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ON THE RELATION BETWEEN THE EMISSION SPECTRA OF ND^{+++} IONS IN PHOSPHORES AND THE ABSORPTION SPECTRA OF THE SAME IN CRYSTALS*

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ABSTRACT. The relation between the emission spectra of Nd^{+++} ions incorporated into colourless ground materials like K_2SO_4, CaO, etc., and the absorption spectra of the same ion in crystals is discussed. Both kinds of spectra are shown to consist of distinct groups of more or less sharp lines. A classification of the absorption spectra of Nd^{+++} ions in crystals, as carried out by the writer previously, is given in which electronic transitions are assigned for the separate groups of lines, one for each group. In accordance with this, electronic transitions are proposed for interpreting the groups of emission lines. The possible transitions are discussed in the light of Van Vleck's theory of the absorption spectra of the rare earth ions in solids. The phosphorescent radiations emitted are regarded wholly quadrupole in nature and the corresponding selection rules are utilised in the assignment of transitions. The proposed transitions explain qualitatively the position of the groups, the intervals between them and their relative intensities. Some of the rare earth ions show line fluorescence in pure condition whether in solution or in crystals; the absence of such fluorescence in the case of Nd^{+++} ions is discussed.

The line emission spectra of the rare earth ions in solids and in solid solutions, *viz.*, the phosphores, have been widely investigated by Tomaschek and his collaborators.[1] In pure solids the visible fluorescence spectra were found to consist of fairly sharp lines at low temperatures, and like the absorption spectra of the same ions in hydrated crystals they divided into distinct groups. It was noticed by these authors that, in general, there is a relation between the emission and absorption spectra of the same ion and they are supposed to arise from a similar type of electronic transitions. Gobrecht[2] recently extended these investigations to the infra-red side and interpreted the origin of the groups of lines as due to transitions from an excited state of the $4f$-electrons to the different levels of the ground term multiplet. But this kind of fluorescence has not been found to occur in all the ions of the rare earth group; only in four out of the fourteen, *viz.*, in Sm, Eu, Tb and Dy, which are symmetrically placed with respect to Gd, this was observed.

The other kind of emission spectra, *viz.*, that given out by the rare earth ions present in phosphores, are known in cases of almost all the ions of the group with

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the exception of Ce^{+++}. The phosphores are prepared by incorporating a minute quantity of the pure salt in colourless ground materials (generally consisting of the oxides and sulphides of the aikaline earth metals) and when excited by strong ultra-violet light or by a beam of cathode rays they give out characteristic spectra. These phosphorescent spectra are very rich in lines, which are extremely sharp even at the ordinary temperature. For those ions which emit both the fluorescent and phosphorescent spectra the centres of the groups of lines emitted were found to coincide nearly, although each group in the latter was somewhat more spread out. This has been regarded as indicating that same electronic transitions were responsible for the two types of emission spectra, while the difference in their finer structure was to be attributed to the influence of the environments in which the ions were placed in the respective cases. Gobrecht has recently analysed the phosphorescent line spectra of Pr^{+++} on this hypothesis. In this paper it is proposed to interpret the spectra emitted by Nd-phosphores on similar lines.

THE ABSORPTION SPECTRA OF Nd^{+++} IONS IN CRYSTALS.

The absorption spectra of Nd^{+++} ions in crystals were partially classified by the writer in a previous communication.[3] Each group of absorption lines was supposed to be due to a single electronic transition from the ground level to an upper excited level in the $4f$-shell; the finer structure inside the groups was assumed to be due to the Stark-splitting of the energy levels as well as to the superposition of lattice oscillations. In Nd^{+++} ions containing three $4f$-electrons the terms allowed by Russell-Saunders coupling are given by $^4(S, D, F, G, I)$ and $^2(P, D, F, G, H, I, K, L)$. The relative positions of the levels of same multiplicity may be denoted according to Hund's rules by

$$^4S > {}^4D > {}^4F > {}^4G > {}^4I \text{ for the quartets}$$

and similarly for the higher doublet levels. Again, the multiplets being all normal here, the ground level, which is the lowest level of the ^4I state, is to be denoted by $^4I_{\frac{9}{2}}$. In the process of absorption, an electron was assumed to jump from this basic level to the components of upper quartet and doublet states, according to the rules of selection laid down for quadrupole and other higher order radiations. In table I the frequencies of the C.G.s' of the groups of absorption lines and the corresponding transitions are given. If the ground term $^4I_{\frac{9}{2}}$ represent the zero in the energy scale, the frequencies given in table I correspond to the absolute energy values of the upper levels, and it is possible to construct with them the energy level diagram for the ions in question.

