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A DIAGRAM OF SOME OF THE ENERGY LEVELS OF GADOLINIUM IV IN THE CRYSTAL LATTICE AS OBTAINED FROM THE ULTRAVIOLET ABSORPTION SPECTRA OF $GdCl_3 \cdot 6H_2O$ AND $GdBr_3 \cdot 6H_2O$

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Abstract

A number of electronic energy levels of the gadolinium ion in the crystals $GdCl_3 \cdot 6H_2O$ and $GdBr_3 \cdot 6H_2O$ were obtained from their ultraviolet absorption spectra. The intervals between these levels were found for the ion in $GdCl_3 \cdot 6H_2O$ and in $GdBr_3 \cdot 6H_2O$ at room temperature and at that obtained with liquid air and in $GdCl_3 \cdot 6H_2O$ also at the temperature reached with liquid hydrogen. Levels were found to be decomposed by a magnetic field into doublets of enormous separations amounting to as much as 15 times the normal Larmor precession. Transitions occurred with large changes in magnetic moment which were different along the different axes of the crystal. The intervals between the electronic levels in the absence of a magnetic field are much smaller than might be expected for an ionic crystal of the rare earths. It has been concluded that the H_2O molecules separate the positive gadolinium ions from the negative ions and that very possibly the feeble fields to which the gadolinium ion is exposed arise in great measure from the polarized H_2O dipoles. Small intervals and large magnetic separations in crystals lead to a "Paschen-Back effect" which is visualized as the incipient uncoupling of the positive ion from the lattice. Since magnetic separations differ along the different axes of the crystal, uncoupling can occur more readily in one direction than in another. No evidence was found for a combination between the oscillation of the ion in the lattice and the frequency of the electronic transition, a possibility imagined by Ehrenfest.

WE POINTED out in our work[3] on the absorption spectra of the rare earths at low temperatures why we selected to study Gd IV in an attempt to obtain the electronic energy levels of an atomic ion in a crystal lattice. It may be sufficient to recall here that Hund[4] had obtained $^8S_{7/2}$ for the basic state of Gd IV in the *gas* by assuming that the seven unbalanced electrons were in the $4f$ shell, the $5s$ and $5p$ being completely full (the Bohr-Stoner assignment) and that Russell-Saunders coupling existed between these electrons. This basic state agreed with the magnetic susceptibility of the *crystals* $Gd_2(SO_4)_3 \cdot 8H_2O$ over an extended temperature range down to 1.3°K.[5] The close agreement showed that within the experimental error all of

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[3] Freed and Spedding, Nature **123**, 525 (1929); Phys. Rev. **34**, 945 (1929); J. Am. Chem. Soc. **52**, 3747 (1930).

[4] Hund, Zeits. f. Physik **33**, 853 (1925).

[5] Woltjer and Kamerlingh Onnes, Leiden Comm. 167 C.; Giauque, J. Am. Chem. Soc. **49**, 1870 (1927).

the ions were in this basic state. Hence of all the rare earths, gadolinium would probably have the simplest absorption spectrum because its basic state is single (in the gas and probably also in the crystal)[6] and the other levels are rather remote from it.

Each level has been established by from five to eight criteria which are, for the most part, peculiar to spectra in crystals. They consist in comparing the spectra of Gd IV in the two salts at the various temperatures[7] and in employing the spectra of $GdCl_3 \cdot 6H_2O$ with different axes in a magnetic field at room temperature.

Bunsen[8] found that the position in wave-lengths of the absorption of rare earth crystals was independent of the direction in which the light traversed the crystal. We have confirmed his conclusion by measuring the absorption spectra of $GdCl_3 \cdot 6H_2O$ along two perpendicular directions.

