Zeitschrift: Helvetica Physica Acta
Band: 38 (1965)
Heft: II

Artikel: Inner 4f-transitions of neodymium tricyclopentadienide at liquid helium temperatures
Autor: Pappalardo, R.
DOI: https://doi.org/10.5169/seals-113586

Inner 4f-Transitions of Neodymium Tricyclopentadienide at Liquid Helium Temperatures

by **R. Pappalardo**

Cyanamid European Research Institute, Cologny (Geneva), Switzerland

(30. X. 64)

Abstract. Optical absorption data are reported for Nd^{3+} tricyclopentadienide in 2-Methyltetrahydrofuran at low temperatures. Transitions are found from levels at ~ 70, ~ 310, ~ 570, and ~ 670 cm^{-1} over the ground state. Some of the observed lines at low temperatures show a pronounced low-energy shift with respect to known Nd^{3+} systems. Two "hypersensitive" lines are found at 16828 and 16986 cm^{-1}.

1. Introduction

WILKINSON and BIRMINGHAM[1)2)] have prepared an interesting series of rare-earth compounds, the rare-earth tricyclopentadienides, where the rare-earth ions are bound to cyclopentadienyl rings.

The same authors also reported[2)] some of the absorption lines of solutions of Er cp_3 and Pr cp_3 at room temperature.

Already from these spectra it appears that the presence of the cyclopentadienyl ring in the coordination sphere of Pr^{3+} or Er^{3+} does not drastically affect the position of the 4 *f*-levels. This in contrast with the pronounced alteration of the 3 d^n levels in the sandwich compounds of the first transition series[3)].

A more detailed study of the optical properties of rare-earth tricyclopentadienides would be appropriate, with a view:

a) to assess the influence of the bonding on the 4*f*-levels,
b) to find whether the bonding to the cyclopentadienyl ring has any favourable effect on the fluorescent properties of some of these systems.

We report here low-temperature optical absorption data of solutions of Neodymium tricyclopentadienide (Nd cp_3) in 2-Methyl-tetrahydrofuran.

2. Experimental

The rare-earth tricyclopentadienides are prepared using the standard procedure of reacting the anhydrous chloride with sodium cyclopentadienide in tetrahydrofuran[1)2)]. Only freshly distilled solvents and reagents were used and all manipulations were performed under nitrogen or under vacuum. The anhydrous $NdCl_3$ was obtained by treating 99.9% Nd_2O_3 (from Lindsay Chemical Division, West Chicago, Illinois) with NH_4Cl at 300 °C. The reaction slurry was dried and sublimed at 200–220 °C at a pressure of 10^{-3} mm. A pale blue sublimate was obtained in the temperature range indicated by BIRMINGHAM and WILKINSON[1)2)].

The blue sublimate was dissolved in freshly distilled 2-Methyl-tetrahydrofuran and transferred to a specially built cell, 2.3 mm thick. This cell was fixed onto a copper block, which was the cold finger of a double Dewar. Thermal contact was improved by means of silver paint.

Immediately afterwards the cryostat was evacuated and cooled first with liquid nitrogen and then with liquid helium. Absorption spectra were taken with a Cary 14 Spectrophotometer. Although no accurate temperature measurements were taken, the cooling of the cell via the cold finger was satisfactory in the visible and ultraviolet region of the spectrum, where dispersed light falls onto the cell. On the contrary, there was considerable heating of the sample due to the undispersed radiation of the Cary source in the infrared range of the instrument. As a result the spectra at liquid helium temperatures in the region from 0.7 to 1.0 μ did not differ very much from the corresponding spectra at 78 °K. For this spectral region, only the data at liquid nitrogen temperature are reported in what follows.

3. The Observed Spectra

The absorption data are collected for convenience in Figure 1 to Figure 13. The line intensities are given in optical density units, with the baseline of the various tracings shifted by appropriate amounts, as required. Typical slitwidths in mm are shown on the curves. Most temperature shifts in the position of the lines, from liquid nitrogen to liquid helium temperatures are not very pronounced and accordingly have not been explicitly given.

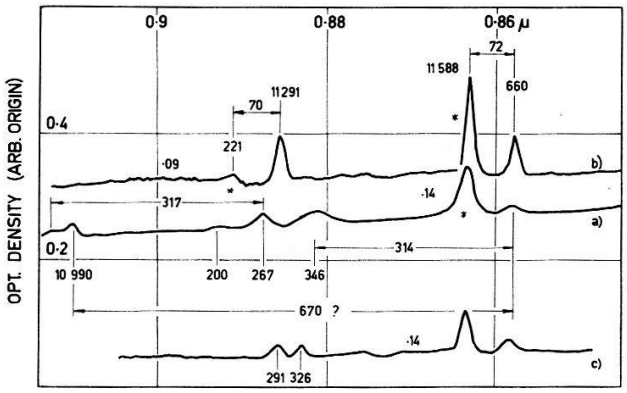

Fig. 1

Line group R. Absorption of 1 cm solution of blue $Ndcp_3$ in 2-Methyl tetrahydrofuran. Sample RB 496 a) at room temperature, b) at 78 °K. The asterisks mark transitions arising from the level at 70 cm^{-1} (see following Figures). A transition from the level at $\sim$ 310 cm^{-1} is also indicated, together with a possible contribution from a level at 670 cm^{-1}. There is a pronounced temperature shift for the group at 11300 cm^{-1}. c) Absorption of 2.3 mm solution of $Ndcp_3$ in 2-Me-THF at 78 °K. Sample RB 353. The low-frequency group differs in the two samples. See also following Figures.

