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ELECTRONIC TRANSITIONS BETWEEN AN INNER SHELL AND THE VIRTUAL OUTER SHELLS OF THE IONS OF THE RARE EARTHS IN CRYSTALS

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Abstract

In the rare earths, the inner 4*f* shell is incomplete and its electrons are much less stable than those in the outer complete 5*s* and 5*p* electronic shells. The rare earths possess sharp absorption lines which are ascribed to initial and final quantum states arising from different orientations of the spin and orbital moments of the electrons within the 4*f* shell. Ce^{+++} has only one electron in this shell giving rise to only one term ^2F, a doublet, with an interval of about 1000 cm^{-1}. Absorption in the ultraviolet must correspond, then, to a transition from the 4*f* shell to virtual outer shells such as 5*d* or 6*s*, or to the lattice. The ultraviolet absorption spectra were taken of single crystals of hydrated cerium chloride and cerium ethylsulfate at room temperatures, at that of liquid nitrogen, and of liquid hydrogen. The crystals varied in thickness from about 0.2 mm to 3 mm, about the same thickness as has been employed in studying the line spectra of other rare earths. Aside from the very faint diffuse band at about 3020A found in one of the chloride crystals and which doubtless exists in the ethylsulfate also, the crystals were completely transparent from the visible to about 2700A and there, absorption set in and occupied the rest of the ultraviolet (to 2000A). To discover whether this continuum was caused by the overlapping of several regions of selective absorption, the cerium ions were diluted in the isomorphous lanthanum crystals which are transparent and possess practically the same electric fields as the cerium crystals. The ratio of Ce^{+++} to La^{+++} in the solution from which the crystals were grown varied from about 1 to 10 to about 1 to 5000. Three new diffuse bands were discovered which remained structureless even at great dilution and at the temperature of liquid hydrogen. The bands were recognized as transitions from a rather sharp inner quantum state ^2F (the electron in the 4*f* shell) to a diffuse outer quantum state ^2D (the electron in the virtual 5*d* shell). The electron of the activated Ce^{+++} is subject to enormous inhomogeneous electric fields because it is very close to the water molecules (and the negative ions) in the lattice. The ^2D term is decomposed by these fields into sublevels of wide separation which are extremely sensitive to all the variations in electric fields. The substitution of one negative ion for another or a change in the fields accompanying thermal contraction displaces the bands in some instances by a hundred times as much as the lines of Gd^{+++} are displaced under similar conditions. Whence, we return to the conclusion that the *lines* of the rare earths in general are associated with inner quantum states. It was predicated that transitions from the 4*f* electron to the outer shells would occur in other rare earths Pr^{+++}, Nd^{+++} etc., but the bands would begin further in the ultraviolet than they do in Ce^{+++}. A band extending from 2280A to 2100A was found in undiluted neodymium chloride which also remained without structure at the temperature of liquid hydrogen. Pr^{+++} exhibited no absorption band within the range of the spectrograph although the existence of one beginning at about 2100A would not have been determined. It is expected that the first band of Pr^{+++} begins somewhere in this region. The breadth of the bands has been discussed.

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* Fellow of the John Simon Guggenheim Memorial Foundation.

IT HAS been proved[1] that the electronic configurations of the rare earths in crystals are the following:

Ionic number*	Ion	Basic term	1*s*, to 4*d*	4*f*	5*s*, 5*p*
54	La^{+++}	^1S	full	0	full
55	Ce^{+++}	^2F	"	1	"
56	Pr^{+++}	^3H	"	2	"
57	Nd^{+++}	^4J	"	3	"
68	Lu^{+++}	^1S	"	14	"

* Ionic number is the atomic number less three.

The energy required to liberate an electron in the 5*s* shell from these ions is about 45 volts and to liberate an electron in the 5*p* shell about 34 volts.[2] However, an extrapolation is necessary to learn the ionizing energies for the electrons in the 4*f* shell. The 4*f* shell becomes less stable than the 5*s* shell at about atomic number 85 and less stable than the 5*p* shell at atomic number 79 and it remains so for all lower atomic numbers. It appears that the energy of the electron in the 4*f* shell of the rare earths may correspond to radiation in the ultraviolet. It would presumably be the least in Ce^{+++} because the effective nuclear charge is probably the least here.