The crystals of $GdCl_3 \cdot 6H_2O$ grow in flat oblong plates and those of $GdBr_3 \cdot 6H_2O$ grow in prisms having two prominent parallel faces. The spectra were usually taken as the light traversed the prominent faces. In our original work, we accepted the crystallographic report of Benedicks[9] that the crystal $GdCl_3 \cdot 6H_2O$ was tetragonal. The nature of the Zeeman effect which we investigated led to the conclusion that the gadolinium ions were not situated in an electric field of tetragonal symmetry. A rotation of ninety degrees about the "optic axis," a line perpendicular to the flat faces, did not leave the Zeeman separations unaltered.[10] As a result, we employed the Zeeman effect in three directions for purposes of identifying levels common to different absorption lines. The levels have been determined (1) by comparing the intervals between the lines of the spectrum of $GdCl_3 \cdot 6H_2O$ at room temperature (2) by observing the corresponding intervals at the temperature obtained with liquid air (3) and with liquid hydrogen. Then (4) a comparison was made with the corresponding intervals in the spectra of $GdBr_3 \cdot 6H_2O$ at room temperature and (5) at that obtained with liquid air. The levels were further identified by the extent to which the lines originating from them were decomposed by a transverse magnetic field when the unique axis of the crystal was perpendicular to the field and when the oblong face of $GdCl_3 \cdot 6H_2O$ was so placed that its length was (6) perpendicular to the lines of force and (7) parallel to the lines of force. We also obtained (8) a spectrum when the unique axis of the crystal ("optic axis"), was parallel to the field. The resolution of our spectrograph was not sufficient to resolve any of the

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[6] Bethe, Ann. d. Physik **3,** 133 (1929); Kramers, Proc. Akad. Weten. Amsterdam **32,** 1176 (1929).

[7] At lower temperatures, the absorption lines shift slightly toward the red and the intervals between the lines composing a multiplet are somewhat increased. This effect of temperature may be correlated with the contraction of the crystal which brings the ions closer together, subjecting them to greater electric fields. Phys. Rev. **34,** 945 (1929).

[8] Bunsen, Pogg. Ann. **128,** 100 (1866).

[9] Benedicks, Zeits. f. anorg. allgem. Chemie **22,** 403 (1900).

[10] Dr. A. Pabst of the Geology Department of this University has kindly communicated to us that his measurements (about to be published) show that $GdCl_3 \cdot 6H_2O$ is actually monoclinic.

Zeeman components in this longitudinal direction. The degree of widening of some of the lines was of aid in several instances.

The relative measurements are accurate to about one cm^{-1} in the absence of the magnetic field but are somewhat less accurate in a magnetic field. It may be seen, then, that the enormous magnetic separations which occur have made our study possible. We shall discuss the magnitude of the Zeeman effect toward the end of the paper. All the lines which have been assigned to levels had a measurable Zeeman separation. We have not wished to assign any lines undecomposed by a magnetic field although there are a number whose intervals are equal to those of the accepted levels in both salts at every temperature. It is likely that other lines would have contributed to an understanding of the energy levels if a greater optical dispersion had been available. This work is now being repeated and extended under much more favorable conditions but we find it desirable to publish the results already obtained.

The lines of the spectra of $GdCl_3 \cdot 6H_2O$ and of $GdBr_3 \cdot 6H_2O$ lie almost entirely in the ultraviolet. There are a few faint lines in the visible all of which sharpen as the temperature is reduced. The lines fall into groups which suggest a multiplet structure and we have interpreted these groups as corresponding to possible lines of the gaseous spectra that have been decomposed by the electric fields of the lattice.[11] We must refer the reader to the previous publications for the enumeration of the lines. Table I gives a list of the lines with which the present paper is concerned.

TABLE I. *List of observed lines.*

Line Number	$GdCl_3 \cdot 6H_2O$ Room Temp. (cm^{-1})	Liquid Air (cm^{-1})	Liq. Hydrogen (cm^{-1})	$GdBr_3 \cdot 6H_2O$ Room Temp. (cm^{-1})	Liq. Air (cm^{-1})
26	35796.5	35792.5	35790.5	35791.5	35785.5
29	35876.5	35874.5	35872.5	35876.5	35873.0
30	36144.0	36136.5	36136.5	36137.0	36128.0
31	36170.5	36165.0	36164.5	36169.0	36163.0
32	36186.5	36181.0	36180.5	36184.0	36177.5
33	36200.0	36196.5	36196.0	36200.5	36194.5
35	36223.0	36219.0	36220.0	36222.0	36219.0
42	36418.5	36411.5	36413.0	36411.5	36402.5
43	36444.5	36438.5	36441.5	36442.0	36437.0
44	36461.5	36458.5	36459.0	36457.0	36452.0