Most tracings pertain to the same sample run at liquid nitrogen and at liquid helium in succession. Other spectra of sublimed material, obtained from different preparations, are also shown. These latter spectra, both at room temperature and at 78 °K, have been used in connection with the spectra at liquid helium, in order to infer the presence of excited levels of the ground manifold of Nd^{3+}, which do not contribute

to the absorption at liquid nitrogen or at liquid helium temperatures. We have noticed in many cases that in cooling from room temperature to 78 °K the lines not only sharpened up, but also that there was an overall increase in their intensity.

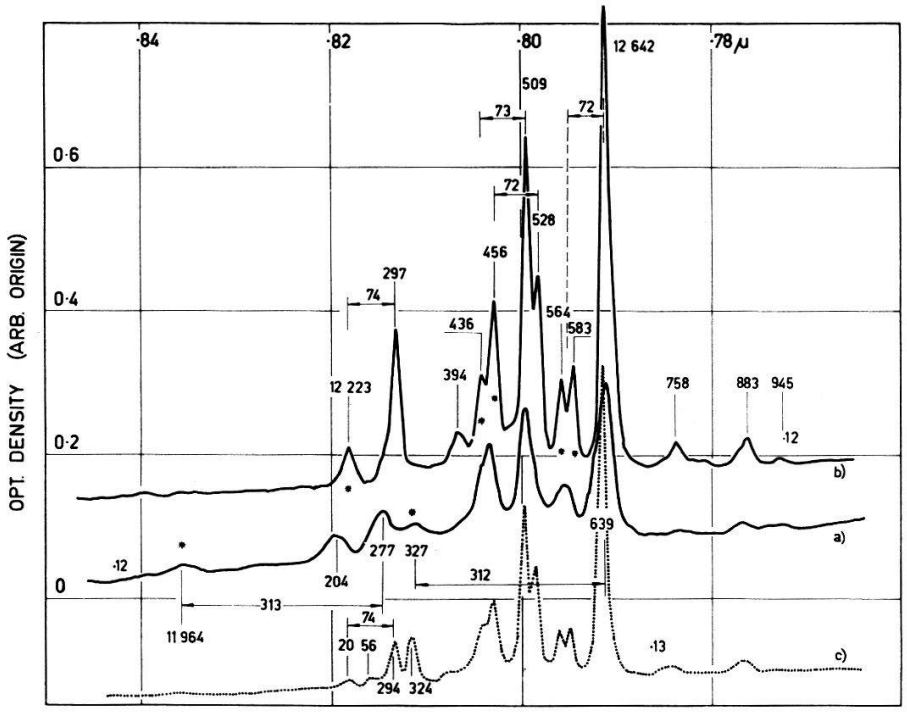

Fig. 2
Line group S. Sample RB 496 a) room temperature, b) 78 °K. There is a $\sim 20\ cm^{-1}$ shift of the group at $\sim 12300\ cm^{-1}$ from a) to b). Finally, c) sample RB 353 at 78 °K.

