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THE LINE SPECTRA OF IONS IN THE SOLID STATE IN THE VISIBLE AND ULTRAVIOLET REGIONS OF THE SPECTRUM. THE ABSORPTION SPECTRA OF $GdBr_3 \cdot 6H_2O$ AT ROOM TEMPERATURE AND AT THAT OF LIQUID AIR AND THEIR COMPARISON WITH THOSE OF $GdCl_3 \cdot 6H_2O$

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It is well known that the absorption spectra of the solutions of colored salts[1] consist of very broad bands and that the detail which the quantum theory requires to analyze them appears unattainable at present. The absorption spectra of crystals are less diffuse and they offer greater hope in this connection because the ions in a crystal lattice are subject to fields of greater regularity than exist in solution. It is a fact that the solutions of the rare earths possess relatively narrow bands and one would expect to find that their crystals would exhibit absorption spectra of exceptional sharpness.[2] In the next few paragraphs we shall attempt to show that the ions of the transition elements (the most common colored ions) should be regarded as polyatomic in the solid state and in solution, while those of the rare earths may be treated as atomic and hence as the simplest for spectroscopic study.

In his work on the spectra of complex atoms and ions in the gaseous state Hund[3] showed how to determine the character of the basic state of an atom (or atomic ion) from the number of the electrons in its various shells. He employed these basic states to calculate the magnetic moments of many ions but for lack of data upon paramagnetic monatomic gases he compared his results with the measured susceptibilities of ions in the solid state and in solution. The agreement was remarkably good in the case of the ions of the rare earths but there was no semblance of agreement with the ions of the iron group (the first long row of the periodic table). It seems then as if

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[1] Jones and Strong, *Carnegie Inst. Wash. Pub.*, No. 110 (1909); No. 130 (1911); No. 160 (1916).

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

[3] Hund, *Z. Physik*, **33**, 853 (1925).

Hund's assumptions do not apply here and it is not difficult to find the reason.[4]

Let us compare a particular example of an ion in the iron group with one in the rare earth group, chromic ion and gadolinium ion. The electronic configurations of these ions in the gaseous state are electronic shells

	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2
Cr^{+++}	2	2	6	2	6	3						
Gd^{+++}	2	2	6	2	6	10	2	6	10	7	2	6

We observe that the ions in the iron group have their incomplete electronic shells in the outermost orbits where they can readily couple with electrons of other substances such as Cl^- or H_2O. It is well known since the work of Werner that Cr^{+++} in solution is really $Cr(H_2O)_6^{+++}$. On the other hand, the unbalanced electrons in the structure of the ions of the rare earths are within the kernel of the ion and are shielded from external coupling by the completely filled 5_1 and 5_2 shells. In fact, the rare earths do not form complex ions and it is well known that their colors are unaffected (or only to a slight degree) by changing the medium in which they are dissolved. The ions of the iron group are extremely sensitive to their medium. For example, the addition of ammonia or cyanide ion completely transforms the colors of chromic ion or cupric ion. We conclude that there is a radical difference between the electronic configurations of these ions in the gaseous state and their configurations in solution. That is, chemical bonds between the water molecules and the metallic ion have transformed the atomic ion into a polyatomic or molecular ion and hence Hund's theory[3] for atomic ions is not applicable. We must have recourse to theories concerning the stationary states of polyatomic molecules, such as have been devised to interpret band spectra. Among the ions of the rare earths, no chemical coupling has occurred, so that these ions are truly atomic in solution and in the crystal. Their magnetic properties establish definitely that they have the same electronic configurations here that they have in the gaseous state. The water molecules are attached to the positive ions by the forces of electrostatic polarization and not by chemical bonds (pairs of electrons whose magnetic moments have neutralized each other).