A study of the data has led to the following conclusions. The interval *26–29* is identical with the interval *30–35* not only because the intervals remain equal at the various temperatures in the two salts but also because three different magnetic separations of the line *26* are equal to those of *30* and the separations of *29* are equal to those of *35*. Hence *26* and *29* arise from one electronic level A' (see Fig. 1) (the designations are arbitrary) and lines *30* and *35* arise from another common level B' and also *26* and *30* have a lower

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[11] The separations between the components in multiplets of the unperturbed Gd IV might be expected to be about 1000 cm^{-1} or more from the formula for relativity doublets derived by Sommerfeld and generalized for multiplets by Goudsmit (Phys. Rev. **31**, 946 (1928)).

level *D* in common while *29* and *35* come from the same lower level *A*. In the same way the intervals *30–31* and *42–43* are identical; that is, the upper[12] level of *31* is identical with that (*B′*) of *30* while *42* and *43* end at the same upper level *C′*.

The segregation of *30, 31, 32,* etc. gives them the general appearance of a multiplet and the lines *42, 43, 44* resemble them closely. The intervals *30–31* and *42–43* have just been discussed. The interval *31–32* appears to be the same as *43–44*. The nearness of *45* to *44* made it impossible to compare the magnetic separations of *44* quantitatively with those of *32* since the magnetic spectra of *44* blurred badly with those of *45*. The interval *31–32* equals *43–44* in both salts at room temperature and at that of liquid air. There appears to be a deviation somewhat greater than the mean error of measurement at the temperature reached with liquid hydrogen, but the lines *44–45* are not clearly resolved. It appears likely that these intervals are truly equal. We have further evidence that *31* and *32* belong to the same multiplet because their energy levels interact in rather strong magnetic fields as is shown by the dissymmetries in position and especially in the intensity of the Zeeman components whereas symmetrical decompositions are obtained when the levels are rather remote from each other. (See Figs. 2 and 3).

INTERVALS

$GdCl_3 \cdot 6H_2O$			$GdBr_3 \cdot 6H_2O$	
Room Temp. cm^{-1}	Liquid Nitrogen cm^{-1}	Liquid Hydrogen cm^{-1}	Room Temp. cm^{-1}	Liquid Nitrogen cm^{-1}
274.5	275.0	276.5	274.5	274.5
374.5	344.0	346.0	345.5	342.5
35796.5	35792.5	35790.5	35791.5	35785.5
26.5	28.0	28.0	31.5	35.0
16.0	15.5	14.0	15.0	14.5
36.5	38.0	39.5	38.0	41.5

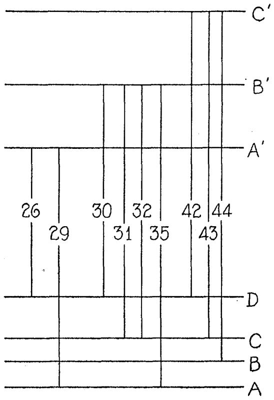

Fig. 1. Energy level diagram.

We have been inclined to believe that *33* is included in this multiplet on account of its magnetic interaction with *32*. However, *33* does not take part in any interval which is equal to another at the various temperatures and hence its inclusion must await further evidence. In addition to the general similarity of the grouping of the lines *30, 31, 32* and *42, 43, 44,* we have further evidence for a common multiplet origin for the lines from their shift with

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[12] If the lower level is assumed identical for both lines 31 and 30, the diagram would not be compatible with the Paschen-Back effect that has been observed; the other conclusions which have resulted from the accepted diagram would follow from this alternative one also.

the temperature and by the change in wavelength produced when the bromide ion is substituted for the chloride ion. A reduction in the temperature brings about a greater separation of the levels as one would expect if the separation was produced by the field or its derivatives[13] upon one electronic level because the ions are then on the average nearer each other and exert stronger fields upon them. The refractive index and the chemical properties of the bromide ion prove that it is considerably more polarizable than the chloride ion. Hence the negative charge induced on the surface of the bromide ion opposite the positive ion would exert a greater field upon the electronic configuration of the positive gadolinium ion, separating the components of