TABLE I.

C. G. of the groups.	Int.	Transitions assigned.	Changes in L and J.
I			
(*i*) 11,553 cm^{-1}	weak	${}^4I_{9/2} \rightarrow {}^4G_{5/2}$	—2 ; —2
(*ii*) 12,509 ,,	strong	$\rightarrow {}^4G_{7/2}$	—2 ; —1
(*iii*) 13,534 ,,	,,	$\rightarrow {}^4G_{9/2}$	,, ; 0
(*iv*) 14,791 ,,	fair	$\rightarrow {}^4G_{11/2}$	,, ; +1
II			
(*i*) 15,980 ,,	weak	${}^4I_{\ /2} \rightarrow {}^4F_{5/2}$	—3 ;—2
(*ii*) 17,120 ,,	strong	$\rightarrow {}^4F_{7/2}$	,, ; —1
(*iii*) 18,900 ,,	,,	$\rightarrow {}^4F_{9/2}$	,, ; 0
(*iv*) 19,622 ,,	fair	${}^4I_{9/2} \rightarrow {}^4D_{5/2}$	—4 ; —2
(*v*) 21,103 ,,	strong	$\rightarrow {}^4D_{7/2}$	—4 ; —1
III			
(*i*) 24,757 ,,	weak	${}^4I_{9/2} \rightarrow {}^2H_{9/2}$	—1 ; 0
(*ii*) 28,486 ,,	fair	$\rightarrow {}^2G_{7/2}$	—2 ; —1
(*iii*) 30,412 ,,	,,	$\rightarrow {}^2H_{11/2}$	—1 ; +1
(*iv*) 33,049 ,,	weak	$\rightarrow {}^2G_{9/2}$	—2 ; 0
III			
v) 34,201 Cm^{-1}	weak	${}^4I_{9/2} \rightarrow {}^2F_{5/2}$	—3 ; —2
vi) 38,283 ,,	,,	$\rightarrow {}^2F_{7/2}$	,, ; —1
vii) 39,759 ,,	very weak	$\rightarrow {}^2D_{3/2}$	—4 ; —3
viii) 42,375	very weak	$\rightarrow {}^2D_{5/2}$	,, ; —2

In a few transitions in table I there are departures from the selection rules of quadrupole radiation. These are possible according to Van Vleck only in strong asymmetric crystalline fields and will be discussed later.

THE EMISSION SPECTRA OF Nd^{+++} IONS IN PHOSPHORES.

The emission lines of Nd-phosphore recorded by Tomaschek under different modes of excitation are given in tables II(*a*) and II(*b*). In table II(*a*) the lines from K_2SO_4Nd under optical excitation are entered and they form only one group of lines in the near infra-red. Table II(*b*) contains the lines obtained from

CaO-Nd phosphore excited by means of cathode rays. It is found that the lines are much more numerous when the phosphore is bombarded by a beam of cathode rays, *e.g.*, the lines in table II(*b*) give rise to several groups in addition to the group in the near infra-red contained in II(*a*). On comparing the wavenumbers of the infra-red lines present in both the tables it will be noticed that they do not, in general, agree. This is of course expected when the ground materials in the two cases are different. In addition to the lines emitted by the phosphores, the emission lines of Nd-glass are also given in the table II(*a*).

TABLE II(*a*).

Infra-red lines from K_2SO_4Nd (at −180°).

'ν'	Int		C.G. of the group.	
11,120 cm^{-1}	4			
201 ,,	3			
286 ,,	2			
387 ,,	3		11,320 cm^{-1}	
429 ,,	3			
444 ,,	2			
482 ,,	6			
513 ,,	4			
564 ,,	2			
*11,396—11,266 ,,	strong band		11,332 ,,	

* Emission from Nd-glass (at −180°)

TABLE II (*b*).

Emission from CaO. Nd. (at + 20°).