According to this reasoning, the absorption spectra of the rare earths resemble the line spectra of monatomic gases, whereas the absorption spec-

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[4] A great deal has been written upon the paramagnetism of the ions of the iron group. Many of the ions in solution and in the solid state display a paramagnetism which can be expressed readily in terms of the Bohr unit of magnetic moment, $eh/\pi m$ where e/m is the ratio of the charge divided by the mass of an electron and h is Planck's constant. This unit is employed constantly in the spectroscopic study of gases. Sommerfeld, "Atombau," Vieweg and Sohn, Braunschweig, 4th ed., **1924**; Stoner, "Magnetism and Atomic Structure," E. P. Dutton and Co., New York, **1926**; Freed, THIS JOURNAL, **49**, 2456 (1927).

tra of the ions in the iron group resemble the band spectra of polyatomic molecules. We actually found in our work on the rare earths, especially in the case of gadolinium, that the absorption spectra consisted of very sharp lines.[5]

It should be remembered that the positive ion in the crystal lattice is constantly in the electric fields of its neighbors. At higher temperatures when the oscillations are more violent the variation in the intensity of the fields will be greater and consequently there is a greater variation in the energy levels of the positive ion which are affected by these fields. That is, different ions will be exposed to fields of different intensities and directions and consequently the light associated with these energy levels will vary slightly in frequency so that the resultant line observed will be broader at higher temperatures. A reduction in temperature will permit a refinement in the absorption spectrum. This influence of temperature was studied by Becquerel.[6]

When the oscillations in the crystal lattice have been so reduced that their effect upon the characteristic absorption is slight, it becomes possible to measure the influence of the size, charge and other properties of the neighbors of the positive ion upon its energy levels. So direct a quantitative study of the influence of one ion (for example) upon another is clearly of great chemical importance. Already vast stores of data have been accumulated showing the influence of chemical combination upon the x-ray energy levels of ions. The unit of energy employed in these investigations is so huge that the influence of chemical combination appears as a slight difference in large magnitudes. X-ray measurements are concerned with the energy necessary to remove an electron from a shell which has its full complement of electrons far inside the kernel of the ion. In the investigation being reported the electrons that are most easily affected by the negative ion come into play, that is, those in the incomplete 4_4 electronic shell. In the x-ray region the smallest detectable energy difference is roughly a thousand times as large as can be detected in the visible region of the spectrum. The quantitative correlation of such magnitudes as heats of solution, etc., with the energy levels of the spectra we are working with is within the range of reasonable expectation.

Experimental Methods and Results.—We are now reporting upon the absorption spectra of $GdBr_3 \cdot 6H_2O$ taken at room temperature and at that of liquid air. We also wish to indicate differences between these spectra and those of $GdCl_3 \cdot 6H_2O$ reported elsewhere.[5] For details as regards some of our apparatus and the method of growing single crystals we must refer to the paper[5] previously mentioned.

The crystals grow in colorless flat rhombohedra. The light was passed

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[5] Freed and Spedding, (a) *Nature*, **123**, 525 (1929); (b) *Phys. Rev.*, **34**, 945 (1929).

[6] J. Becquerel, Gedenkboek H. Kammerlingh Onnes, Leiden, 1922.

perpendicular to two parallel sides which did not require polishing. It has been known for a long time that the frequency of the light absorbed is the same along the different axes of a crystal. The intensities, however, may be different.[7]

The source of the continuous radiation in the ultraviolet was a hydrogen discharge tube with aluminum electrodes, as described by Bay and Steiner.[8] The spectrum was continuous and rather uniform in intensity down to 2000 Å.—the limit of our spectrograph.

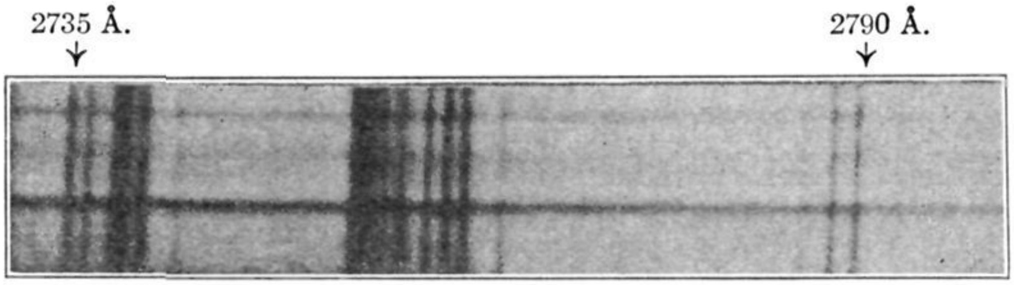

Fig. 1.—Absorption spectrum of $GdBr_3 \cdot 6H_2O$ at room temperature.