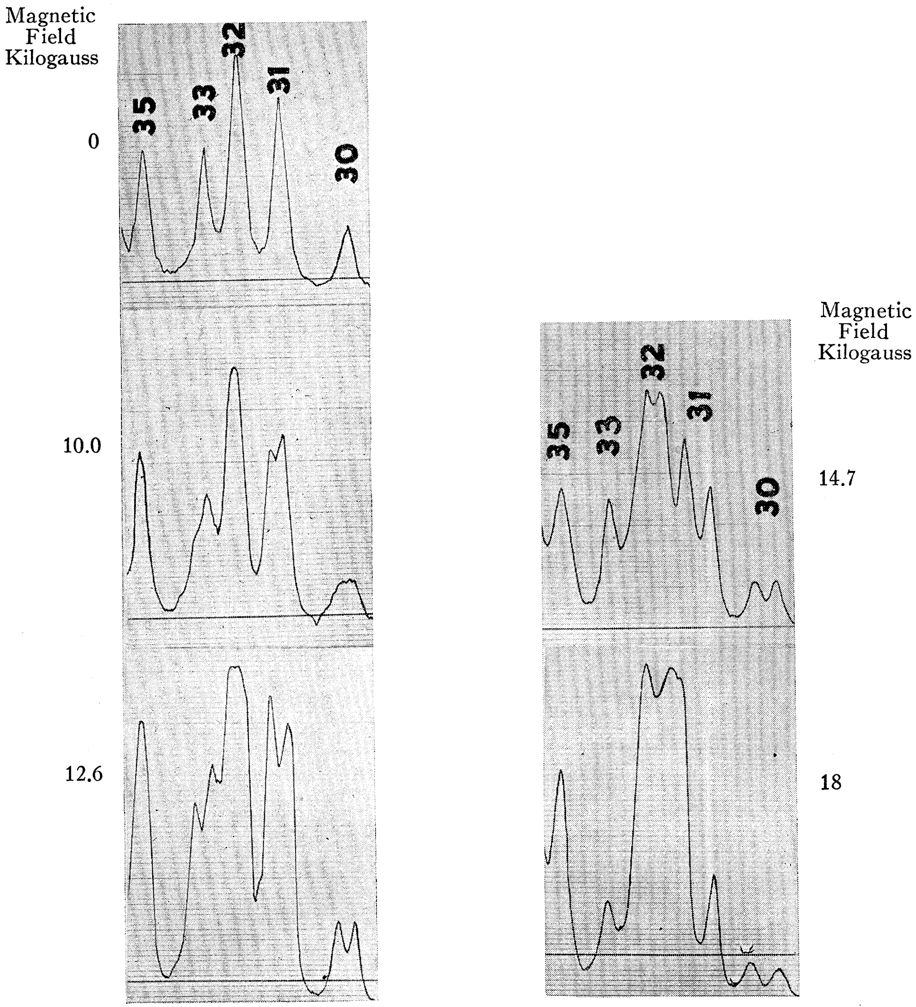

Fig. 2. Microphotometer curves of absorption spectra of $GdCl_3 \cdot 6H_2O$. Unique axis perpendicular to field, parallel to light ray. Long axis perpendicular to field.

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[13] Stern, Phys. Zeits. **23,** 476 (1922).

the "electric" multiplet further. The magnetic separations of *42* and *43* are equal to those of *30*, *31*, and *32* and consequently all their decompositions take place at the lower levels only and their upper levels are not decomposed within the limits of our measurements. It is then not surprising that with an interval of 16 cm^{-1} between *31* and *32* and with magnetic separations of about 16 cm^{-1} at fields of 23,000 gauss a Paschen-Back effect was observed.[14] The spectra show, then, the astonishing regularity that all the upper levels do not decompose in a magnetic field with the crystal in this direction while the three levels, B, C, D, decompose equally with separations of about 0.7 cm^{-1} per kilogauss, about 15 times the normal Larmor precession.