The extraordinary sharpness of the absorption lines of the rare earths in crystals has been ascribed to stationary states arising from the electrons within the inner (4*f*) shell. The different states owe their origin to the different orientations of the orbital and spin moments of the electrons in this shell. Because of the enormous positive charge acting on these internal electrons, they are doubtless close to the nucleus and rather distant from the fluctuating perturbations of the oscillating molecules and ions. In addition the completely filled 5*s* and 5*p* shells serve as screens against these perturbations. Ce^{+++} has but one electron in the 4*f* shell and it can give rise to but one basic term.[3] Any absorption in the ultraviolet must imply a transition of the 4*f* electron to outer electronic shells such as 5*d*,—, 6*s* etc. The possibility is open, of course, that the electron may end in the closely spaced quantum states which are equivalent to ionization in the lattice.

The absorption lines of most of the rare earths are diffuse at room temperature but they sharpen remarkably at lower temperatures. As a rule they are

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[1] Hund, Linienspektren, Springer, Berlin (1927).

[2] The actual values differ little from one ion to another. Those given here apply to Nd^{+++} and were read from the Bohr-Coster diagram. See, for example, Ruark and Urey, Atoms, Molecules and Quanta, p. 253, McGraw-Hill, New York (1930).

[3] The basic term is ^2F, a doublet, with an interval of about 1000 cm^{-1} as calculated from Sommerfeld's formula for relativity doublets. These levels are further decomposed by the inhomogeneous electric fields of the surrounding molecules and ions. The magnitude of the electrical separation cannot be as much as several hundred cm^{-1} when the positive ions are surrounded with H_2O dipoles since the magnetic susceptibilities of these ions are almost the same as Hund calculated for the gaseous ions. If the separations reached any such order of magnitude, deviations from Curie's law would have been serious at room temperature. Kramers Proc. Acad. Amsterdam **32,** 1176 (1929).

fine at the temperature of liquid nitrogen. The total intensity of the diffuse lines seems to be concentrated within a very narrow range so that the lines are easy to observe. As a precaution, the temperature was reduced even further to that of liquid hydrogen where the intensification progresses still further.

The apparatus employed was a quartz Dewar tube furnished with four plane quartz windows. The single crystals were always immersed in the refrigerating liquid and were held in a metallic strip fastened to a tube of German silver which could be raised and lowered. In this way any one of several crystals could be placed in the path of the light. The source of continuous radiation in the ultraviolet was a hydrogen discharge tube similar to the type recommended by Bay and Steiner.[4] It was constructed of Pyrex glass and permitted the continuous use of more than 500 milliamperes. An E_2 spectrograph from Hilger was employed through the kindness of Professor Blanksma of the Organic Chemical Laboratory of this university. It contained one quartz prism and had a dispersion of about 5A per mm at 2500A.

Crystals of the following salts were investigated: cerium chloride, cerium ethylsulfate, cerium acetate, praseodymium chloride, neodymium chloride, lanthanum chloride. All contained water molecules of crystallization. The cerium salts were recrystallized many times; the chloride from absolute alcohol. The cerium chloride was obtained as the hydrated chloride "pur" from the Societé des Produits Chimiques des Terres Rares. The ethylsulfate of cerium and the acetate were made from a hydrated nitrate "reinst" of the Auer Gesellschaft. *All* the chemical operations and crystallizations were carried out at practically room temperatures to avoid oxidation. The oxidation of cerium, observed by the yellowing of the solution, sets in rapidly if the solution is boiled in air, but this reaction does not occur in alcohol. (It was later found reported that the oxidized cerium salt reverts easily in the presence of alcohol to the form desired for this work.)[5]

Thereafter, all crystallizations were performed at room temperature from solutions containing considerable concentration alcohol. The crystals were grown by the slow evaporation of a saturated solution in a dessicator containing calcium chloride.

