Physics. — *Introduction to a theory of magneto-optic phenomena in crystals.* By Jean Becquerel. (Communication Suppl. N⁰. 68*a* from the Physical Laboratory at Leiden. (Communicated by Prof. W. J. de Haas.)

§ 1. *Remarks on the nature of the absorption spectra in crystals of rare earths.*

It is known, that crystals show different absorption spectra according to the orientation of the light vibration (electric vector) in the interior of the crystal [1]). In uniaxial crystals two principal spectra exist: the ordinary spectrum corresponding with vibrations normal to the optical axis and the extra-ordinary spectrum corresponding with vibrations parallel to the axis.

In the present paper we shall consider the crystals of rare earths, which show absorption bands remarkably fine and distinct especially at very low temperatures [2]).

The first question to be answered is that of the nature of the absorption spectra in these crystals. Have we to do with „line spectra" as in the atoms (or ions) of vapours or with „band spectra" i. e. with molecular spectra, due to the transitions of electrons as well as to the rotations of the molecules and to the oscillations of the constituent atoms ? Several reasons are in favour of an approach to the linespectra of ions [3]).

1⁰. Different salts or different crytals containing the same rare earth as a cation have very similar absorption spectra. It is remarkable that the differences for different salts relate to the detail structure of the lines only. The grouping of rays lie in the same spectral regions (the isolated rays have nearly the same place), so exactly that for any salt it is possible to identify at first sight the rare earth cation it contains. This fact proves that the spectrum is due essentially to the cation ant not to the molecule as a whole or to a complex ion [4]). It is however evident, that the different compounds or the different crystals have not identically the same spectrum, the energy levels and especially the "transition-probabilities" being neces-

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[1]) Henri Becquerel Ann. de Ch. et de Phys. VI, **14**, 170, 1888 and thèse de doctorat.

[2]) Jean Becquerel, le Radium **4**, 328, 1907. Jean Becquerel and H. Kamerlingh Onnes, Comm. N⁰. 103, le Radium **5**, 227, 1908.

[3]) The expression generally used of "absorption bands" must not give rise to confusion: it would have been more accurate to speak of "rays more or less diffuse". At very low temperatures several of these rays are nearly as fine as the rays of vapours.

[4]) This is in agreement with M. O. Laporte (Zs. f. Phys. **47**, 767). In this question I cannot agree with Mr. G. Joos (Ann. d. Phys. **81**, 1076, 1926).

sarily modified by the influence of the ions which constitute the molecule together with the cation or by that of neighbouring ions in a crystal lattice.

We must remark now, that a profound difference exists between the spectra of the combinations of rare earths and the band spectra like those of the uranyl compounds. The latter (absorption spectra and phophorescence emission spectra) have a regular structure ; groups of homologous lines are lying at constant intervals throughout the whole spectrum [1]). The existence of these equidistant groups is due to oscillations of the atoms in the complex-ion UO_2 [2]). Moreover, for uranyl crystals (and for crystals only) in the groups of rays one little interval (of the order of 200 cm^{-1}) occurs, which varies from one crystal to the other and is due to oscillations of the crystal lattice [3]).

In the crystals of rare earths which we consider here (xenotime, tysonite, parisite, bastnaesite, apatite...) the rare earth ion lies isolated at a knot of the lattice ; no complex ion exists and therefore no groups of rays are found at intervals following a regular law. Such groups exist neither in the spectra of the solutions. Thus one of the fundamental characteristics of band spectra fails.

It remains however an open question, whether the oscillatory energy of the lattice plays a role in the production of the absorption rays. Now it is certain, that at the lowest temperatures reached (1.3° K.), at which temperatures the specra still exist [4]), we cannot imagine an initial oscillation in the non-excited state, but it is not impossible, that the production of an oscillation of the lattice and the transition of an electron are produced at the same time. This question can only be answered after a profound investigation of the distribution of the rays, especially at very low temperatures.

The difference between the spectra of the crystals of the rare earths and of those of uranyl is again accentuated by the fact that the first ones gave a considerable Zeeman-effect, while the "bandspectra" of the uranyl compounds were proved to be insensible to the action of a magnetic field.

[1]) EDMOND BECQUEREL, Ann. de Ch. et de Phys. V, sér. **10**, 5.

HENRI BECQUEREL, C.R. **101**, 1252, 1885.