	Int.	C.G.		Int.	C.G.
10,609 Cm^{-1}	3		21,316 Cm^{-1}	w	
657 ,,	3		453 ,,	m	
711 ,,	4		686 ,,	w	21,730 cm^{-1}
760 ,,	4		852 ,,	st	
880 ,,	2		22,142 ,,	w	
965 ,,	2	11,000 cm^{-1}	721 ,,	w	
11,082 ,,	6				
196 ,,	10		23,276 ,,	v.st	
296 ,,	10		413 ,,	—	
382 ,,	3		634 ,,	v.st.	23,586 ,,
			690 ,,	st.	
11,695 ,,	2		860 ,,	st	
736 ,,	3				
786 ,,	2	*	25,118 ,,	st,	25,310 ,,
874 ,,	2		503 ,,	st.	
909 ,,	1				
12044 ,,	4		36,446 ,,	m	
163 ,,	5	12,140 ,,	619 ,,	m	
211 ,,	1		985 3,	m	
288 ,,	3		37,136 ,,	st	
334 ,,	2		261 ,,	m	37,028 ,,
477 ,,	2		568 ,,	m	
584 ,,	2		611 ,,	m	
13,206 ,,	2	13,276 ,,			
346 ,,	2				

In table III a classification of these emission lines is proposed as arising out of transitions between term levels of the Nd^{+++} ions which were obtained from an analysis of its absorption spectra. The table contains the C. G.'s of the different line groups, their average intensities, the proposed electronic transitions and the corresponding frequencies as calculated from the absorption data.

TABLE III.

C. G. of the groups.	Int.	Transitions possible.	Changes in 'L' and 'J'.	Calculated from absorption.
I.				
(a) 11,332 Cm^{-1}				
(b) 11,320 ,,	v strong	${}^4G_{\frac{5}{2}} \rightarrow {}^4I_{\frac{9}{2}}$	+2 ; +2	11,552 Cm^{-1}
11,000 ,,				
II.				
12,140 ,,	weak	${}^2H_{\frac{9}{2}} \rightarrow {}^4G_{\frac{7}{2}}$	−1 ; −1	12,236 ,,
13,276 ,,	v. weak	$\rightarrow {}^4G_{\frac{5}{2}}$	−1 ; −2	13,192 ,,
III.				
21,730 ,,	medium	${}^2H_{\frac{9}{2}} \rightarrow {}^4I_{\frac{13}{2}}$	+1 ; +2	—
23,586 ,,	strong	$\rightarrow {}^4I_{\frac{11}{2}}$	+1 ; +1	—
25 310 ,,	medium	$\rightarrow {}^4I_{\frac{9}{2}}$	+1 ; 0	24,745 ,,
IV.				
(c) 27,129 ,,	weak	${}^2G_{\frac{7}{2}} \rightarrow {}^4I_{\frac{9}{2}}$	+2 ; 1	28,475 ,,

(a) Emission spectra of Nd-glass excited by light.
(b) Do of K_2SO_4 -Nd ,, do.
(c) Additional group emitted by Al_2O_3 – Nd under cathode ray excitation

DISCUSSION.

It is found that the majority of the groups of emission lines conform to the scheme of classification shown above, which is very similar to that adopted for the absorption spectra ; also they are capable of being represented by transitions in the energy level diagram constructed for Nd^{+++} ions from the absorption data as shown in figure 1. In both of these cases, *viz.*, emission and absorption, the changes which '*L*' and '*J*' undergo in each transition are given in the corresponding table. It is found that according to the selection rules given by Laporte most of the specified transitions are forbidden. They can thus hardly be expected to give rise to lines of appreciable intensity, observed in absorption as well as in emission.

Recently Van Vleck[1] has discussed this question with special reference to the absorption spectra of the rare earth ions in solids. He regarded the transitions as all more or less forbidden in ordinary dipole radiation and calculated the probability of transition in all the other forms of radiation, which the ions can possibly emit under the influence of the crystalline field. These are tabulated below together with the allowed changes of 'L' and 'J' in each case.

TABLE IV.

	Forms of radiation	Selection rules.	
1.	Quadrupole	$\Delta L = 0, \pm 1, \pm 2 \ (0 + \longrightarrow 0)$	4 sec^{-}
		$\Delta J = 0, \pm 1, \pm 2 \ (0 + \longrightarrow 0, 1)$	
2.	Magnetic Dipole	$\Delta L = 0, \pm 1 \ (0 + \longrightarrow 0)$	
		$\Delta J = 0, \pm 1 \ (0 + \longrightarrow 0)$	
3	Electric Dipole (caused by distortion of the electronic motion due to crystalline fields).	ΔL or ΔJ may be equal to even 4 or 5	(a) 1 sc (no centre of symmetry) (b) 10 ,, (dissymmetry caused by vibration).

As shown in the table the probability of transition is very low in each case being of the order of about one-millionth of that in the ordinary dipole radiation. This is in agreement with the experimental results of Becquerel,[5] who found that the intensity of absorption of these ions (specially Pr^{+++} and Nd^{+++}) is extremely low and obtained values of $\sigma \backsim$ 10 to 100 sec^{-1}. They are of the same order of magnitude as in the four cases cited above, as according to Van Vleck the calculation may be easily out by the order of 10 to 100. The apparent intensity of the absorption lines is due to the high concentration of the ions in the solid crystals.