The crystals of the three cerium salts varying in thickness from about 0.2 mm to 3 mm showed similar absorption spectra at all temperatures. They were completely transparent from the visible region of the spectrum to about 2700A and then absorption began rather abruptly and occupied the rest of the ultraviolet region (until about 2000A, the limit of transparency of the quartz spectrograph). The absorption edge moved toward the red with increasing thickness of crystal.

It was inferred at this stage of the work that the continuum corresponded to an ionization of the ion, a transition of the electron immediately to the lattice rather than to an outer shell such as 5*d*, . . . , or 6*s* etc. Transition to the latter would presumably have resulted in broad lines or bands since the

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[4] Bay and Steiner, Zeits. f. Physik **45**, 337 (1927).

[5] Treadwell-Hall, Analytical Chemistry, p. 471, Vol. I, New York (1916).

outer shells are susceptible to the oscillating electric fields of the water molecules. (Additional broadening influences will be discussed later.)

It was of course necessary to establish that the absorption was not due to the negative ions. For this purpose salts of other rare earths containing the same negative ions were examined so as to be entirely assured that the fields emanating from the positive ion, that is, the fields associated with the size and charge of Ce^{+++} could not displace the "natural" obsorption of the negative ions into the observed spectral region. (It is hardly necessary to remark that the ionic radii of the rare earths are almost identical, the well-known difficulty of separating them attests to the minutest differences.)

Lanthanum *chloride* was found to be completely transparent throughout the entire spectral range. This behaviour was expected since the chloride ion is known to be transparent here and lanthanum with no electrons in the $4f$ shell would require for the disruption of the completed shell many times the energy available in the shortest wave-lengths. Apart from a line spectrum, praseodymium *acetate* was also found to be transparent down to the shortest measurable wave-lengths. Dysprosium *ethyl sulfate* behaved similarly.

It was still possible that the unbroken continuum was really the superposition of several absorption bands either because of an interaction of neighboring cerium ions or because of an enormous intrinsic absorption of these ions. The consequences of both these influences could be obviated by separating the Ce^{+++} in the crystal lattice and by keeping the thickness of the resulting crystal about the same as in the previous experiments. The cerium ions were separated from each other by making mixed crystals of the cerium salts with the same lanthanum salts, the cerium comprising but a small fraction of the total. Mixed crytals of cerium and lanthanum chlorides and of cerium and lanthanum ethyl sulfates were investigated. La^{+++} was selected for the dilution because of its complete transparency. Mixed crystals of the La^{+++} and Ce^{+++} salts can be made in all proportions because the radii of these ions are almost identical. In the ethylsulfates and in the chlorides, both the Ce^{+++} ions and La^{+++} ions are immediately surrounded, with the same number of water molcules probably as $La(H_2O)_6{}^{+++}$, $Ce(H_2O)_6{}^{+++}$ and the fractional differences in the radii of these increased ions is even less than in the unhydrated ions. In addition the slight difference between the action of one cerium upon another and that of a lanthanum ion upon a cerium ion is lessened by the negative ions between them in the crystal lattice.[6]

Crystals prepared from a *solution containing* about ten times as much lanthanum chloride as cerium chloride exhibited a new faint diffuse absorption band with a maximum at about 3025A at room temperature and the continuum occurred in approximately the same region as before. This ab-

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[6] The research of J. Becquerel (Gedenkboek H. Kammerling Onnes (1922)) shows that many absorption lines of the rare earths are sharp even in complicated mixtures such as minerals. The substitution of Br^- for Cl^- in $GdCl_3\ 6H_2O$ (Freed and Spedding, Jour. Am. Chem. Soc. **52**, 3747 (1930)) shifted the absorption lines of Gd^{+++} on an average by about $4cm^{-1}$. The substitution of La $(H_2O)_6{}^{+++}$ for Gd $(H_2O)_6{}^{+++}$ would doubtless produce so small a displacement that it would be scarcely measurable with the quartz spectograph employed in this work.

sorption was never observed in crystals containing Ce^{+++} in smaller concentration such as are about to be discussed.[7] These crystals varied in thickness from about 0.3 mm to 2 mm. When the concentration of cerium in solution was about two percent of that of lanthanum, the continuum previously noted decomposed into three diffuse bands which remained as diffuse at the temperature of liquid hydrogen as at room temperature. The corresponding ethylsulfates showed similar absorption spectra. When the Ce^{+++} in solution was diluted further, about one hundred fold relative to the La^{+++}, the same absorption bands persisted, became fainter and narrower but showed no structure either to the eye or to a microphotometer. Lowering the temperature to that of liquid hydrogen did not perceptibly alter the diffuseness of the bands. (See Table I.)