HENRI and JEAN BECQUEREL and H. KAMERLINGH ONNES, Comm. Leiden N⁰. 110, 1909.

E. L. NICHOLS and H. L. HOWES in collaboration with E. MERRITT, O. T. WILBER and Miss F. G. WICK. Publications of the Carnegie Institution of Washington N⁰. 298 (1919). The American physicists have established that in the absorption spectrum the interval of the homologous rays is smaller than in the emission spectrum. The values of these intervals, slightly varying from one composition to the other, are approximately 700 cm^{-1} and 830 cm^{-1} resp.

[2]) G. H. DIEKE and A. C. S. VAN HEEL, Comm. Leiden Suppl. N⁰. 55a, 1925.

[3]) A. C. S. VAN HEEL. Thesis, Leiden; Comm. Leiden, Suppl. N⁰. 55b.

[4]) In fact, the spectra are very simplified ; but they do not show any tendency to vanish. The rays that remain at very low temperatures generally are very intense ones. It seems as if the whole absorption is concentrated progressively, according as T diminishes in these rays of low temperature. As to the variations of the intensity with the temperature see the remarks of P. EHRENFEST, in Livre jubilaire de KAMERLINGH ONNES, Leiden 1922.

II.   *Zeeman-effect in crystals. Recapitulation of the fundamental facts.*

We are only going to consider the case of a uniaxial crystal and we shall suppose the magnetic field to be parallel to the optical axis.

Longitudinal effect.   When the light-beam has the same direction as both the axis and the field, the decompositions of the rays of the ordinary spectrum (the only one visible) differ from the Zeeman-effect of vapours by three essential factors [1].

1[0].   In the spectra of the atoms (or of the ions) of the vapours all components corresponding with an absorption of circular vibrations of the same sign as the current producing the field are displaced towards the increasing frequencies. Here in the spectra of the crystals of the rare earths however these displacements and such of sign opposite to them are equally frequent (fig. 1).

2[0].   For the rare earths that are highly paramagnetic the distance between the components can reach very large values. For certain absorption rays of erbium in xenotime for example *this distance obtains 8.6 times the normal value, in one sense as well as in the other with respect to the circular polarisation.*

The large distances are equally frequent for both senses of the phenomenon.

A fact probably not fortuitous is, that in all crystals investigated until now the ratios of the largest distances to the normal are of the same order of magnitude as the ratio of the magnetic moment of the ion in its fundamental state to the BOHR magneton. The number for erbium given above is an example.

3[0].   The decompositions consist of doublets. Sometimes however at the

fig. 1.   fig. 2.
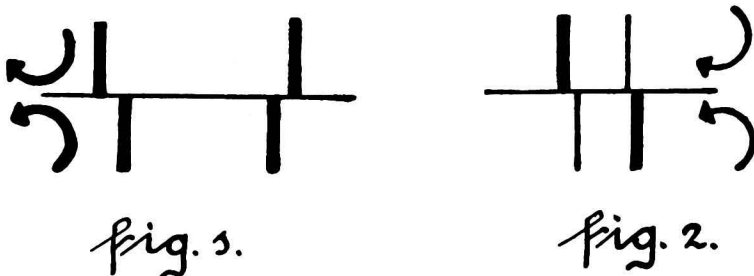
side of a principal doublet a secondary doublet is observed much less intense and generally with nearly the same distance as the principal one [2]. These four lines might be called a quadruplet, but I think it more exact to consider each doublet individually. They are circularly polarised in opposite senses (fig. 2); moreover their centres do not coincide; finally either both doublets, show an asymmetry in the positions with respect to the initial ray

[1]) JEAN BECQUEREL, C. R. de l'Ac. des Sc. 9 avril 1906. Le Radium, **4**, 49, 1907; **5**, 5, 1908.

[2]) JEAN BECQUEREL, Comm. Leiden Suppl. 20, le Radium **6**, 327, 1909.

or at least, one doublet does so; the asymmetries in the intensities are different too. The two doublets are therefore at least partly independent; it is probable that the secondary doublet is due to a satellite ray too near the principal ray to be separated from it without magnetic field.

No explanation of these facts has been given in the quantum theory notwithstanding the recent development of the theory of the Zeeman-effect. Still it is evident that we have here to do with a phenomenon of the same nature as the Zeeman-effect. We may even say with a phenomenon more simple in some respects, no complex decompositions having been found.