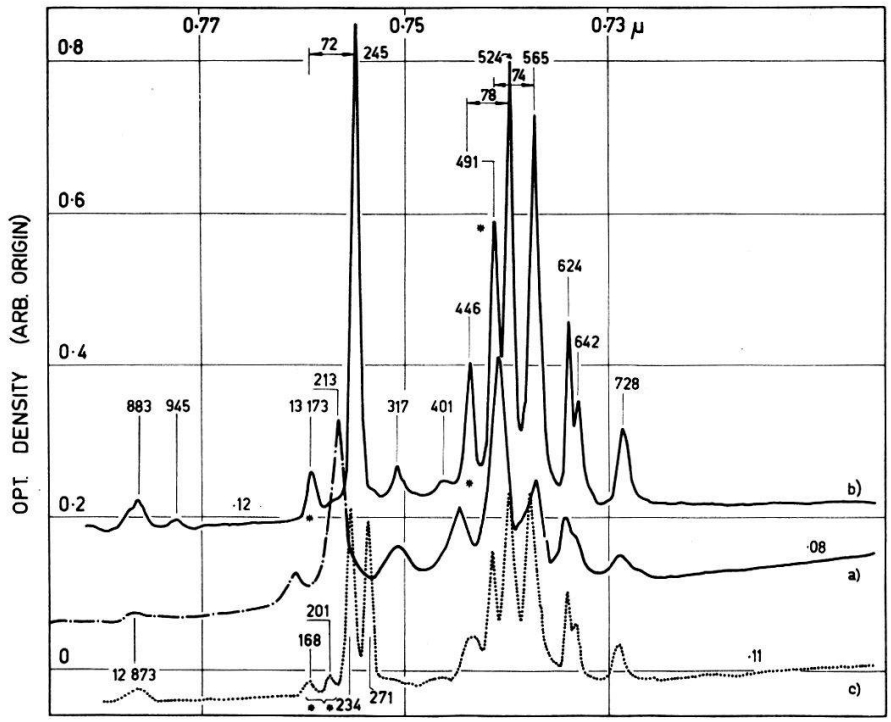

Fig. 3
Line group A. Sample RB 496 a) room temperature, b) 78 °K. Again the long-wavelength group shows a pronounced temperature shift. c) RB 353 at 78 °K.

A general remark concerning the Nd cp_3 spectra is the following. Especially for the first line groups a pattern seems to exist, whereby a line component is usually strongly shifted to low frequencies, with respect to other known Nd^{3+} spectra, and has a pronounced temperature-dependent position. Furthermore, this component has usually a different fine-structure in the sample studied at liquid helium, from what it has in the remaining samples studied.

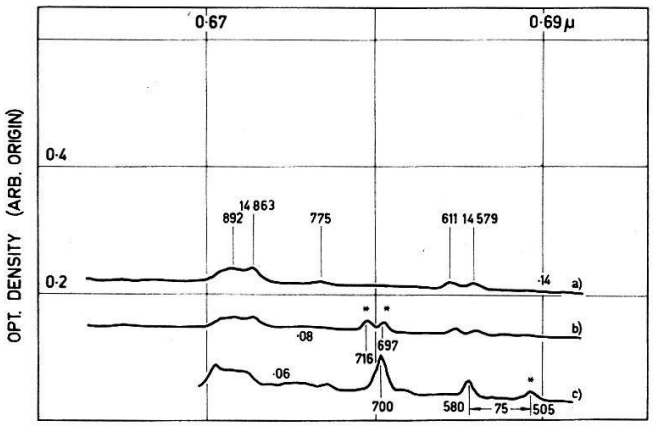

Fig. 4

Group B. The direction of scanning is inverted starting from this figure. a) Nd cp_3 in 2 MeTHF, mm 2.3, sample RB 353 at liquid helium, b) same at liquid nitrogen, c) sample RB 496 at 78 °K.

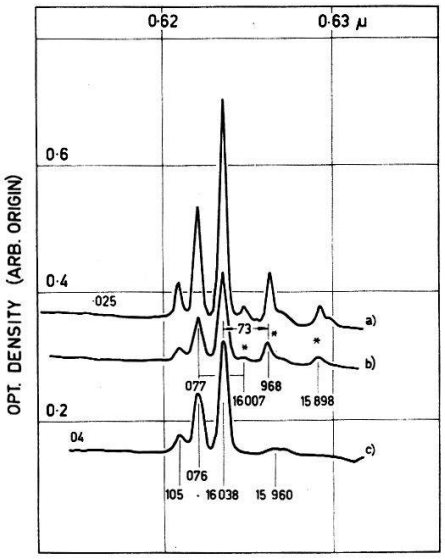

Fig. 5

Group C. a) Sample RB 496, 78 °K, b) sample RB 353 at 78 °K, c) sample RB 353 at liquid helium.

One would conclude that more than one absorbing species is present, were it not for the fact that the anomalous lines in question show the same low-energy satellites, arising from the crystalline splitting of $^4I_{9/2}$, as do the remaining lines.

In what follows, we shall briefly comment on the composition of the various line groups of Nd cp_3, by comparing them with the absorption data of $LaCl_3$:Nd reported by CARLSON and DIEKE[4]) and those of Nd ethylsulphate, reported by GRUBER and SATTEN[5]).

Ground Manifold $^4I_{9/2}$

From the temperature dependence of the absorption lines, one can derive that levels are located at 70 cm^{-1}; 310 cm^{-1}; 570 and 670 cm^{-1} in Nd cp_3. These last two are found at room temperature as low-energy satellites of some lines, especially the very intense transition at $\sim 0.6\,\mu$, and their assignment is not unambiguous. In this connection it should be added that rare-earth tricyclopentadienides show intense infrared absorption in the 650 cm^{-1} region. If some of these levels over the ground state were vibrational, and not crystalline components of $^4I_{9/2}$, they should also be in evidence as high-energy satellites of the electronic transition. This is not apparent in our spectra. By comparison, two of the Nd^{3+} systems most extensively studied[4)5)], both possessing trigonal symmetry for the Nd^{3+} site, $LaCl_3$:Nd and neodymium ethylsulphate $Nd(C_2H_5SO_4)_3 \cdot 9H_2O$ show a splitting of $^4I_{9/2}$ into five components as follows:

$LaCl_3$:Nd	O;	115.39;	123.21;	244.40;	249.35 cm^{-1}
$[Nd(C_2H_5SO_4)_3 \cdot 9H_2O)$	O;	149 ;	154 ;	279 ;	311 cm^{-1}

If our assignment is correct, then the baricenter of $^4I_{9/2}$ is stabilized at least twice as much as in the corresponding two Nd^{3+} systems.

