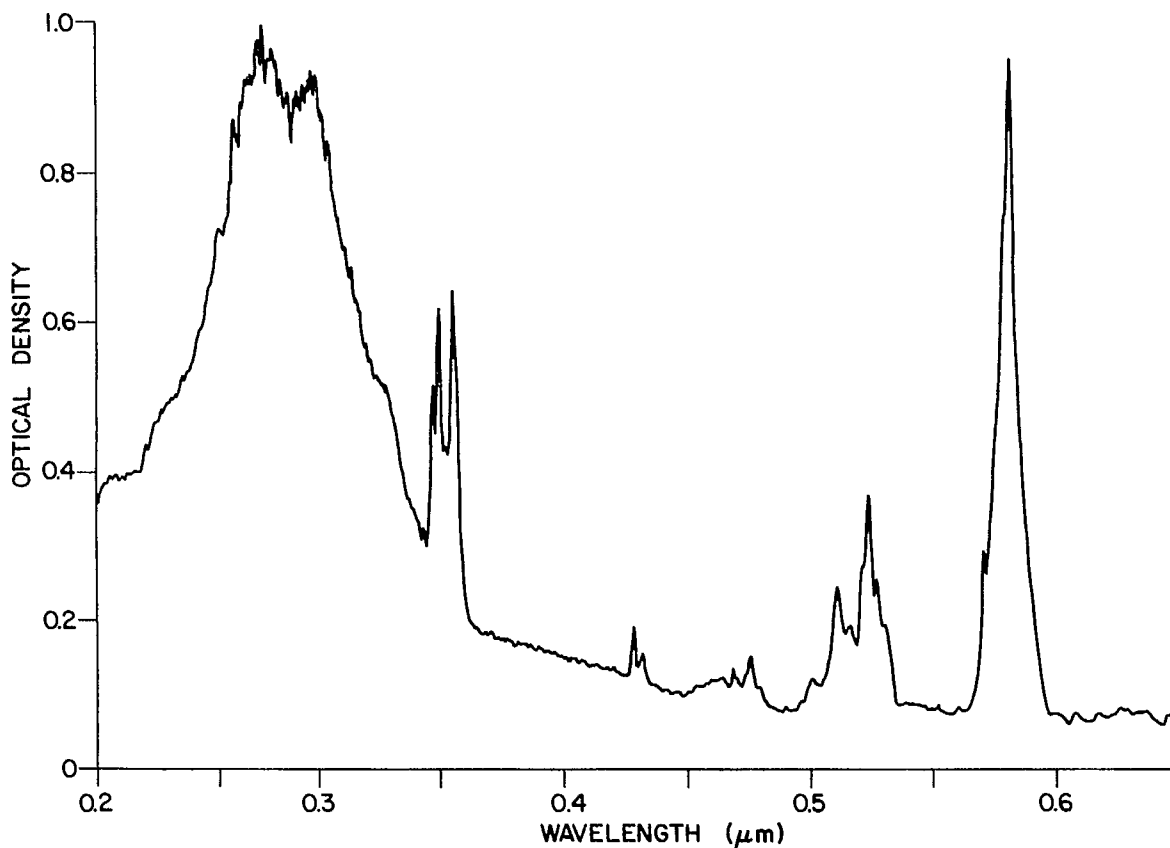


Fig. 8. A portion of the absorption spectrum of  $\text{POCl}_3:\text{ZrCl}_4$  codoped with  $\text{Nd}^{3+}$  and  $\text{UO}_2^{2+}$  ions.

## 5. ACKNOWLEDGEMENTS

The author thanks R.G. Lamont for providing excellent technical assistance throughout the course of the experiments. Assistance was also provided by D. Landheer during two summers as a research assistant.

## 6. REFERENCES

1. Dieke, G.H. *Spectra and energy levels of rare earth ions in crystals*. Interscience Publishers, New York, 1968.
2. Wybroune, B.G. *Spectroscopic properties of rare earths*. Interscience Publishers, New York, 1965.
3. Heller, A. *A high-gain room-temperature liquid laser: trivalent neodymium in selenium oxychloride*. *Appl. Phys. Lett.* 9, p. 106, 1966.

4. Lempicki, A. and A. Heller. *Characteristics of the Nd<sup>3+</sup>:SeOCl<sub>2</sub> liquid laser*. Appl. Phys. Lett. 9, p. 108, 1966.
5. Heller, A. *Liquid lasers--design of neodymium-based inorganic ionic systems*. J. Mol. Spectroscopy 28, p. 101, 1968.
6. Heller, A. *Liquid lasers--fluorescence, absorption and energy transfer of rare earth ion solutions in selenium oxychloride*. J. Mol. Spectroscopy 28, p. 208, 1968.
7. Schimitschek, E.J. *Laser emission of a neodymium salt dissolved in POCl<sub>3</sub>*. J. Appl. Phys. 39, p. 6120, 1968.
8. Heller, A. *Liquid lasers. Preparative techniques for selenium oxychloride based solutions*. J. Am. Chem. Soc. 90, p. 3711, 1968.
9. Lamont, R.G., Watanabe, A. and J.G. Chambers. *A dry inert-gas glove box for the handling of hygroscopic and corrosive materials*. CRC Report No. 1244, 1973.
10. Watanabe, A. *A spectroscopic determination of the induced-emission cross section of the  $^3P_0 \rightarrow ^3F_2$  and  $^3P_0 \rightarrow ^3H_6$  transitions of the Pr<sup>3+</sup> ion in SeOCl<sub>2</sub>:SnCl<sub>4</sub>*. CRC Report No. 1243, 1973.
11. Dieke, G.H. and H.M. Crosswhite. *The spectra of the doubly and triply ionized rare earths*. Appl. Opt. 2, p. 675, 1963.
12. McClure, D.S. *Electronic spectra of molecules and ions in crystals*. Solid State Physics 9, p. 400, 1959.
13. Tolstoi, M.N., Lyubimov, E.I. and I.M. Batyaev. *Spectroscopic properties of Nd<sup>3+</sup> luminescent centers in SnCl<sub>4</sub>-POCl<sub>3</sub>*. Optics and Spectroscopy 28, p. 389, 1969.
14. Brecher, C. and K.W. French. *Comparison of aprotic solvents for Nd<sup>3+</sup> liquid laser systems: selenium oxychloride and phosphorus oxychloride*. J. Phys. Chem. 73, p. 1785, 1969.
15. Dexter, D.L. *A theory of sensitized luminescence in solids*. J. Chem. Phys. 21, p. 836, 1953.
16. Van Uitert, L.G. and L.F. Johnson. *Energy transfer between rare-earth ions*. J. Chem. Phys. 44, p. 3514, 1966.
17. Stroud, J.S. *Concentration quenching of Nd<sup>3+</sup> fluorescence*. Appl. Opt. 7, p. 751, 1968.
18. Gandy, H.W., Ginther, R.J. and J.F. Weller. *Radiationless resonance energy transfer from UO<sub>2</sub><sup>2+</sup> to Nd<sup>3+</sup> in coactivated barium crown glass*. Appl. Phys. Lett. 4, p. 188, 1964.

19. Neeland, J.K. and V. Evtuhov. *Measurement of the laser transition cross section for  $Nd^{3+}$  in yttrium aluminum garnet.* Phys. Rev. 156, p. 244, 1967.
20. Samelson, H., Heller, A. and C. Brecher. *Determination of the absorption cross section of the laser transitions of the  $Nd^{3+}:SeOCl_2$  system.* J. Opt. Soc. Am. 58, p. 1054, 1968.