The absorption spectra of $GdBr_3 \cdot 6H_2O$ at room temperature were taken with a spectrograph having two quartz prisms with a dispersion of 3.5 Å. per mm. at 2350 Å. and 20 Å. per mm. at 4000 Å. This spectrograph was not available when the spectra at the temperature of liquid air were taken. The latter were photographed with a large Hilger spectrograph containing a single quartz prism. Its dispersion was 6 Å. per mm. at 2350 Å. and 34 Å. per mm. at 4000 Å.

The bromide is extremely hygroscopic and its handling was made easier by covering the crystal with a very thin layer of collodion, which was transparent in the spectral regions investigated.

It happened that the most satisfactory spectra of the bromide were obtained from a particular crystal about 0.8 mm. thick which originated from c. p. gadolinium oxalate procured from the Welsbach Company and twice reprecipitated and recrystallized. If any lines had appeared in the bromide which did not have their counterpart in the chloride, we should have been inclined to attribute them to slight impurities. (However, such was not the case.) Our chloride was made from a sulfate especially purified for us under the direction of Professor B. S. Hopkins of the University of Illinois, who was kind enough to give us also the following chemical history of the sulfate.

"Gadolinium material accumulated in this Laboratory (University of Illinois) from various rare earth sources was repeatedly precipitated as hydroxide by the addition of ammonia to a solution of the chlorides. The

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[7] Bunsen, *Pogg. Ann.*, **128,** 100 (1866); H. Becquerel, *Ann. chim. phys.*, **6,** 170 (1888).

[8] Bay and Steiner, *Z. Physik*, **45,** 337 (1927).

mixture was then treated with hydrogen sulfide, filtered, and the rare earths in the filtrate were precipitated as oxalates with oxalic acid, ignited to the oxides, dissolved in hydrochloric acid, precipitated as hydroxides by ammonia, and finally converted to the nitrates by dissolving in nitric acid. Bismuth nitrate was added and the mixture was subjected to fractional crystallization of the simple nitrates in nitric acid solution. After prolonged fractionation, part of the material was precipitated as oxalate, ignited, and dissolved in nitric acid with the addition of sufficient magnesium oxide to form the double rare earth magnesium nitrate. This material was subjected to further fractional crystallization. All the gadolinium free from the other rare earths was then precipitated twice as oxalate to remove magnesium, then dissolved in hydrochloric acid and treated repeatedly with hydrogen sulfide to remove bismuth until no further precipitate of bismuth sulfide was obtained. The gadolinium was precipitated as oxalate, ignited, dissolved in nitric acid and fractionally crystallized five times as simple nitrate. The material was then precipitated as oxalate, ignited for twenty-four hours, and the oxide was suspended in a large volume of water to which sulfuric acid was added. The sulfate solution was evaporated slowly and the crystals were dried in an oven at 110°.

"The samarium present was estimated spectroscopically to be approximately 0.2%. No indication was observed of europium, while there was a possible trace of terbium, although no spectroscopic evidence of its presence was obtained. The sulfuric acid had the following limits of impurities (%)

HCl	0.00005	Heavy metals	0.0005
Fe	.00008	Non-volatile	.0006
As	.000001		

TABLE I

WAVE LENGTHS OF $GdBr_3 \cdot 6H_2O$ AND $GdCl_3 \cdot 6H_2O$

$GdBr_3 \cdot 6H_2O$				$GdCl_3 \cdot 6H_2O$					
Room temperature		Liquid air temperature		Room temperature		Liquid air temperature		Liquid hydrogen temperature	
(Å.)	(cm.$^{-1}$)	(Å.)	(cm.$^{-1}$)	(Å.)	(cm.$^{-1}$)	(Å.)	(cm.$^{-1}$)	(Å.)	(cm.$^{-1}$)
		4646.3	21516	4644.9	21523.0	4646.62	21515.0	4647.05	21513.0
		4154.7	24062[a]			4157.9	24044		
		4153.6	24069			4157.2	24048		
						4152.7	24074	4156.84	24036.5
						4152.3	24076	4153.28	24070.5
		4074.0	24539[b]			4073.7	24541		
		4073.5	24542			4072.7	24547	4074.11	24536.5
?		4029.0	24813	4026.6	24026	4026.2	24830		
		4028.5	24816	4024.5	24841	4024.8	24839	4025.75	24833.0
?		4012.5	24884	4016.4	24891	4014.1	24905	4014.10	24905.0
		4016.8	24888			4013.6	24908		
						4012.8	24913		
				4011.4	24922	4011.9	24919	4012.61	24914.5
3118.10	32061.5	3118.90	32053.5	3117.04	32072.5	3117.52	32067.5	3117.67	32066.0
3114.85	32095.0	3115.40	32089.5	3114.87	32094.0	3114.95	32094.0	3115.19	32091.5
3112.10	32123.5	3112.50	32119.0	3112.14	32123.0	3112.13	32123.0	3112.33	32121.0