TABLE I. *Data of mixed crystal of lanthanum and cerium ethylsulfate and mixed crystal of lanthanum and cerium chloide.*

Temperature	Number of band	$La^{+++}(Ce)^{+++}(C_2H_5SO_4)_3 \cdot 9H_2O$		$La^{+++}(Ce)^{+++}Cl_3 \cdot 6H_2O$	
		Center of band	*Width of band A	Center of band A	Width of band
Room	I			3020	
	II	2565	110	2575	50
	III	2380	100	2455	50
	IV	2200	50	2300	very wide
Liquid nitrogen	II	2550	80		
	III	2370	60		
	IV	2230	60		
Liquid nitrogen	II	2540	115	2540	80
	III	2365	90	2440	65
	IV	2245	very wide	2300	45

* The width of the band is only of qualitative significance since it varies with the time of exposure, especially in the wider bands.

Different crystals gave roughly the same maxima within 10A for the narrow bands and 15A for the wider ones. This is about the reproducibility with which the maxima of any single bands are known.

The same crystal of the ethylsulfate was employed at the three temperatures. It was grown from a solution containing about fifty times as much lanthanum as cerium.

The same crystal of the chloride was also employed at the two temperatures but it is possible that at room temperatures there was some moisture on the faces of the crystal. The chlorides differ from the ethylsulfates in being very hygroscopic.

The diffuseness of the bands, the magnitude of their separations the great displacement in their positions when one negative ion is substituted for another or when the temperature is reduced, confirm the expectations that the absorption represents a transition from the 4*f* shell to virtual outer shells of the ion. There is no escape from this interpretation if the final quantum

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[7] After this research was finished, this band was recognized faintly in the spectrum of a crystal of cerium chloride undiluted with lanthanum.

states are to be identified with the positive ion. The diffuseness of the bands may be attributed to the outer quantum state or states. (I shall refer to an "outer quantum state" when I mean the quantum state of the ion if the electron is in an outer shell.) The latter is exposed to all the perturbations of the neighbors of the positive ion and to all the oscillations that the neighbors experience. In addition, the unordered electric fields resulting from the strains in the crystal exercise a broadening on these sensitive levels. Even more important in this connection, the electronic levels probably couple with the oscillational levels of the water molecules of the crystal lattice in a way such as has already been anticipated.[8,9] On the other hand, the inner quantum state, the basic state, is relatively free from these oscillating perturbations. The coupling between the electronic motion in the 4*f* shell and the oscillational motion of the lattice is weak and judging by the sharpness of the absorption lines of the other rare earths such as Nd^{+++}, Gd^{+++}, Dy^{+++} etc., we would estimate the energy of the coupling to be less than the width of a rather sharp absorption line. The energy of this coupling must fall off rapidly with distance.

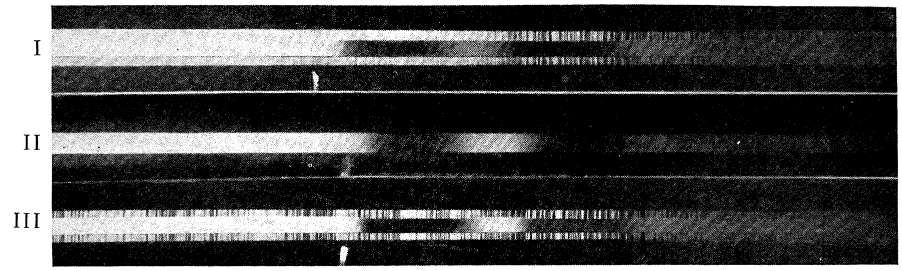

Fig. 1. Mixed crystal of lanthanum and cerium ethylsulfate. I. Room temperature, II. Temperature of liquid nitrogen, III. Temperature of liquid hydrogen.