Group R ($^4F_{3/2}$)

Although this is a quartet-quartet transition, the observed intensity is relatively quite low (Figure 1). We have no liquid helium data for this group, yet the probable transitions from the ground state are the lines at 11290 and 11660 cm^{-1} (sample

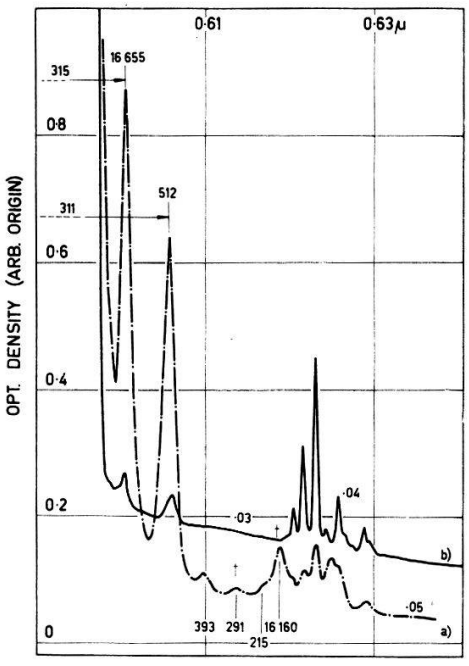

Fig. 6

Sample RB 496. a) Room temperature, b) at 78 °K. The curves show the low-frequency satellites of the two "hypersensitive" lines located at room temperature at 16970 and 16823 cm^{-1}. The transitions arising from the level at 310 cm^{-1} are quite evident. The daggers show the possible transitions from the level at $\sim$ 670 cm^{-1}. The line at 16393 and the shoulder at 16215 still remain to be accounted for.

RB 496). If so, the separation of these two Stark levels is far too large, compared with the data for Nd ethylsulphate (two levels at 11538 and 11556 cm^{-1}) and for $LaCl_3$:Nd (two intense lines at 11423.90 and 11453.91 cm^{-1}).