TABLE I (*Concluded*)

Room temperature		Liquid air temperature		Room temperature		Liquid air temperature		Liquid hydrogen temperature	
(Å.)	(cm.$^{-1}$)	(Å.)	(cm.$^{-1}$)	(Å.)	(cm.$^{-1}$)	(Å.)	(cm.$^{-1}$)	(Å.)	(cm.$^{-1}$)
3109.90	32146.0	3110.25	32142.5	3109.86	32146.5	3109.91	32146.0	3110.10	32144.0
3061.20	32657.5	3061.90	32650.0	3060.54	32664.5	3061.00	32659.5	3060.82	32661.5
3057.25	32699.5	3057.85	32693.0	3057.08	32701.5	3057.27	32699.5	3057.17	32700.5
3053.60	32738.5	3053.95	32735.0	3053.61	32738.5	3053.53	32739.5	3053.53	32739.5
2793.15	35791.5	2793.60	35785.5	2792.67	35796.5	2793.07	35792.5	2793.22	35790.5
2790.20	35829.0	2790.70	35823.0	2790.10	35830.5	2790.49	35825.5	2790.72	35822.5
2788.20	35850.0	2788.95	35845.5	2788.70	35848.5	2788.90	35845.5	2789.08	35843.5
2786.50	35876.5	2786.90	35873.0	2786.52	35876.5	2786.68	35874.5	2786.83	35872.5
?	?	2767.9	36118	?	?	2767.77	36119.5	2767.66	36121.0
2766.45	36137.0	2767.10	36128.0	2765.90	36144.0	2766.47	36136.5	2766.47	36136.5
?	?	2765.9	36144	2765.06	36155.0	2765.63	36147.5	2765.63	36147.5
2764.00	36169.0	2764.45	36163.0	2763.86	36170.5	2764.29	36165.0	2764.33	36164.5
2762.85	36184.0	2763.35	36177.5	2762.65	36186.5	2763.07	36181.0	2763.10	36180.5
2761.60	36200.5	2762.05	26194.5	2761.62	36200.0	2761.88	36196.5	2761.92	36196.0
2760.45	36215.0	2761.20	36205.5	2760.93	36209.0	2761.23	36205.0	2761.31	36204.0
2759.95	36222.0	2760.15	36219.0	2759.86	36223.0	2760.17	36219.0	2760.09	36220.0
2759.40	36229.0			2759.08	36234.5	2759.37	36229.5	2759.40	36229.0
2758.85	36236.5		[c]	2758.53	36240.5	2758.87	36236.0	2758.83	36236.5
2758.30	36243.5			2758.11	36246.0	2758.46	36241.5	2758.42	36242.0
2757.85	36249.5			2757.66	36252.0	2758.03	36247.0	2758.00	36247.5
2757.45	36255.0			2757.20	36258.0	2757.62	36252.5	2757.62	36252.5
2756.80	36263.0	2757.15	36258.5	2756.59	36266.0	2756.93	36261.5	2756.85	36262.5
?	?	2747.75	36382.5	2745.05	36418.5	2745.57	36411.5	2745.46	36413.0
2745.60	36411.5	2746.25	36402.5			2744.71	36423.0	2744.33	36428.0