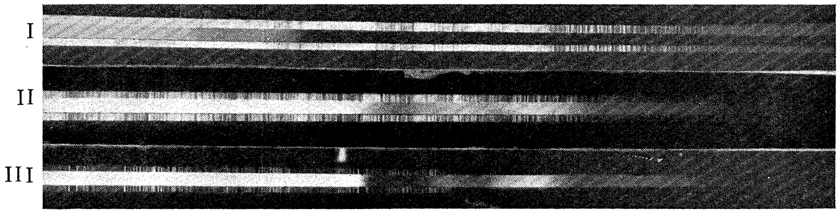

Fig. 2. Mixed crystal of lanthanum and cerium chloride. I. Room temperature: crystal grown from solution containing about ten times as much lanthanum as cerium. II. Room temperature: crystal grown from solution containing about 200 times as much lanthanum as cerium. III. Temperature of liquid hydrogen: crystal containing same concentration as II.

The H_2O molecules may be fairly well represented as dipoles in their action upon the relatively distant 4*f* electron. However, the proximity of the

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[8] Ehrenfest, Gedenboek, H. Kammerling Onnes (1922).

[9] Frenkel, Phys. Rev. **37,** 17 and 1276 (1931).

H_2O groups to the outer electron of the activated Ce^{+++} brings into play their detailed electronic structures with their stupendous inhomogeneous electric fields. The influence of the negative ions also becomes more intense. We find that an alteration in the dipole attending the substitution of one negative ion for another displaces the bands of the Ce^{+++} by as much as 1000 cm^{-1} whereas a similar substitution displaces the lines of Gd^{+++} by less than 10 cm^{-1}. The contraction of the crystal, induced by lowering the temperature, with the resulting change in the electric fields, also effects a disproportionate readjustment of the inner and outer shells. In Gd^{+++} where both the basic and the activated states are in all probability inner states an absorption lines shifts about 6 cm^{-1} when the temperature is reduced from room temperature to that of liquid hydrogen.[10] Under like conditions we find a displacement in Ce^{+++} of from 200 cm^{-1} to 500 cm^{-1}. There is no reason for believing that transitions to outer shells are restricted entirely to Ce^{+++}. We should expect Pr^{+++}, Nd^{+++} etc. to have similar bands in their absorption spectra. Pr^{+++} and Nd^{+++} with higher nuclear charges than Ce^{+++} probably hold the 4*f* electrons more strongly and require more energy for analogous transitions. (Such is the ordinary progression in gases also.) Hence we should expect to find their bands further in the ultraviolet region of the spectrum. No bands were found in a hydrated crystal of praseodymium chloride which Professor Urbain had kindly purified for the Cryogenic Laboratory. Nd^{+++} ("Reinst" Auer Gesellschaft) definitely possessed such a band in our extreme ultraviolet. The band of the hydrated neodymium chloride extended from 2280A to 2100A and showed no structure even at the temperature of liquid hydrogen. It is probable that Pr^{+++} can be similarly activated but its first band lies just out of range of the quartz spectrograph. A faint band near 2100A would not have been detected for the general intensity of the radiation was feeble in this region.

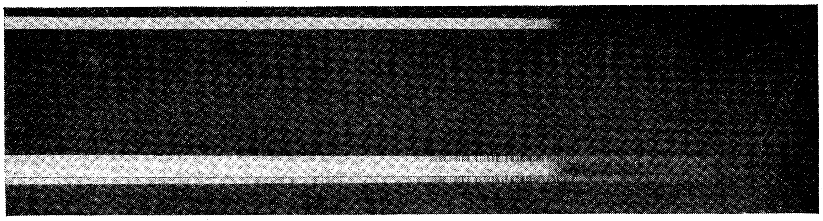

Fig. 3. Absorption spectrum of Nd^{+++} in $NdCl_3 \cdot 6H_2O$ at 20°K. Band begins at about 2280A and ends at about 2100A, (very faint).