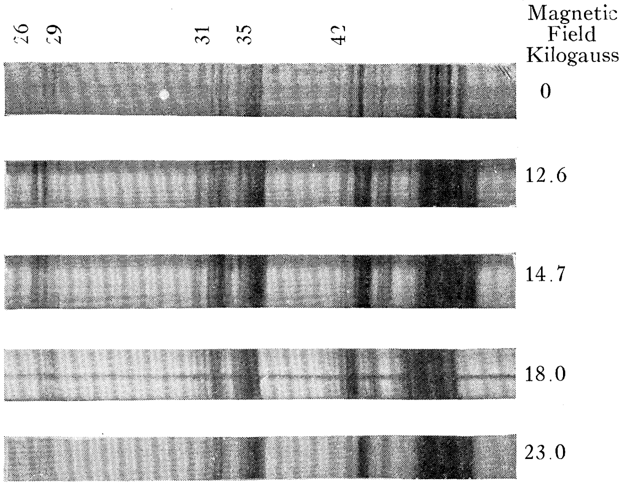

Fig. 3. Absorption spectra of $GdCl_3 \cdot 6H_2O$. Unique axis perpendicular to field, parallel to light ray. Long axis perpendicular to field.

If the level A had been decomposed to the same degree it would have been natural to assume that the lower multiplet was really the $^8S_{7/2}$ level of Gd IV in the gas decomposed by the electric fields of the lattice. (The theories of Bethe[15] and the first approximation of Kramers[66] expect S levels to remain undecomposed in the crystal lattice.) Such a possibility would have been especially attractive since the extreme separations of $^8S_{7/2}$ amounts to $2 \times 7/2 \times 2 = 14$ times the normal Larmor precession equal, to the observed within the experimental error ($g=2$ and $j=7/2$ and the factor 2 results from the symmetrical extremes $m=7/2$ and $m=-7/2$). The assumption would have been further supported by the results of Bethe who showed that only those levels with j (or rather w a magnitude associated with j) odd or half-integral (as 7/2) can be decomposed by a magnetic field. However magnetism in crystals is still an obscure subject and much further work is necessary.

The model employed for visualizing the Paschen-Back effect in gases is roughly the following. A multiplet results from the different relative orienta-

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[14] Freed and Spedding, Phys. Rev. **35**, 1408–9 (1930).

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

tions of the spin and orbital moments of the electrons, each level of the multiplet representing a fixed relative orientation. (It is perhaps better to say that the vectors of spin and orbital momenta precess about each other at definite angles.) When the levels are so close together that the decompositions produced by the magnetic field approach the intervals between the levels, the dissymmetries in the resulting Zeeman patterns express the uncoupling of the orbital and spin momenta of the electrons. Somewhat similarly, each electronic level of an "electric" multiplet in the crystal, that is, a multiplet produced by the lattice, may be regarded as representing the mutual energy of the ion in a definite direction and the crystal lattice.[16] When the electric fields are weak, the magnetic separations may approach the intervals between the components of the electric multiplet and then dissymmetries set in which may be said to represent the disorienting of the ion from the lattice. The data show that the magnitude of the separations varies with the axes of the crystal so that the incipient uncoupling of the ion from the lattice is more readily possible in one direction than in another. When the electric fields of the lattice are strong, a magnetic field may produce a Paschen-Back effect of another character under special conditions. In this case, the lattice is strongly coupled with the orbital momentum of the electron (because of its electric moment) and the energy between the magnetic field and the magnetic moment of the orbital motion will be small compared with the coupling energy of the lattice and orbit. However, the magnetic field may be strong enough to uncouple the spin moment from the orbital moment. Such a Paschen-Back effect would probably manifest itself in the interaction between a component of one electric multiplet and a component of another.

Kramers[6] has computed the decomposition produced by the lattice upon the level associated with the electron in the $4f$ shell of Ce IV in the mineral xenotime and obtained intervals of several thousand cm^{-1}. Bethe[15] concluded that separations of several hundred cm^{-1} would probably result from the electric fields of ionic crystals Our levels have much smaller intervals, in keeping with the current ideas on the crystal structure of such a substance as $GdCl_3 \cdot 6H_2O$. In all probability the H_2O molecules immediately surround the gadolinium ion, shielding it from the negative ions. That is, the negative ions are relatively distant from the positive ion and it is indeed possible that the feeble field to which the gadolinium ion is exposed originates in great measure at the polarized H_2O molecules.

