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LINE ABSORPTION SPECTRA OF SOLIDS AT LOW TEMPERATURES IN THE VISIBLE AND ULTRA-VIOLET REGIONS OF THE SPECTRUM

A Preliminary Study of $GdCl_3 \cdot 6H_2O$ from Room Temperature to that of Liquid Hydrogen

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Abstract

This work is the beginning[1] of a systematic investigation of the absorption spectra of solids, particularly single crystals of the ions of the rare earths, over a range of temperatures. We expected that the ions of the rare earths in the solid state would exhibit line absorption spectra because their magnetic moments agreed quantitatively with theories[2] which had been successful in elucidating the line spectra of gases. The latter definitely established that only the 4_4 electronic shell is incompletely filled and extrapolation of the energies from x-ray data led to the conclusion that the energy necessary to remove a 4_4 electron might possibly be measured through quartz.

The absorption spectra of the synthetic uniaxial crystal $GdCl_3 \cdot 6H_2O$ were the first to be taken because the spectrum of Gd^{+++} would presumably be the simplest, its basic electronic level ^8S being single. Its spectrum was found actually to consist of very sharp lines, sharp even at room temperature. They were almost all in the ultraviolet. The appearance of the spectrum changed little as the temperature was reduced except that there was a general slight shift of the lines toward the red and also that there were greater separations between the lines comprising each multiplet. This behavior is primarily due to the contraction of the crystal which brings the ions closer together. That is, the electrostatic fields of the constituents of the crystal surrounding the positive ion become more intense when the constituents approach each other. Many lines allow themselves to be systematized into multiplets by means of the constant frequency intervals that occur but we are postponing the attempt to obtain a unique energy diagram until measurements of the Zeeman Effect now in progress will have been completed. We have also studied the effect of changing the electrostatic fields to which the positive ions are exposed, for example, by substituting bromide ion for the chloride ion, etc., but shall publish these results later.

A simple new method for growing crystals from solution is described.

We HAVE outlined[1] reasons for believing that the absorption spectra of the rare earths in the solid state would resemble the line spectra of ions in the gaseous state. We shall briefly review those reasons here. Hund[2] calculated the magnetic moments of the ions of the rare earths on the basis that:

(a) Their electronic configurations were those postulated by Stoner in his scheme for the Periodic System.

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[1] Freed and Spedding, Nature, **123**, 525 (1929), where a brief summary of some of our results on Gadolinium, Samarium and Erbium are given.

[2] Hung, Zeits. f. Physik, **33**, 853 (1925).

(b) "Normal multiplet coupling" between the electrons subsisted even in the solid state and in solution.

(c) The magnetic moments calculated from the basic electronic levels derived from the above assumptions would be those possessed by the ions in the solid state and in solution.

His results checked the measured susceptibilities very satisfactorily. It appears then that the water of solution or of crystallization does not disturb the nature of the electronic coupling in the free ion nor affect the number of electrons coupled.[3]

The electronic configurations established by Hund are:

Atomic No. of ion	Ion	No. of electrons in shells $1_1 \cdots 4_3$	4_4	5_1	5_2
54	La^{+++}	full	0	2	6
55	Ce^{+++}	″	1	2	6
|	|				
61	Gd^{+++}	″	7	2	6
|	|	″			
68	Lu^{+++}		14	2	6

When we extrapolate x-ray data of the heavier elements to the rare earths we find that an electron of the rare earths possesses less energy in the N_6 (N_7) shells than it does in the O shells. That is, an electron in the 4_4 shell is held less tightly than an electron in the 5_1 or 5_2 shells. It appears from this extrapolation that the energy needed to remove an electron from an ion of the rare earths corresponds to frequencies which can probably be measured through quartz. Many of the rare earths are colored so that the frequencies associated with electronic activations actually lie in the visible region of the spectrum.

For each ion we can assume with confidence that the basic electronic level is that confirmed by Hund with magnetic data.

The work of Becquerel and his associates[4] is of considerable importance for our present point of view. They obtained absorption spectra of minerals which contained mixtures of rare earths. In 1906 Becquerel had found that the narrow absorption bands displayed by these substances at room temperature became much narrower when the temperature was reduced. At the temperature of liquid hydrogen some of the bands attained a sharpness comparable with lines in the spectra of gases. Becquerel and his associates focused their attention upon individual lines or bands, that is, their polarization in a magnetic field, etc. They made no recorded attempt to identify particular lines or bands with the individual constituents of the crystal responsible for them. Hence the problem of evaluating their spectra hardly presented itself. Their crystals were enclosed in glass (Dewar tubes) which limited the range of their spectra particularly on the side of short wave-lengths. Each of the minerals contained several rare earths and in addition it

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[3] The molecules of water are held presumably by the forces of electrostatic polarization and not by chemical bonds, that is, not by bonding pairs of electrons.

[4] J. Becquerel. Gedenkboek H. Kammerling-Onnes. Leiden 1922.

probably contained other positive and negative ions in solid solution. Such irregularities in the crystal lattice doubtless produced strains which tended to blur the absorption lines. Indeed, we have obtained photographs showing that different negative ions shift the position of the absorption lines of a positive ion to unequal degrees so that an absorption "band" in a mineral might really be the unresolved effects of two or more negative ions.

In order to get spectra of solids as free as possible from the influences of perturbing fields, we studied synthetic uniaxial crystals of individual rare earths in as high a state of purity as we could procure. We are now reporting work of a preliminary nature on the spectra of $GdCl_3 \cdot 6H_2O$, a synthetic uniaxial crystal. The spectra were taken at room temperature, at that of liquid air, and at that of liquid hydrogen.