?	?	2744.85	36421.0	2743.09	36444.5	2743.54	36438.5	2743.31	36441.5
2743.30	36442.0	2743.65	36437.0			2742.45	36453.0	2742.37	36454.0
2742.15	36457.0	2742.40	36452.0	2741.81	36461.5	2742.03	36458.5	2742.00	36459.0
2741.55	36463.5	2742.05	36458.0			2741.02	36472.0	2741.05	36471.5
2739.95	36486.5	2740.20	36483.0					2740.45	36479.5
2738.75	36502.0	2739.05	36498.0	2739.85	36487.5	2740.19	36483.0	2740.08	36484.5
2736.75	36529.0	2738.10	36511.0					2739.48	36492.5
2735.20	36551.0	2737.30	36521.5	2738.69	36503.0	2738.95	36499.6	2738.76	36502.0
2734.35	36561.0	2735.50	36545.5[d]	2737.12	36524.0	2737.83	36514.5	2737.94	36513.0
2733.65	36570.5	2734.05	36565.0	2735.80	36541.5	2736.33	36534.5	2736.26	36535.5
2732.90	36580.5	2733.20	36576.5					2735.36	36547.5
2731.90	36593.5	2732.30	36588.5	2734.68	36556.5	2735.06	36551.5	2734.95	36553.0
2731.15	36603.5	2731.25	36602.5	2734.12	36564.0	2734.38	36560.5[e]		
2730.80	36608.5					2733.75	36569.0		
2730.30	36615.5	2730.05	36618.5	2732.70	36583.0	2733.11	36577.5	Unresolved band due to structure in source	
2729.70	36623.2			2731.73	36596.0	2732.18	36590.0		
2729.10	36631.0	2729.30	36628.5			2731.17	36603.5		
						2730.24	36616.0		
				2726.84	36637.5	2729.31	36628.5	2728.78	36635.5
2727.80	36648.5	2727.85	36648.0	2727.48	36653.0	2727.82	36648.5	2727.79	36649.0
2727.00	36659.5	2727.05	36658.5	2726.85	36661.5	2727.07	36658.5	2727.0	36659.5
2530.35	39508.5	2530.50	39506.0	2530.05	39513.0	2530.30	39509.0		
2529.40	39523.5	2529.55	39520.5	2528.90	39531.0	2529.10	39528.0		
2527.10	39559.0	2527.15	39558.5	2526.40	39570.0	2526.60	39576.0		
2525.25	39588.0	2525.20	39589.0	2524.70	39597.0	2524.85	39594.5		
2523.20	39620.5	2523.25	39619.5	2522.50	39631.0	2522.70	39628.5		
2464.00	40572.0	2464.00[f]	40572.5	2463.15	40586.0	2463.25	40584.5		
2463.05	40588.0	2463.20	40585.5	2462.30	40601.0	2462.35	40599.0		
2446.75	40858.0	2446.90	40855.5	2446.10	40868.0	2446.50	40862.5		
2441.75	40941.5	2441.85	40940.0	2441.25	40950.0	2441.35	40948.0		