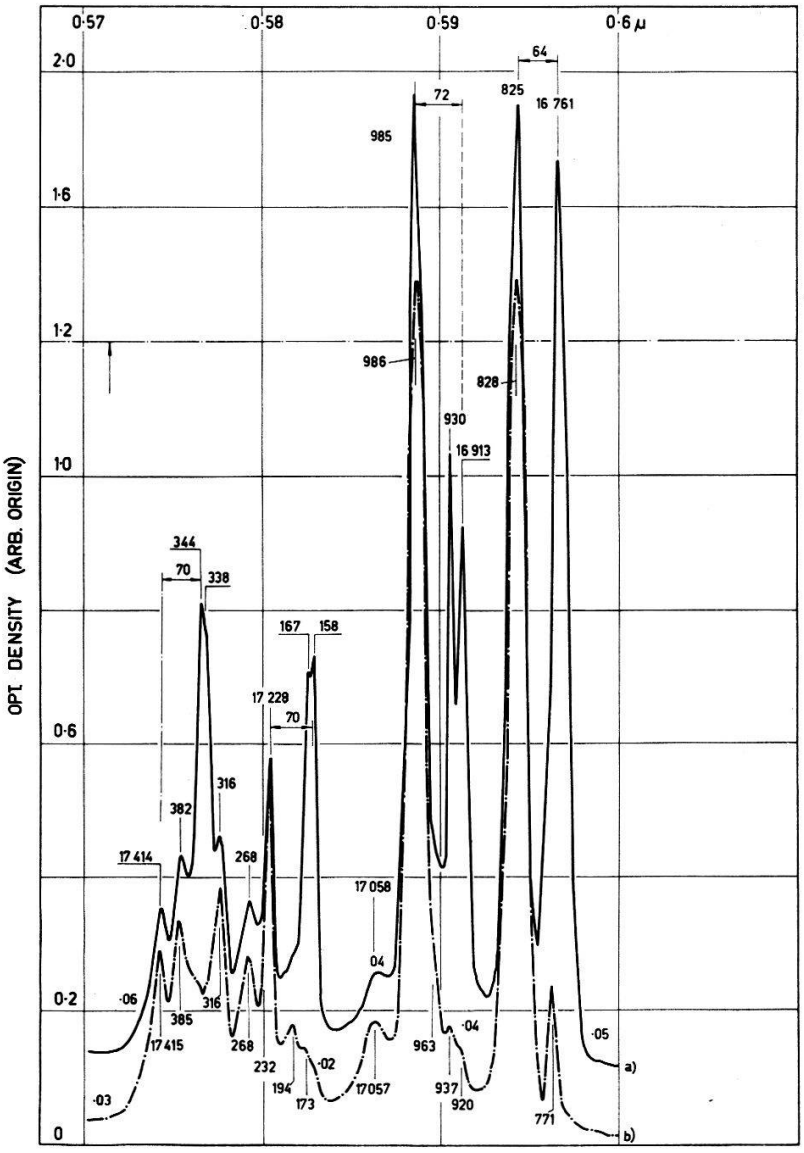

Fig. 7

Sample RB 353. a) At liquid nitrogen, b) at liquid helium. There is a change in the ordinate scale at D = 1.2 (arrow). The intense, sensitive lines at ~ 16830 and 16990 cm^{-1} are responsible for the blue coloration of the compound.

We start noticing in this group the curious feature, mentioned before. At the low-energy side of the group there are lines which show a strong temperature shift from room temperature to liquid nitrogen, and usually show doublet structure in sample RB 353. Also, while the high-energy components are located at approximately the position of the corresponding lines of the two neodymium systems we are using as reference, the low-energy components are strongly shifted towards lower frequencies.

Group S ($^4F_{5/2}$ and $^2H_{9/2}$)

The following lines (Figure 2b) probably represent the transition from the ground level: 12297; 509; 528; 642 cm^{-1}. Except for the first line, the frequencies are not far off from those of the corresponding lines in the two systems mentioned:

$LaCl_3$:Nd	12458.37;	480.65;	487.47;	536.14;	555.73;	643.52;	662.91
$Nd(C_2H_5SO_4)_3 \cdot 9H_2O$	12568;	587;	595;	615;	738;	755	

At least three lines groups at $\sim 0.8\,\mu$ show splittings of 20 cm^{-1}. The line at 12642 is asymmetric on the short-wavelength side (Figure 2b).

The "anomalous" line at 12297 cm^{-1} (Figure 2b) shows doublet structure in sample RB 353 (Figure 2c).

Group A ($^4F_{7/2}$ and $^4S_{3/2}$)

The situation here is quite similar to that of the previous two groups. An "anomalous» line is located at 13245 cm^{-1}. The other lines are fairly close in position to the lines of Nd ethylsulphate.

Group B ($^4F_{9/2}$)

The anomalous doublet (Figure 4a) has quite a similar splitting as in the previous groups. Although this group is due to a quartet-quartet transition, its intensity is remarkably low.

Group C ($^2H_{11/2}$)

Both samples show an identical spectrum (Figure 5). The position of the transitions corresponds fairly well to that of the two Nd systems we are using as reference. It is interesting to note that the splitting pattern in Nd cp_3 is quite similar to that of $Nd[(C_2H_5SO_4)_9\ 9H_2O]$ with one line followed by a triplet of equidistant lines (15957; 16013; 16033; 16050 cm^{-1}). The spacing is roughly double in Figure 5c.

Group D and D' ($^4G_{5/2}$ and $^2G_{7/2}$)

One intense line is found at 17095 cm^{-1} for $LaCl_3$:Nd, followed by an intense, diffuse triplet at 17165.17; 17228.75 and 17297.44 cm^{-1}. Figure 7 shows a very intense doublet shifted by ~ 300 cm^{-1} from the lines of $LaCl_3$:Nd. Again samples RB 353 shows some doublets absent in other samples, such as samples RB 412b (Figure 8) and sample RB 496.

In view of the fact that rare-earths "hyper-sensitive" lines are associated[6]) with the selection rule $\Delta L = 2$; $\Delta J = 2$, the two intense lines should correspond to $^4G_{5/2}$ Stark levels. In fact, according to CARLSON and DIEKE, even in intermediate-coupling $^4G_{5/2}$ is nearly pure.

The intense group D is suitable for the detection of transition from the excited levels of $^4I_{9/2}$. In Figure 6 the transitions from the level at 310 cm^{-1} are quite evident. Still weaker transitions are in evidence, which could be assigned to contributions from levels at ~ 570 cm^{-1} and 670 cm^{-1}.

These intensely absorbing groups should also be suitable for the detection of vibronic replica of the "pure" electronic transition. Actually a large number of diffuse lines (Group D') appear in the region from ~ 17600 to $\sim 18350\ cm^{-1}$. Neither CARLSON and DIEKE, nor GRUBER and SATTEN mention esplicitly the presence of lines in this region.

Even if these lines are overtones of group *D*, any correlation to the lines of group *D* is far from evident in Figure 9.