In the case of emission spectra it is sufficient to assume that their origins are due to quadrupole radiation involving changes of 'L' and 'J' not greater than 2 units. In the case of the absorption spectra on the other hand, the origin of certain faint lines have been found to involve larger changes of these two quantum numbers and are according to the views of Van Vleck to be ascribed to electric dipole radiations arising out of forbidden transitions in an unsymmetrical crystalline electric field. Van Vleck has discussed two different ways in which such a field can arise. In emission the electronic transition usually occurs between the excited states and the different levels of the ground term. But it will be noticed that the transitions do not take place from all the different levels of the upper multiplets but only from their lowest levels. The electron, when in any one of the upper level, is first brought down to the lowest level of the multiplet in question by thermal collisions, and from there it jumps back to the ground state. Many of the transitions possible in absorption do not therefore appear in emission ; thus it is possible to find out the multiplet separations of many of the upper states from the absorption data, but the emission data help only in obtaining the same for the ground state. In table III the possible transitions obeying the rules of quadrupole radiation are given. In the following it will be seen how far they can explain the intensity of the different groups as also the intervals between them. For convenience we shall divide the transitions assigned into three classes, *viz.*,

(*a*) Transitions among the quartet levels : In the table only one such transition is specified, *viz.*, $^4G_{\frac{5}{2}} \rightarrow {}^4I_{\frac{9}{2}}$. It is easy to see that other transitions of this type are all excluded, since transitions from $^4G_{\frac{5}{2}}$ to other levels of ^4I will involve a change in ' J ' by more than two units while in transitions from other quartet levels both ' L ' and ' J ' will have to change by more than two units. The intensity of this group is the highest as shown in the table. This is to be anticipated, because in this transition there is not only no change of multiplicity but also the changes in L and J are in the same sense.

(*b*) Transitions from the doublet levels to the ground state. The allowed transitions of this kind are

$$(i)\ {}^2H_9 \longrightarrow {}^4I_{\frac{9}{2},\ \frac{11}{2},\ \frac{13}{2}}.$$

$$(ii)\ {}^2G_{\frac{7}{2}} \longrightarrow {}^4I_{\frac{9}{2},\ \frac{11}{2}}.$$

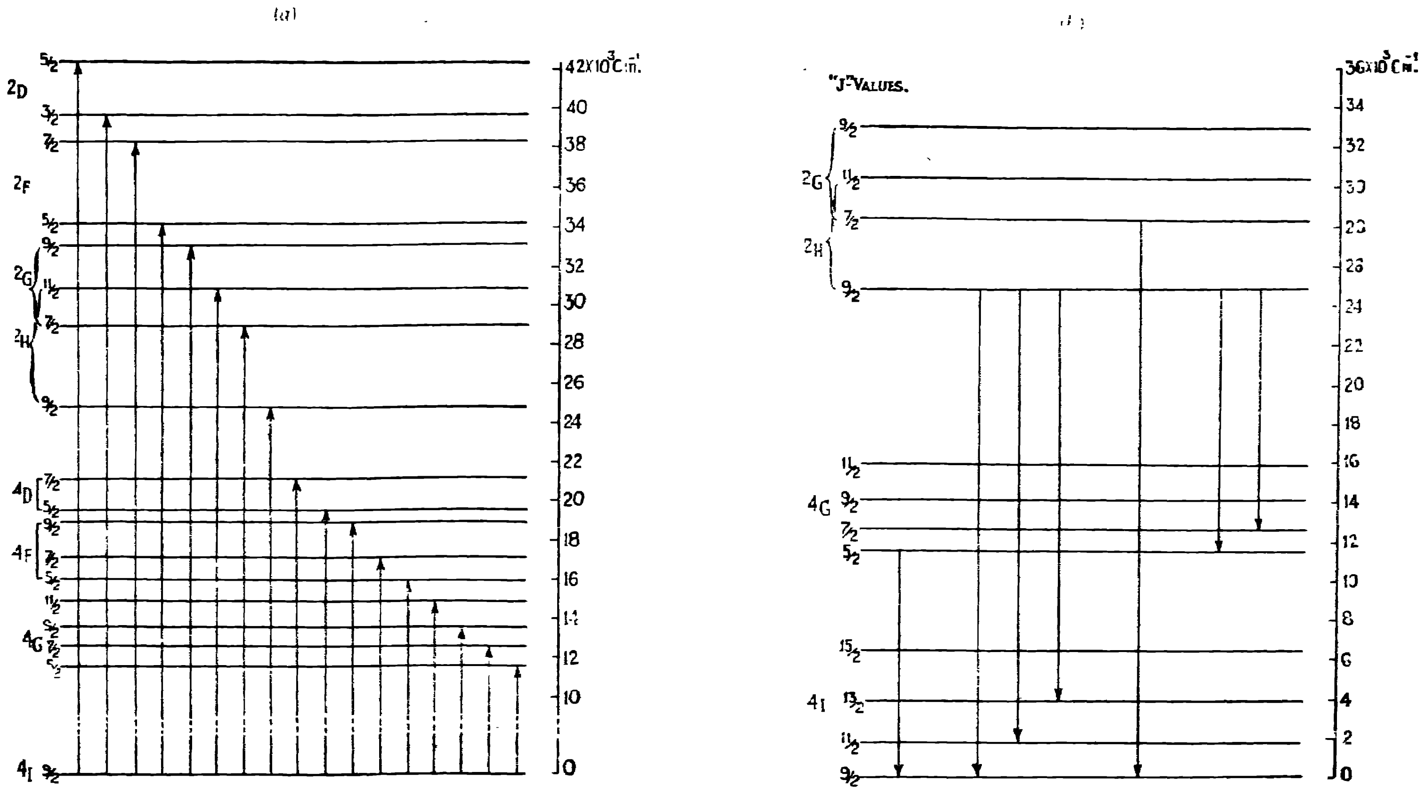
In the table the three groups corresponding to (*i*) are given. It is expected that the intervals between these groups should give the splitting of the ground term multiplet. The separations between these levels calculated according to the well-known formula are given by