III. *Interpretation of the observed facts.*

From the experimental results the following conclusions are readily deduced.

a. The simplicity of the decompositions proves, that the rays are less degenerated than the spectral rays of the vapours. They are partially decomposed already. As without a magnetic field an electric field alone can give rise to a decomposition, *we are inclined to consider the absorption rays of the rare earths as components due to a natural Stark effect.*

Here we may remark, that probably in this case certain rays would be due to transitions forbidden in the absence of an electric field.

The internal electric field to which the ion is subjected is non-homogeneous; it necessarily has axial symmetry with respect to the direction of the optical axis [1]). In the absence of a magnetic field, the only possible orientations of the ions are those determined by the quantum number m of the component of the momentum in the direction of the electric field, while the axis of momentum has a precession motion about the direction of the electric field.

The existence of an internal field immediately explains the two spectra: the ordinary spectrum corresponding with the transitions $\triangle m = \pm 1$ the extraordinary spectrum corresponding with the transitions $\triangle m = 0$.

In the electric field alone the energy levels corresponding to $+ m$ and to $- m$ are confused; a magnetic field is needed to separate them. Supposing the magnetic field to be parallel to the axis, considering the ordinary spectrum and applying the selection rule $\triangle m = \pm 1$ to the two levels risen from the duplication of the initial state and the two levels of the final state, we find a doublet (fig. 3), which really is the type of the decomposition observed.

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[1]) Though, to speak accurately, the Stark effect is produced by a homogeneous field, I follow the example of W. PAULI Jr. in extending the designation to the case of a non-homogeneous field. This problem has been treated by O. STERN Phys. Z.S. **23**, 476, 1922 and has been exposed by W. PAULI in Handbuch d. Physik **23**, 248. For the calculations the electrostatic potential has been supposed to be a quadratic function of the coordinates, the nucleus being taken as origine of coordinates.

[2]) JEAN BECQUEREL, C.R. 26 mars, 9 avril 1906. Le Radium, **4**, 49, 1907.

If the preceding ideas are right, we must expect a great variability of the Zeeman-effect for one and the same ray of absorption according to the
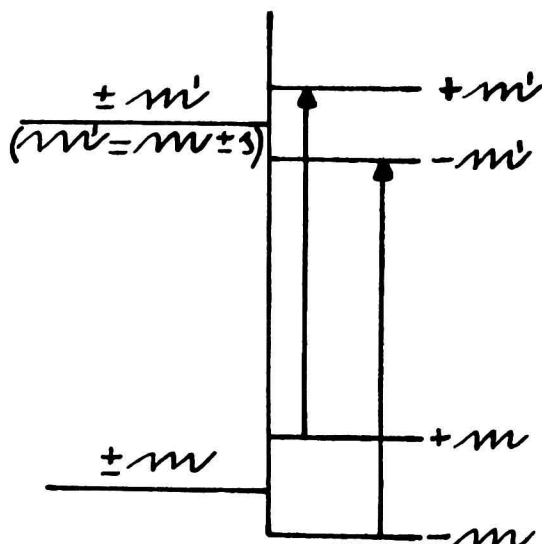

fig. 3.

orientation of the magnetic field with respect to the optical axis. This is what has long been observed: for one and the same ray of the ordinary spectrum with vibrations normal to the magnetic field, we have doublets with distances absolutely different according as the field is parallel or normal to the optical axis.

Moreover the phenomenon must become more complicated, when the magnetic field and the electric field form any angle [1]). In fact, when the magnetic field is oblique with respect to the optical axis, we observe new components [2]).

NIELS BOHR [3]) has shown, that for the hydrogen atom subjected both to an electric and a magnetic field with axial symmetry round the same axis,

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[1]) N. BOHR. Ueber die Quantentheorie der Linienspektren (Uebers. P. HERTZ) p. 137. The problem treated by BOHR however relates to a uniform electric field and to the hydrogen atom.

[2]) JEAN BECQUEREL, le Radium 5, 5, 1908. Compare the figures 2, 4 and 5. In fig. 2 a large doublet (8.6 times the normal distance) is to be seen, formed by the components of the ray 5221 of the erbium (ordinary spectrum of xenotime). the field being parallel to the axis.

In fig. 4 for the same orientation of the vibration with respect to the field the same ray gives a small asymmetrical doublet, the field being here normal to the axis.