[a] Looks like two lines. Very faint band. [b] Very faint band, looks like two lines. [c] Band unresolved due to smaller dispersion. [d] Barely resolved due to small dispersion. [e] Not completely resolved due to smaller dispersion. [f] Background so faint lines difficult to measure.

Discussion of Results.—The absorption spectra even at room temperature consisted of extremely sharp lines, as may be seen from the photograph and the precision with which the frequencies could be determined (see table). The spectra lay almost entirely in the ultraviolet region except for a few faint diffuse lines in the visible. These lines became markedly finer at the temperature of liquid air.

The magnetic measurements of Kammerlingh Onnes and his associates[9] show that the magnetic behavior of Gd^{+++} in the solid state conforms with that expected theoretically from a "perfect magnetic" gas throughout the entire temperature range, from room temperature to 1.3°K. This "gas" (Gd^{+++}) consists of a single species having ^8S for its basic electronic level.[10]

It follows that the other electronic levels are rather far removed in terms of energy from the ^8S, for, otherwise, the ions having the electronic configurations corresponding to these levels would have contributed to the measured susceptibility and produced deviations from the theoretical curve. The latter had assumed that only one species was present.

The Hund theory predicts that other electronic levels belonging to systems of lower multiplicity than ^8S originate from the seven 4_4 electrons of Gd^{+++}. They correspond to different relative orientations of the spin and orbital moments of the seven equivalent electrons. Goudsmit[11] has shown that the relativity doublet separation given by the formula of Sommerfeld employed in the x-ray region of the spectrum

$$\Delta\nu = \frac{R\left(\frac{2\pi e^2}{hc}\right)^2 (Z - \sigma)^4}{n^3 l(l + 1)}$$

can often be applied in the optical region to such electronic configurations in order to obtain the separations between the multiplets. $\Delta\nu$ is the difference in frequency between the doublet levels, R is Rydberg's constant, e is the charge of the electron, h is Planck's constant, c is the velocity of light, Z is the atomic number of the atom, σ is the screening constant derived from x-ray measurements, n is the total quantum number of the electron and l is its orbital quantum number. The separations expected in the rare earths are of the order of magnitude found between the *groups* of the Gd^{+++} spectrum. It appears probable even at this early stage of study that each group of lines would be a single line (if the ion were gaseous) corresponding to a transition from the basic level to a multiplet level and that this single line has been decomposed into a group of lines by the electric fields within the crystal. However, some of the levels have not been

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[9] Woltjer and Kammerlingh Onnes, Leiden Comm. No. 167C.

[10] (a) Hund, *Z. Physik*, **33**, 853 (1925); (b) Giauque, THIS JOURNAL, **49**, 1870 (1927).

[11] Goudsmit, *Phys. Rev*.. **31**, 946 (1928).

decomposed into their maximum number of components. We have already found from spectroscopic measurements in a magnetic field (Zeeman Effect on Solids) that further decomposition of some of the lines (or levels) can be effected.[12]

It is easy to tabulate many of the lines of the Gd^{+++} spectrum into multiplets having constant energy differences. Such a tabulation need not lead to unique energy levels even in the spectra of gases unless further information such as is furnished by the study of the Zeeman Effect, etc., is available. It is with the aim of getting unique energy relations that our work on the Zeeman Effect in crystals is being undertaken.

We have also made polarization spectra (which we shall publish later together with the work on the Zeeman Effect) which show that the lines are polarized in relatively different directions. Such a behavior cannot be attributed to any crystalline dissymmetry, for then all the lines would be polarized more or less uniformly.

It is characteristic of the Stark Effect, that is, the interaction of an electric field with radiant matter, that it produces lines which are polarized. The polarization of the spectral lines definitely expresses the electrical influence of the neighbors of the positive ion upon its spectrum. The identification of the polarization of the lines with that observed in the Stark Effect on gases is the same as the interpretation previously advanced[13] that the polarization discloses the regular orientation of the observing ions by the crystalline forces. In the Stark Effect the external field brings about an orientation or a quantization of the ion with respect to the direction of the field and then the transitions between the resultant states of the ion give rise to light which is polarized.

The astonishing sharpness of the lines in the spectrum of Gd^{+++} even at room temperature shows that the Gd^{+++} is not sensitive to the variation in the perturbing action of the external electric fields. One would expect that the thermal oscillation of the constituents in the crystal lattice would produce a great broadening, for example, such as is found in Sm^{+++}, Er^{+++}[14] at room temperature. The shielding of the 4_4 electrons by the complete shells of the 5_1 and 5_2 electrons is particularly effective in Gd^{+++}. As has been previously mentioned, the basic level of Gd^{+++} is an ^8S which implies that the orbital momenta of all seven electrons in the 4_4 shell have completely neutralized each other. Such a neutralization leads to a distribution of electron density having spherical symmetry, according to the quantum mechanics; that is, the electrons are probably grouped compactly inside the shielding 5_1 and 5_2 shells of electricity. In the language of

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[12] Becquerel (Ref. 6) in studying the influence of a magnetic field upon the polarization of the light absorbed by his substances observed a splitting of some of the lines.

[13] Brunetti, *Physik. Z.*, **29**, 571 (1928).

[14] Freed and Spedding, *Nature*, **123**, 525 (1929).

orbits, we may say that the average time in which the 4_4 electrons are close to the perturbing agents is slight. In the less symmetrical electron distributions which exist among ions such as Eu^{+++} or Sm^{+++}, the eccentricity of their orbits implies that the electrons are very close to the sources of perturbation a considerable fraction of the time. Hence their energy levels are capable of great variation since they accompany the oscillations of the perturbing agents. Their spectral lines are more diffuse.