On the other hand one might assume that the separation in the levels B, C, D (all of which appear to have the same magnetic moment) can be attributed to different oscillational frequencies of the ion in the crystal lattice. The possibility of a combination of the electronic frequency of an ion and its oscillational frequencies in the lattice was imagined by Ehrenfest.[17] We are not in a position to disprove the existence of such a combination in the gadolin-

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[16] This idealization is valid when cylindrical symmetry is approximated by the lattice as in elongated tetragonal symmetry. Analogous but more complicated models would be necessary for a close approximation to other crystalline forms.

[17] Ehrenfest, Gedenkboek H. Kamerlingh Onnes, 1922.

ium crystal, but the evidence we feel, is definitely against such a combination of frequencies. In the first place, one would expect some regularity in the spacing of the levels if they arose from oscillations. Indeed, one would expect the lattice oscillations to deviate regularly (and only slightly) from a

TABLE II. *Magnetic decomposition of the lines.*

Observation transverse to field; unique axis perpendicular to field; long axis of crystal $GdCl_3\cdot 6H_2O$ perpendicular to field.

Line number	Field kilogauss	Shift towards longer wave-lengths cm^{-1}	Shift toward shorter wave-lengths cm^{-1}	Total separation cm^{-1}	Total separation per kilogauss cm^{-1}
26*	18	6	5	11	0.6
	23	7	9	16	0.7
29*	18	0	0	0	0
	23	0	0	0	0
30	18	6	6	12	0.7
	23	7	8	15	0.7
31	18	5.5	5.5	11	0.6
	23	7	10.5	17.5	0.76
32 33	Large separation—blur with 31				
35	12	0	0	0	0
	23	0	0	0	0
42	20	5	6	11	0.6
	23	6	8(?)	14	0.6
43	15	6	5	11	0.7
	23 blurs with 44				
44	Blurs with 45 even with low field strengths.				

Note: While some of the lines sharply divide into two components as the field is increased, e.g., *26 30* etc., others tend to blur as they widen, e.g., 27. Still others tend to fade out so that it is difficult to observe them, e.g., *29*. See Fig. 1.

Unique axis perpendicular to field; observations transverse to field; long axis of crystal $GdCl_3\cdot 6H_2O$ parallel to field.

Line	Field kilogauss	Shift toward longer wave-lengths cm^{-1}	Shift toward shorter wave-lengths cm^{-1}	Total separation cm^{-1}	Total separation per kilogauss cm^{-1}
26	23	3	3	6	0.27
29	23	5	5	10	0.43
30	18	2	2	4	0.22
	23	3	3	6	0.26
31	18	2	2	4	0.22
	23	3	3	6	0.26
32 33	Decompose and blur together				
35	18	4	5	9	0.5
	23	5	7	12	0.5
42	20	3	3	6	0.3
	23	4	3	7	0.3
43 44	Decompose and blur together				

Observations parallel to field; unique axis parallel to field.

26 no visible effect,
29 widened
30 no visible effect,
31 widened
32 clearly double
35 widened
42 no visible effect
43 widened
44 doubled (?)

harmonic character and the corresponding intervals would then be almost equal (or multiples of some obvious fundamental frequency). The oscillations of a lattice composed of bromide ions would probably be considerably different from one of chloride ions. For example, the reststrahlen[18] of KCl lie at 63.4μ and those of KBr at 82.6μ, a difference of 36.6 cm^{-1}. The reststrahlen of TlCl (a heavier chloride) lie at 91.6μ and of TlBr at 117.0μ, a difference of 23.7 cm^{-1}. There is but little difference, however, between the frequencies of gadolinium chloride, 36.5 cm^{-1}, 16.5 cm^{-1}, 26.5 cm^{-1} and the corresponding frequencies of the bromide, 38 cm^{-1}, 15 cm^{-1}, and 31 cm^{-1}. It is much more natural to regard these intervals as due to the electric fields of the lattice and as arising in part from the chloride ions in one case and from the bromide ions in the other, both kind of ions, however, being made ineffective by the H_2O molecules which intervene between them and the positive gadolinium ion.

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[18] Rubens, Sitz. Preuss. Akad. Wiss., Berlin (1917), p. 47.