In fig. 5 finally, relating to an oblique field, a triplet is to be seen for the vibration normal to the field. The middle component of the triplet occurs in oblique fields only.

[3]) N. BOHR, loc. cit. p. 129.

the two circularly polarised components of a magnetic doublet must be symmetrical with respect to the initial ray and of the same intensity if the magnetic field is weak. An asymmetry both in position and in intensity must appear as soon as the disturbing influence of the magnetic force becomes of the same orders of magnitude as the electric force.

I may recall here, how much I previously insisted on the asymmetries in the positions of the components of the doublets occurring when the magnetic field is parallel to the optical axis. These asymmetries rapidly grow when the field becomes stronger. Moreover I established the existence of weak asymmetries in the intensities connected with those in the position [1]).

It is probable, that the considerations developed by BOHR with respect to the hydrogen atom may be generalized and that they relate to the case considered here. The ensemble of the facts cited above seems characteristic of the simultaneous influence of an electric field and a magnetic field. I do not think we need doubt of the nature of the phenomenon.

The usually very distinct separation of the neighbouring bands shows that the non-homogeneity of the electric field must be great at the knots of the crystal lattice. We know that in a non-homogeneous field the changes of the energy levels are functions of the gradient of the electric field.

b.   The quantum theory of the Zeeman-phenomenon shows that, of the variation of mg ($g =$ decomposition factor) from the initial to the final state has the same sign as the variation of m, we have the effect in the ordinary sense. This is the case in all known examples of the Zeeman-effect in vapours. But if the variations of mg and of m have opposite signs, we obtain the effect with opposite sign.

In fact, indicating by accentuated letters the numbers referring to the final state (after the absorption) and taking for unit of distance the absolute value of normal distance and for unit of momentum the absolute value of the Bohr-magneton, we have

$$\triangle \nu = m'g' - mg.$$

If, for example $m' - m = + 1$, the circular vibration has the same sign as the current that produces the field. If $m'g' - mg$ has the same sign as $m' - m$, $\triangle \nu$ is positive : this is the ordinary case. The contrary is the case of $m'g' - mg < 0$.

c.   From the preceding formula it is evident, that the large distance of certain doublets (for the circular vibrations and for field parallel to the axis) are a manifestation of large jumps of the projection on the axis mg of the magnetic moment.

Thus the problem is reduced to the finding of the values for the decomposition coefficient that render account of the consequences b. and c., which were deduced from the experiments and from the quantum theory

[1]) JEAN BECQUEREL, le Radium, **6**, 327, 1909.
     W. PAULI, loc. cit.

of the Zeeman-effect. The coefficients of Landé do not suffice. Further on I shall come back to this question [1]).

IV. *Rule for the asymmetries in the intensities of paramagnetic origin. Interpretation with the quantum theory.*

It is known, that in all crystals of rare earths *the paramagnetic orientation becomes manifest* in the form of asymmetries in the intensities between the two circularly polarised components of a magnetic doublet [2]). These asymmetries are the origin of the paramagnetic rotatory power. At low temperatures they are generally more intense than the asymmetries connected with the asymmetries in the positions, considered above. For instance for several rays of the erbium in xenotime, at the temperature of liquid helium one of the components of the doublet vanishes in a rather weak field (of the order of 10.000 gauss) [3]).

For these crystals, as well as for the ruby, a rule exists with only very few exceptions. *In every doublet the paramagnetic orientation becomes manifest by the predominance of the components displaced towards the high frequencies* for either sense of the Zeeman-effect with respect to the circular polarisation.

Apart from rare exceptions it is evident from this rule, that towards the side of the low frequencies the paramagnetic rotation due to an absorption band has the negative sign, when the Zeeman-effect has the ordinary sense, and positive in the opposite case. The inverse senses occur towards the side of the high frequencies [4]).

We are now going to interpret the rule for the paramagnetic asymetries.