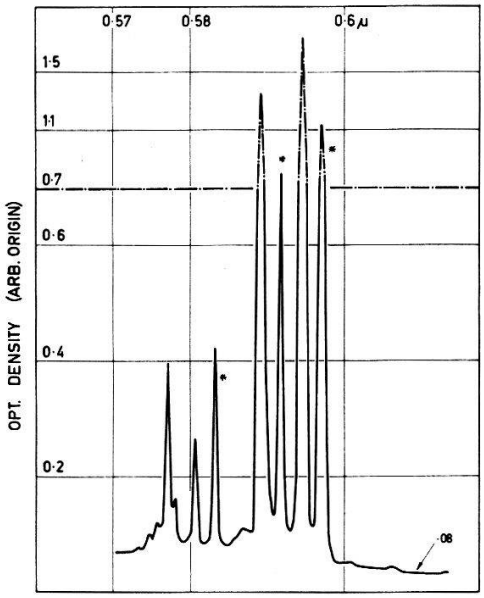

Fig. 8
Sample RB 412b at 78 °K. There is a change in the ordinates at D = 0.7. By comparison with Figure 7 the doublet structure is missing at ~ 16920 and $17268\ cm^{-1}$.

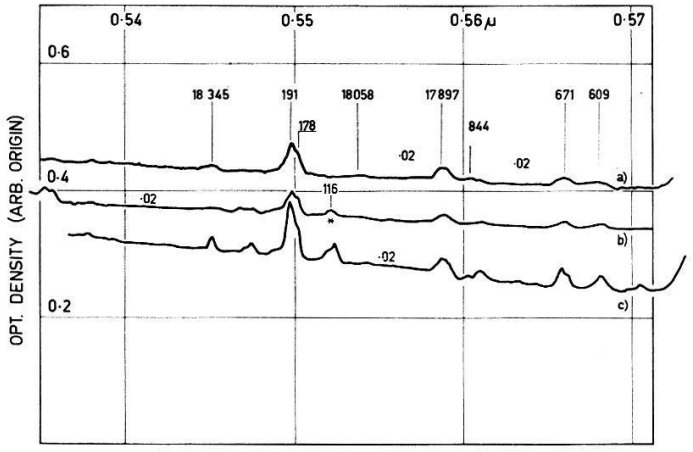

Fig. 9
Sample RB 353. a) At liquid helium, b) at liquid nitrogen, c) sample RB 496 at 78 °K.

Group E ($^4G_{7/2}$)

Comparison of Figure 10b with the spectrum of RB 496 at 78 °K, shows that in the latter the line at $\sim 18744\ cm^{-1}$ is sharper and that there is no doublet structure at $\sim 18870\ cm^{-1}$.

The corresponding lines in $LaCl_3$:Nd and $Nd[(C_2H_5SO_4)_3 \cdot 9H_2O]$ are shifted to higher energies by ~ 250 cm^{-1} and ~ 380 cm^{-1} respectively. Both facts suggest that the three intense lines on the right-hand side of Figure 10 are "anomalous".

Group F

This group starts at 19430.93 cm^{-1} in $LaCl_3$:Nd and at 19570 cm^{-1} in Nd ethylsulphate. The assignments vary. According to CARLSON and DIEKE this group is due to $^2G_{9/2}$ and according to GRUBER and SATTEN to $^4G_{9/2}$. In Nd cp_3 the two lines at 19565 and 19581 cm^{-1} have comparable intensity to those of group E ($^4G_{7/2}$), suggesting the presence of quartet levels. Both in this group and in the previous ones there is a large number of lines unaccounted for, unless vibrational components are considered.

Group G

In $LaCl_3$:Nd this group ranges from 21029 cm^{-1} to 21651 cm^{-1}, and is attributed to $^4G_{9/2}$, $^2(P, D)_{3/2}$ and $^4G_{11/2}$.