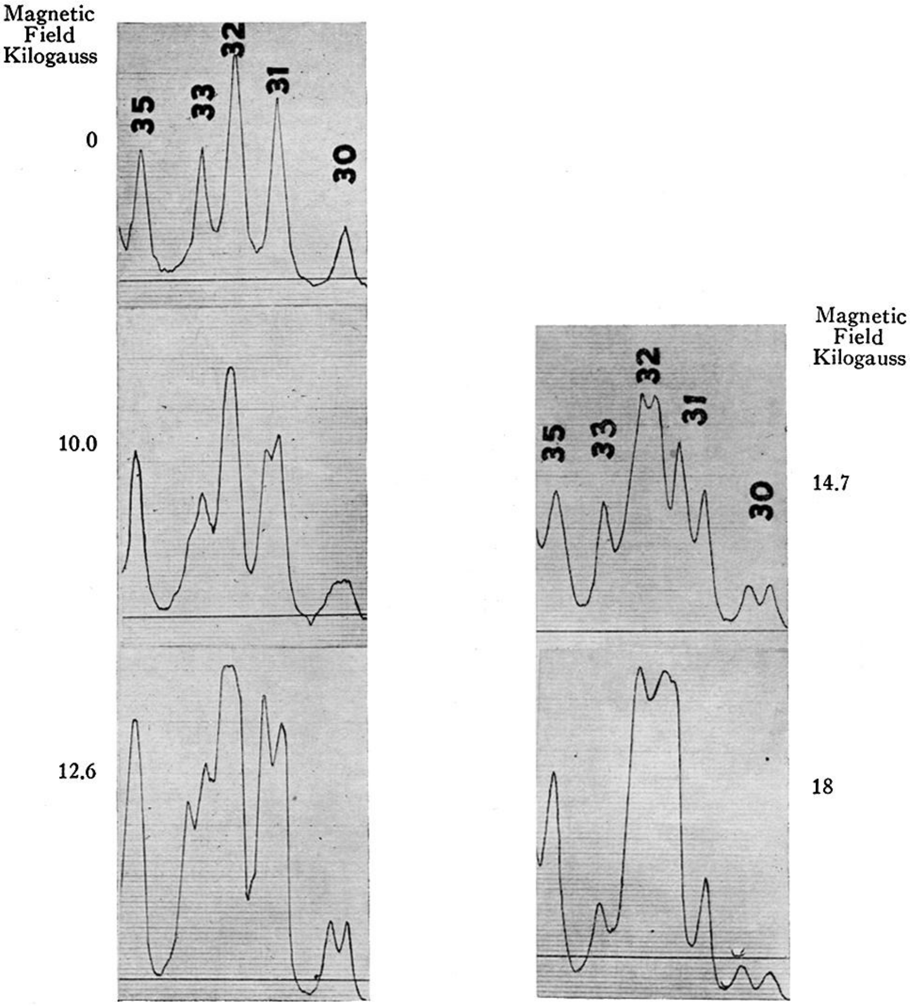

Fig. 2. Microphotometer curves of absorption spectra of $GdCl_3 \cdot 6H_2O$. Unique axis perpendicular to field, parallel to light ray. Long axis perpendicular to field.

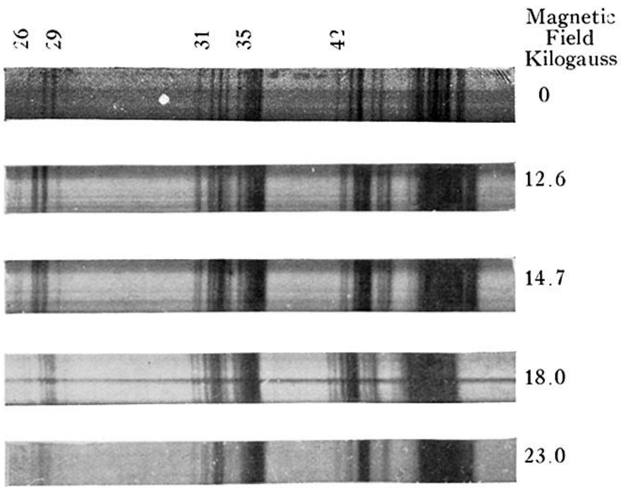

Fig. 3. Absorption spectra of $GdCl_3 \cdot 6H_2O$. Unique axis perpendicular to field, parallel to light ray. Long axis perpendicular to field.