So symmetrical an arrangement of the seven electrons leads to a coupling of great stability. That is, the energy level corresponding to this coupling is considerably lower than any other (a sort of maximum stability). It is probable that the nearest energy level to which any rearrangement would correspond is so far above its basic level that ultraviolet light is necessary for any transition. (In other words, it would be surprising if any transitions could be brought about in absorption by means of infra-red radiation. If it occurs it would probably be faint and due to a transition from an activated level. We are inclined to believe that the faint diffuse lines in the visible are of a similar origin. Their very diffuseness suggests that the transition begins at an electronic state of less stability than the basic ^8S.)

At the low temperature, there is a general readjustment of the energy levels so that the lines shift slightly toward the longer wave length regions of the spectrum. This change (already discussed in our communication on $GdCl_3{\cdot}6H_2O$) may be attributed to the thermal contraction of the crystal. The constituents of the crystal are on an average nearer each other at the lower temperature and the closer approach of a bromide ion, for example, has probably shifted the outer energy level (corresponding to the activated state of Gd^{+++}) more than the inner. That is, the energy levels have approached each other (in terms of energy) and a transition between them corresponds to a smaller change in energy than at the higher temperature. The light is of longer wave length.

Comparison of Spectra of $GdBr_3{\cdot}6H_2O$ and $GdCl_3{\cdot}6H_2O$.—There appears to be a complete parallelism among the spectra of the bromide and the chloride, that is, a line for line correspondence in their spectra. It is fairly certain from analogies with salts of similar composition that the six molecules of water are grouped more or less symmetrically about the gadolinium ion. Hence any difference in the spectra of $GdCl_3{\cdot}6H_2O$ and $GdBr_3{\cdot}6H_2O$ can be ascribed to a first approximation to the difference in character between the bromide ion and the chloride ion. The results show that the corresponding lines in the two spectra are very nearly the same, a fact in keeping with the supposition that the molecules of water are between the negative ions and the gadolinium ion. The spectra indicate that the bromide ion induces a slight approach in the gross energy levels (that is, the hypothetically "unsplit" energy levels) of the gadolinium ion, as follows from the general displacement of the lines toward longer wave lengths as compared with the corresponding chloride lines. The bromide ion also brings about a slightly greater separation (on the average) between the lines comprising a group. We have attributed the existence of these groups to the electric fields surrounding the gadolinium ion (fields presumably arising principally from the polarized water molecules). Upon this basis, the displacement toward the red and the greater separation induced by the bromide ion can be related to the well-known deformability of the bromide ion, which would produce a greater negative charge upon the surface opposite the gadolinium ion than would the chloride ion.

Summary

We have discussed the possibility of applying the quantum theory of the line spectra of gases to ions in the solid state. We have concluded that the ions of the rare earths exhibit line spectra comparable with those of atomic ions in the gaseous state under the influence of external electric fields.

The absorption spectra of the crystal $GdBr_3 \cdot 6H_2O$ were taken at room temperature and at that of liquid air. Its spectra even at room temperature consist of lines of extreme sharpness comparable with the lines of the iron arc which were used for comparison. The spectra lie almost entirely in the ultraviolet. There are a few faint diffuse lines in the visible.

At the temperature of liquid air there is a slight shift of the lines toward longer wave lengths and a greater separation between lines comprising each group. These displacements can be related to the thermal contraction of the crystal which brings the constituents of the crystal closer together. The fields due to the neighbors of the Gd^{+++} become then more intense than at the greater average distance at higher temperatures. The few diffuse lines in the visible become narrower and sharper at the temperature of liquid air. The spectra consist of groups of lines and these groups are separated by rather large intervals. We have regarded each group as corresponding to one line of the spectrum of Gd^{+++} ions in the gaseous state. This line has been decomposed into several lines by the electric fields arising from the neighbors of the Gd^{+++} ions in the crystal lattice.

Some of the potentialities of such investigations are sketched. The influence of bromide ion upon the positive ion is roughly compared with that of chloride ion (a preliminary communication on the spectra of $GdCl_3 \cdot 6H_2O$ was published in *Phys. Rev.*, **34,** 945 (1929)) and this difference is related to the greater deformability of the bromide ion.

We are continuing and extending the study of the spectra of the ions of the rare earths with the hope of obtaining unique energy levels.

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