For an absorption ray not decomposed by a magnetic field two quantum numbers correspond to the initial state of the ion $\pm m$ and two to the final state of the ion $\pm m'$. Besides, we have the selection rule $\triangle m = \pm 1$. In

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[1]) I had expected to find the solution by assuming an electrostatic binding between the rotating nucleus and the electron envelope, the nucleus being asymmetrical and the envelope strongly polarised by the internal electric field. In their book "Introductoin à la Physique des rayons X et ;" p. 114, MAURICE and LOUIS DE BROGLIE have raised the question of an "embrayage" between nucleus and electron layers, when one of the latter is displaced. For quantum numbers of rotation for the nucleus of the same order of magnitude as the number obtained by BACK and GOUDSMIT for the bismuth nucleus, decomposition coefficients are found rendering account of the phenomena observed in the crystals of rare earths (both senses and the large distances). But Mr. H. A. KRAMERS made the true objection, that the electric field opposes such a binding between the nucleus and the envelope, as the nucleus can only have a very small electric moment.

[2]) JEAN BECQUEREL, le Radium **5**, 5, 1908; **6**, 330, 1909.
   JEAN BECQUEREL and H. KAMERLINGH ONNES, Comm. Leiden N⁰. 103, 1908.

[3]) JEAN BECQUEREL, H. KAMERLINGH ONNES and W. J. DE HAAS, Comm. Leiden N⁰. 177, 1925. See the fig. (1) and (2) of this Comm.

[4]) It is to be remembered that upon the paramagnetic rotation the diamagnetic one is superposed, which has the same sign at both sides of a band (positive in the case of the ordinary ZEEMAN-effect, negative in the other case).

the magnetic field the most intensive component is that due to a transition starting from the state of lowest energy, this state being the most probable one. Assuming g positive in this initial state ; the lower level is the level $(-m)$; the rule now teaches us, that the component displaced towards the high frequencies correspond to a transition starting from $(-m)$, which may be the sense of the Zeeman-effect.

1. If the Zeeman-effect has the ordinary sign, this component has a positive circular polarisation ; we thus have

$$\pm m' + m = + 1.$$

With the exception of the particular cases $m = 0$ and $m = \frac{1}{2}$[1]), this condition can be fulfilled only then when the final state has a negative quantum number $(-m')$, so that we must write :

$$- m' + m = + 1.$$

As on the other hand the variation of mg has the same sign as that of m, we have

$$m'g' < mg.$$

2. If the Zeeman-effect has the inverse sense, we have

$$- m' + m = - 1.$$

and as the variation of mg is of sign opposite to the variation of m, we find again the preceding inequality.

We may remark, that this condition is necessarily fulfilled, if g' is negative.

If we had supposed g to be negative, we should have found that as a rule the law is followed that g' is positive or negative with the condition

$$m' \mid g' \mid < m \mid g \mid$$

Summarizing : if we exclude the very special case [2]) $\pm m = \pm \frac{1}{2}$ and $\pm m' = \pm \frac{1}{2}$, the rule for the asymmetries has the following meaning. For values of the same sign for the quantum number of orientation in the

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[1]) For $m = 0$, the initial state is not redoubled and there is no asymmetry. For $m = \frac{1}{2}$, the case is different from the general case as the final state in the above equation corresponds to $+ m' = \frac{1}{2}$, while for m superior to the equation necessarily gives the negative value $(-m')$ for the quantum number of the final state. A complete discussion of the case $m = \frac{1}{2}$ would show, that an asymmetry occurs of the sense indicated under one of the following conditions

$m' = \frac{1}{2}$ with g and g' of the same sign,
$m' = \frac{1}{2}$ with g and g' of opposite sign and also $m'|g'| < m|g|$.
$m' = \frac{3}{2}$ with g and g' of opposite sign,
$m' = \frac{3}{2}$ with g and g' of the same sign and $m'|g'| < m|g|$.

The two last conditions $(m' = \frac{3}{2})$ only lead to the same conclusions as in the general case $(m > \frac{1}{2})$.

[2]) With this case corresponds an absorption ray that has not exactly the same position and a different intensity in the ordinary and the extra-ordinary spectrum.

initial and in the final state, the projection of the magnetic moment in the final state is smaller than that in the initial state, whether the projection on the axis of the magnetic moments in these two states have the same sign or opposite signs.

The rule for the asymmetries must be kept in view in the investigation of the transitions to which the absorption spectra of the crystals of rare earths are due.

V. *Transverse effect. Extra-ordinary spectrum.* When the light-beam is normal to the common direction of the axis and of the field, the modifications of the ordinary spectrum are the same as in the case of longitudinal observation with this single difference that the components are linearly polarised. Thus we have to consider the extra-ordinary spectrum only (electric vector parallel to the optical axis and to the field).