It was surprising to observe so little contraction in the bands at the temperature of liquid hydrogen. The breadth of the bands which can be related to thermal oscillations (namely, the variation in the external electric fields and the coupling with the oscillations themselves) are doubtless greatly reduced. However, the low temperature would be accompanied by an in-

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[10] Freed and Spedding, Phys. Rev. **34,** 945 (1929).

crease in the number and in the intensity of the strains and their "surface" fields would undo the normal effects of reduced temperatures.[11]

We have mentioned[3] that the separation between the levels of the basic doublet ^2F is expected to be about 1000 cm^{-1}. Corresponding to this difference in energy about 5 percent of the total Ce^{+++} ions would be activated and in the upper level at room temperature. At the temperature of liquid hydrogen, only one Ce^{+++} ion out of 10,000,000 would be activated. Transitions beginning at this activated level would produce faint bands at room temperature and they would disappear at the temperature of liquid hydrogen. Since there is little change in the relative intensities of the bands, we must accept that practically all the Ce^{+++} occupy the basic level or levels so close together that they behave as one relative to the width of the bands.[12] This statement, while almost certainly true, is not necessary for the conclusion that the electron occupies the $5d$ shell. It is sufficient and it makes the discussion more direct. The necessary condition is that the Ce^{+++} ions in these dilute crystals are not present in appreciable amounts at the temperature of liquid hydrogen in more than three levels 2500 cm^{-1} or more apart. There is no question but that this condition is rigorously fulfilled.

If we look at the electronic configurations of the metals of the rare earths, we observe that one $5d$ electron and two $6s$ electrons had been removed in the process of ionization. The $5f$ shell does not become a stable shell for an electron until the atomic number 90 (thorium) is reached and no atom has an electron in the $5g$ shell. We shall try to decide between the $5d$ shell and the $6s$ shell as the final state of the electron. The former would give rise to a ^2D term and the latter to a ^2S term. It is known[13,14] that S terms are not decomposed by electric fields (or as Kramers points out, only to a degree of several cm^{-1}) and since they are single, a transition to the $6s$ shell from the basic level could account for only one band. However at least four bands exist and hence we must conclude that the electrons of many cerium ions end in the $5d$ shell. The final state is then $^2D_{3/2,5/2}$ decomposed further by the electric fields of the lattice. On grounds of symmetry Bethe[13] has concluded that a $D_{3/2}$ term is decomposed into three terms in a hexagonal crystal (ethyl sulfate) and in tetragonal crystals and into at least as many in crystals of lower symmetry. (The chloride is probably monoclinic.) The $D_{5/2}$ term will be decomposed into more than three.

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[11] These strains are only feebly effective in broadening the lines associated with inner quantum states. Er^{+++} with an ionic number of 66 exhibits very broad and diffuse bands at room temperature which undergo a striking refinement into sharp lines at lower temperatures such as that of liquid nitrogen (Freed and Spedding Nature, **123,** 525 (1929)).

[12] Possibly, the faint band observed at room temperature in some crystals of the chloride, originates at this activated level. The intensities referred to have been shown by the same crystal of the ethylsulfate at the three temperatures. Here we can see little difference in the relative intensities. In the chloride, band II has apparently gained somewhat in intensity at the expense of band III at the temperature of liquid hydrogen. The chlorides, however, are very hygroscopic. At room temperature, there was possibly a little moisture on the faces of the crystal which would influence the absorption and hence make comparison of the intensities, invalid.

[13] Bethe, Ann. d. Physik **3,** 133 (1929).

[14] Kramers, Proc. Acad. Amsterdam **32,** 1176 (1929).

Transitions from the $2F$ term to $D_{3/2}$ and $D_{5/2}$ states would conserve the selection rules of $\Delta j = \pm 1$ and 0 and $\Delta l = \pm 1$ and such transitions would be highly probable. Only very high probabilities of transitions can accord with such enormous intensities in the absorption as have been found. Transitions to the $6s$ shell would introduce $\Delta j = 2$ and $\Delta l = 3$ which would be of much lower probability.[15] The high positive charge on Ce^{+++} would probably make the $5d$ electron more stable than the $6s$, $6p$ etc. electrons. (The concept of many virtual orbits in the crystals becomes more and more vague.) There are numerous examples in gases where a high nuclear charge stabilizes an inner shell. The best known are the iso-electronic gases K and Sc^{++} and their electronic configurations are