$$\Delta\nu\,({}^4\mathrm{I}_{\frac{9}{2}} \longrightarrow \tfrac{11}{2}) = 1814\ \mathrm{cm}^{-1}$$

$$\Delta\nu\,({}^4\mathrm{I}_{\frac{11}{2}} \longrightarrow \tfrac{13}{2}) = 2144\ \text{,,}\quad ,$$

If it be assumed that the screening constant $\sigma = 34$. The corresponding intervals from the table III will be found to be 1724 cm^{-1} and 1856 cm^{-1} respectively, showing thereby a fair agreement. The relative intensities of the groups are also in accordance with the theory for the middle group where both ' L ' and ' J ' increases by ' 1 ' is stronger than the other two where ' J ' either remains same or increases by 2 units. Of the remaining transitions in (*ii*) only one is

FIGURE I.



Energy level diagram for Nd^{+++} ions which accounts for several of the observed frequencies of absorption and emission spectra of the ion.

(a) For absorption in crystals.

(b) For emission from phosphores.

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present in the table, which gives rise to a group of weak lines observed only in Al_2O_3·Nd.

(*c*) Transitions where the final level is an excited level: The table contains two such transitions, *viz.*, $^2H_{\frac{9}{2}} \rightarrow {}^4G_{\frac{5}{2}, \frac{7}{2}}$. The frequency interval between the corresponding groups of lines agrees fairly well with the separation between the $^4G_{\frac{5}{2}}$ and $^4G_{\frac{7}{2}}$ levels, as obtained from the absorption data. The probability of such transitions is, however, very low from what has been said above, and this is shown by the extremely low intensity of these groups of lines, although the changes in '*L*' and '*J*' are quite favourable.

In the above portion we have seen that there is a good deal of similarity between the absorption and the emission spectra of Nd^{+++} ions, even when in different states of aggregation. But there are also a few points of distinction between the two and it seems desirable to discuss them here. It is found that although the general nature of the absorption spectra remains practically same whether the Nd^{+++} ions are in solutions or in crystals, or whether they are embedded in glass or other colourless ground meterials, it makes a lot of difference in emission. Thus whereas the Nd^{+++} ions in glass or in the phophores give rise to the groups of emission lines in the visible, the pure ions whether in solution or in crystals have not been found to emit any. This naturally leads one to postulate the influence of the foreign atoms present in bringing about the corresponding transitions in emission. But such an assumption will not in general be valid for all the rare earth ions, as it has already been referred to above that some of these show line fluorescence in pure condition whether in solution or in crystals. On the other hand, many of the transitions shown in the energy level diagram in figure 1 are reversible appearing both in the process of absorption and emisssion, which indicates that the corresponding radiations should behave more or less like the resonance radiation of free atoms. It seems thus extremely difficult to explain why there will be no line fluorescence in ions like Nd^{+++} when in pure condition either in solution or in crystals.

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