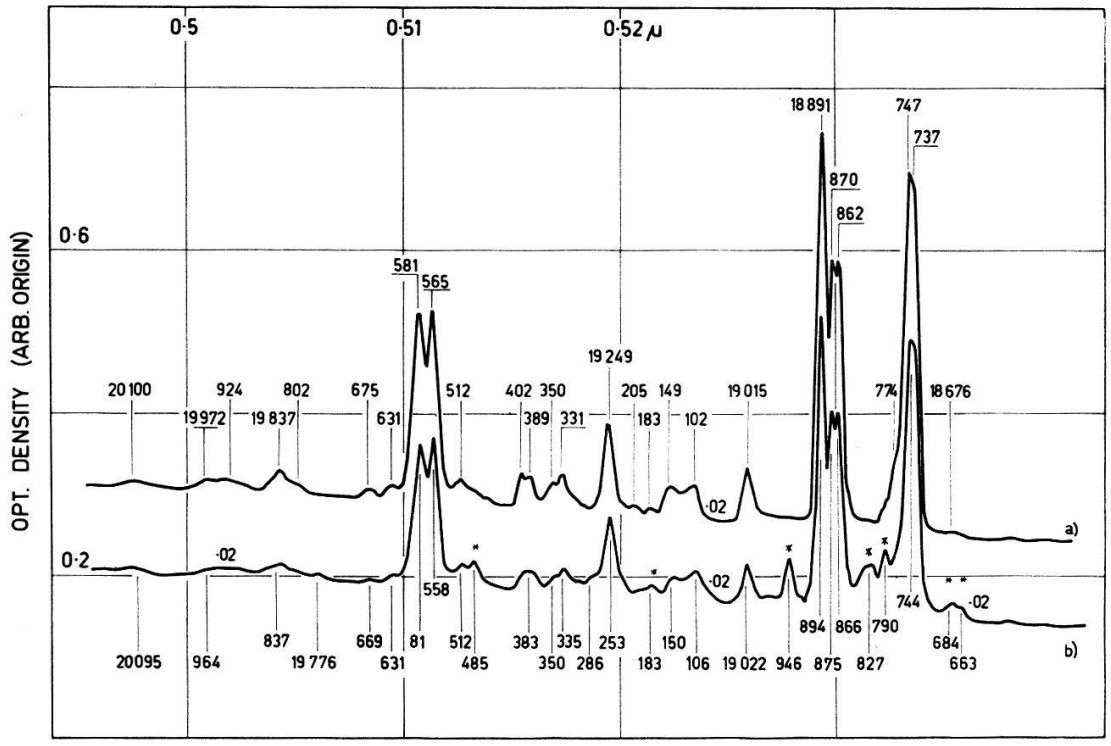

Fig. 10
Sample RB 353. a) At liquid helium, b) at liquid nitrogen.

In $Nd[C_2H_5SO_4]_3 \cdot 9H_2O$ it contains lines from 20983 to 21303 cm^{-1}, and is assigned to $^2G_{9/2}$ and $^2D_{3/2}$, these latter data, though, pertain to 78 °K.

The main characteristic of this group in $Ndcp_3$ is its weak intensity (Figure 11).

Group I ($^2P_{1/2}$)

It has been established that this weak group is due to the singlet $^2P_{1/2}$. Hence it is very suitable, in sufficiently absorbing samples, to the study of temperature-dependent

lines and of the splitting of $^4I_{9/2}$. We assign the weak absorption at 23078 to the $^2P_{1/2}$ transition (Figure 12a). Then transitions arising from levels at ~ 70; ~ 310; ~ 670 cm^{-1} are in evidence in Figure 12e. Only in the strongly absorbing RB 412 sample can one detect an absorption due to the $^2D_{5/2}$ level.

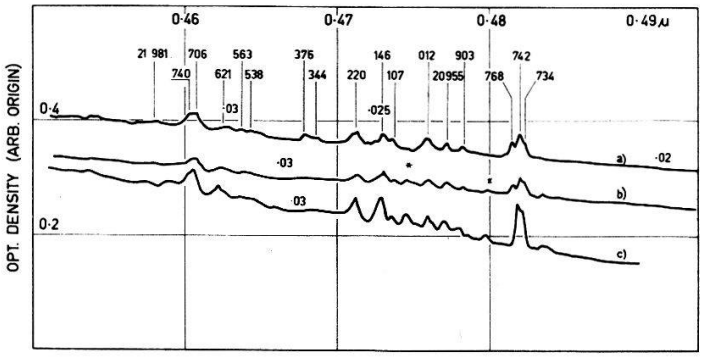

Fig. 11
Sample RB 353. a) At liquid helium, b) at liquid nitrogen, c) RB 496 at liquid nitrogen (Group G).

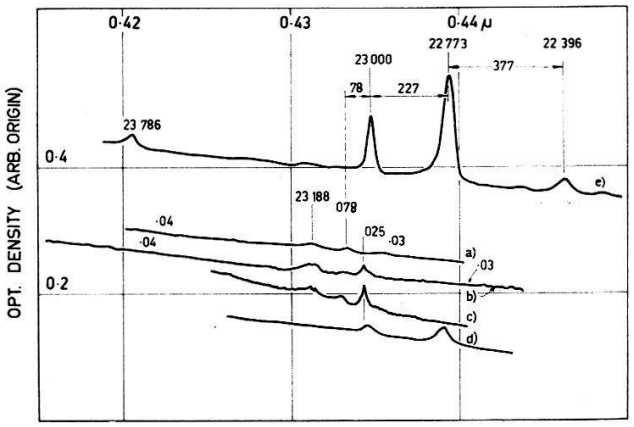

Fig. 12
Group I. a) RB 353 (liquid helium), b) same, liquid nitrogen, c) RB 496, liquid nitrogen, d) same, room temperature, e) RB 412, room temperature. The $^2P_{1/2}$ level is located at 23078. In curve e) frequency differences of ~ 78, ~ 315, ~ 680 cm^{-1} are in evidence. Curve a) shows also evidence for a transition to the $^2D_{5/2}$ group.