	$1s$ to $3p$	$3d$	$4s$
K	full		1
Sc^{++}	"	1	

In a recent letter to this review[16] Spedding advanced the hypothesis that the sharp absorption lines of the rare earths are due quite generally to transitions from the inner $4f$ shell to the outer shells $5d$, $-6s$, etc. He was led to this supposition because the transitions between the states arising within the $4f$ shell in Gd^{+++} must result in intercombination lines, that is in transitions between ^8S and ^6P, for example, intercombination lines occur frequently in the heavier gases free from perturbations and hence there is no reason to dismiss such possibilities in ions imbedded in a lattice where many influences are still unknown. It was observed that the intensity of the absorption bands in Ce^{+++} was much greater than in Nd^{+++} or Pr^{+++} since upon diluting Ce^{+++} with La^{+++} and Nd^{+++} with La^{+++} the bands of Ce^{+++} persisted long after the lines of Nd^{+++} had disappeared. The greater intensity confirms the view that the bands of Ce^{+++} arise from permitted transitions while most of the lines of Nd^{+++} are transitions of less probability, such as intercombination lines. The extreme sensitivity of the bands of Ce^{+++} to external conditions shows clearly that electrons close to the sources of perturbation are responsible for the absorption. In Gd^{+++} the initial and final states are either insensitive to the surrounding molecules or are almost equally sensitive to them. They must then have almost identical electron distributions and hence both the initial and final states of the absorption lines are due to electrons in the $4f$ shell.

I should like to express here my gratitude to Professor W. J. de Haas and to all in his laboratory for their kind hospitability.

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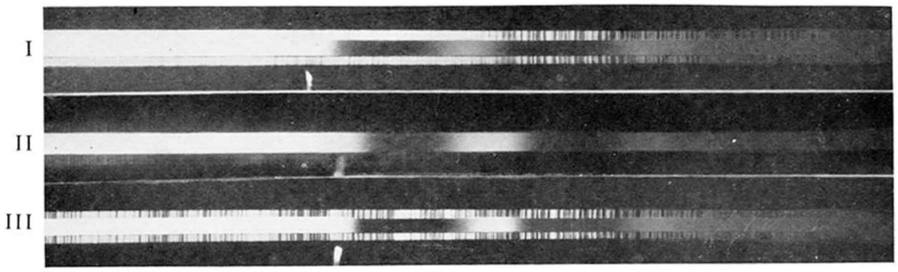
[15] As Bethe observes, the presence of the electric fields introduces different quantum numbers and a selection principle applies to them. Nevertheless, the above discussion on transition probabilities is qualitatively valid since in the limit of feeble fields, the above considerations are approximated.

[16] Spedding, Phys. Rev. **37**, 777 (1931).



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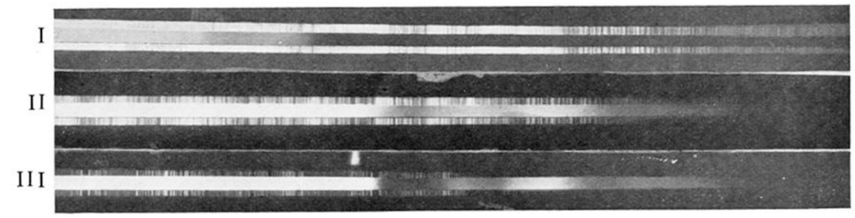

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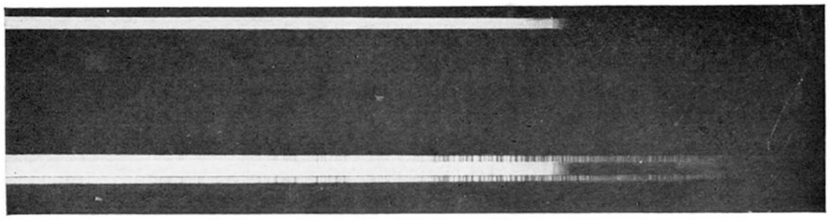

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