According to our theory the extra-ordinary spectrum must be given by the transitions $\pm m' = \pm m$. In the magnetic field the transitions corresponding with $+ m$ and with $- m$ give a doublet, which is in agreement with the experiments.

But for the state of polarisation, no difference must exist in the nature of the magnetic modifications of the rays of the extra-ordinary spectrum and those of the ordinary spectrum, if the magnetic field is parallel to the axis. In fact the largest distances of the doublets are of the same order of magnitude in the two cases. Moreover, the asymmetry in the intensities of paramagnetic origin [1]) is the same as in the ordinary spectrum; the experiments show that, but for a few exceptions, the rule for the asymmetries is the same.

We shall not consider the much more complicated case, that the magnetic field is normal to the optical axis. I will only insist on the fact, that the modifications of the rays are essentially variable with the orientation of the field with respect to the axis, as has been mentioned already. It may be remarked also, that no asymmetry in the intensities of paramagnetic origin occurs (at least not to a perceptible degree) for an orthogonal position of the field and the axis.

VI. *Remarks on the Zeeman-effect in the crystals of the rare earths.*
We mentioned, that the large distances of the doublets and the existence of two opposite senses of the circular polarisation of these doublets seem inexplicable with the aid of the decomposition coefficients of Landé. It is not impossible that the internal electric field produces an effect analogous to the Paschen-Back effect [2]). This will be the case, if the action of the electric field on the resulting orbital moment (quantum number l) predominates over the reciprocal action (ls) ; but it is not possible as

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[1]) To this asymmetry an asymmetry of an other nature is superposed as in the case of the ordinary spectrum (see above).

[2]) This hypothesis was suggested to me by Mr. H. A. KRAMERS.

yet to solve the question, a profound study of the succession of the absorption rays being necessary, while on the other hand the energy differences for the terms of the multiplets are not known for the ions of the rare earths.

It is evident, that an electric Paschen-Back effect would change the magnetic moments of the ions; this might explain why for the ion Ce^{+++} in tysonite and in parisite we found 1 Bohr magneton [1]) from measurements of the paramagnetic rotatory polarisation (instead of $gj = 2.14$, which value follows for the fundamental state from the measurements of CABRERA [2]) and of ST. MEYER [3]) and also from an investigation of HUND [4])). In the ion Ce^{+++} only one, the electron responsible for the magnetism exists ($s = \frac{1}{2}$) and as the moment is equal to one magneton, it is obvious, that the moment of this electron only plays a role. If under the influence of the electric field the binding (ls) is ruptured and if moreover the minimum energy in the fundamental state corresponds to $m_l = 8$, the orbital moment no longer plays a role. But this interpretation is very hypothetical. It is not clear however, how to explain the great decompositions with the two senses of the Zeeman-effect, while keeping to the rule $\triangle m_s = 0$ which has always been observed in the magnetic Paschen-Back effect. Another question is that of the nature of the transitions to which the absorption bands are due. It seems certain, that for the triple ions of the rare earths in the initial state which at very low temperatures (1.3° K.) is the fundamental state (modified and decomposed by the electric field), the active electrons are those of the incomplete layer ($n = 4$, $l_i = 3$); the variation in the energy by the transitions to the layers $n = 5$ or $n = 6$ seem to be too great to give absorption rays in the visible spectrum [5]). So that we obviously have to do with a reorganisation of the incomplete layer under the action of the light: the anomalies in the Zeeman-effect should then be an indication of great variations of the magnetic moment by this reorganisation.

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[1]) JEAN BECQUEREL and W. J. DE HAAS, Comm. Leiden N⁰. 193a, 199a.

[2]) B. CABRERA, C.R. **180**, 668, 1925.

[3]) ST. MEYER, Phys. Z.S. **26**, 1, 478, 1925.

[4]) F. HUND, Z.S. f. Phys. **33**, 855, 1925. Linienspektren und periodisches System der Elemente p. 179, 1927.

[5]) The transitions to $n = 5$ might give the ultraviolet bands, which are the origin of the great paramagnetic rotatory power as e.g. the extremely intense band which, according to the law of Mr. LADENBURG, must lie at about $\lambda = 2370$ Å for the Ce^{+++} in tysonite and in parisite (J. BECQUEREL and W. J. DE HAAS loc. cit.).