Group K

In sample RB 412 (room temperature run) three weak absorptions are found at 25805; 26020 and 26270 cm^{-1}.

Group L

This group is discussed only by CARLSON and DIEKE and not in reference 5. For $LaCl_3$:Nd it is reported that lines belonging to this group stretch from 27972.88 to 29327.76. Their assignment implies the presence of a $^4D_{3/2}$ and $^4D_{1/2}$ manifold.

The presence of quartet terms is in agreement with the intensity of the lines in Figure 13. We might note here that in Nd cp_3 the group in question appears to be shifted roughly 1000 cm^{-1} from the corresponding group in $LaCl_3$:Nd. The temperature dependence of the line at 28129 cm^{-1} (Figure 13b) is also remarkable.

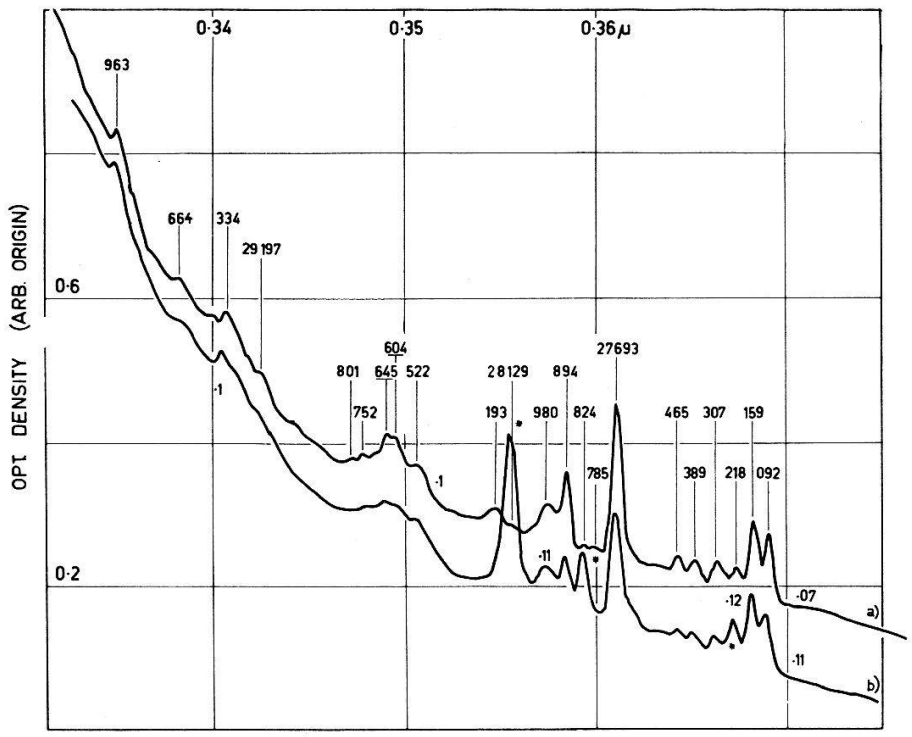

Fig. 13
a) RB 353 at liquid helium, b) RB 353 at liquid nitrogen.

Conclusion

The optical preliminary data presented here point to the existence of four excited levels at 70 cm^{-1}; 310; 570 and 670 cm^{-1}. Of these, the last three could very well be of vibrational nature. Until this question is solved by a comparative study of other rare-earth cyclopentadienides, it will not be easy to decide whether the general shift of the excited levels of Nd cp_3, compared with $LaCl_3$:Nd and $Nd[(C_2H_5SO_4)_3 \cdot 9H_2O]$ is due to a decrease in the electronic repulsion parameters F_K or mainly to the increased stabilization of the ground state in Nd cp_3.

Anomalies in the fine structure of some lines, that is the doublet structure of some "anomalous" lines of the sample studied at liquid helium temperature and absent in other samples, will have to be clarified.

Absorption data at liquid helium, for the line groups in the near infrared region, should be of great help in the interpretation of the crystalline splitting of the free-ion J-levels.

Acknowledgement

I am greatly indebted to Dr. F. Calderazzo for useful advice on the preparation of the samples, to Dr. C. K. Jørgensen for useful discussion and to Mr. S. Losi for valuable technical assistance.

References

[1]) G. Wilkinson and J. M. Birmingham, J. Amer. chem. Soc. *76*, 6210 (1954).
[2]) J. M. Birmingham and G. Wilkinson, J. Amer. chem. Soc. *78*, 42 (1956).
[3]) F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience Publishers 1962, page 644.
[4]) E. H. Carlson and G. H. Dieke, J. Chem. Phys. *34*, 1602 (1961).
[5]) J. Gruber and R. A. Satten, J. Chem. Phys. *39*, 1455 (1963).
[6]) C. K. Jørgensen and B. R. Judd, Mol. Phys. *8*, 281 (1964)