We are continuing this work with a grating of high dispersion and are also investigating the Zeeman effects on these spectra with a view of getting a unique energy level diagram. The gadolinium chloride was made from the sulfate octahydrate $Gd_2(SO_4)_3 \cdot 8H_2O$ purified to atomic weight purity under the direction of Professor B. S. Hopkins of the University of Illinois, to whom we wish to express our gratitude. The chemical history of the substance will be published later in our paper on the absorption spectra of $GdBr_3 \cdot 6H_2O$.

Preparation of Crystals

In order to get sharp and well defined absorption lines it was necessary to have fairly large single crystals, and the following method proved very satisfactory in obtaining them. Small seeds were first prepared by dissolving almost all of a conglomerate of crystals in conductivity water at about 60°C. The solution was then placed on a thick piece of asbestos in a sheltered corner of the laboratory where it was protected from shock and sudden temperature changes. The following morning the solution was poured off through a porous Jena glass filter into a beaker, and a drop of water added to dissolve any microscopic seeds. The filters, funnels, and beakers had all previously been thoroughly cleaned with hot chromic acid and dried in an electric oven free from dust. The best of the seeds were then selected with the aid of a magnifying glass and put into the filtered solution. This was immediately placed in a vacuum dessicator, which contained a little calcium chloride. If the dessicator is connected directly to the vacuum pump the seeds grow but in a chaotic fashion resulting in opaque clusters. We found this could be avoided by inserting a small capillary about 0.001 mm in diameter between the dessicator and the pump. Under such conditions the crystals grow smoothly and perfectly. Crystals 1.5 cm long and 1 cm wide can be obtained in four days and have actually been obtained in as little as two days. No further precautions need be taken as the capillary irons out fluctuations in pressure, and the fluctuations in room temperature are minimized by the poor heat conduction into the evacuated dessicator.

Sources of Light and Spectrographs

We used a 500-watt tungsten lamp as a source of continuous light in the visible region of the spectrum. This light after passing through the crystal was focused on the slit of a three-prism Steinheil spectrograph which had a dispersion of 3.2A per mm at 4000A and 26A per mm at 6000A.

A condensed discharge between tungsten electrodes as described by Barnes and Fulweiler[5] served as the source of our continuous radiations in the ultra-violet in our earlier work. This source gave a good continuous spectrum down to 2500A and one less satisfactory to 2200A. In the latter region the absorption spectrum of the tungsten tended to mask our absorption spectra. A rapid flow of pure water through the discharge chamber was found necessary to obtain a satisfactory spectrum even down to 2500A.

In our later work we used a discharge through hydrogen between aluminum electrodes as described by Bay and Steiner[6] and we found it very satisfactory. The spectrum was continuous and uniform in intensity down to 2000A, the limit of our instrument.

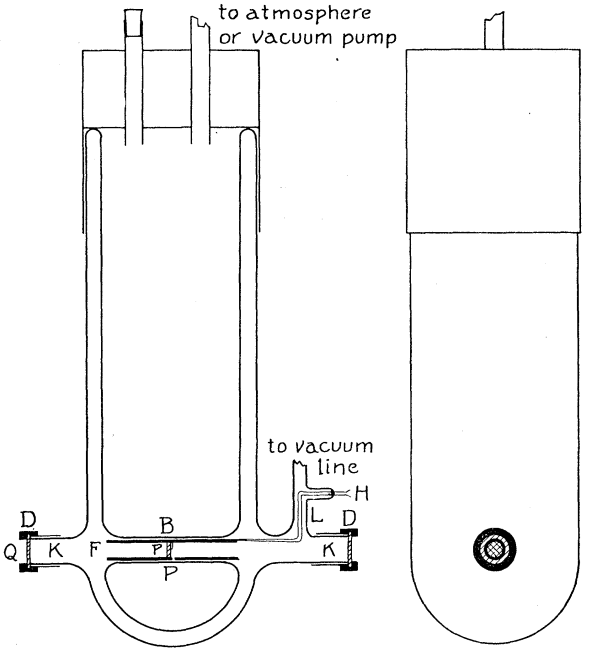

Fig. 1. Dewar tube for maintaining the crystal at low temperatures.

A large Hilger spectrograph containing a single quartz prism was used in this region. It gave a dispersion of 6A per mm at 2350A and 34A per mm at 4000A.

Apparatus for Maintaining Crystal at Low Temperatures

The Dewar tube (Fig. 1) for maintaining the crystals at low temperatures was made of Pyrex glass. It was so designed that by using the quartz windows *QQ* a beam of ultra-violet light could be passed horizontally through

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[5] Fulweiler and Barnes, J. Franklin Inst. **194,** 83 (1922).

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

it near the bottom. The inner tube of the Dewar was pierced near the bottom by a glass cylinder (*B*), 25 mm in diameter. The tubes *KK* were sealed on the outside shell so as to be a continuation of this cylinder. The quartz windows were sealed by means of de Khotinsky cement on the ends of two short brass tubes which slipped over the cylinders *KK*. Caps *DD* screwed down over the windows so as to protect them from mechanical jolts. By having the brass tube warm and a thick layer of de Khotinsky on the tube *K*, a vacuum tight joint could rapidly be made by slipping the tube into place.

The crystal *P* was mounted on the end of a copper cylinder and held in place by means of cap made of aluminum foil.

The cylinder was then wrapped with aluminum foil and wedged into place at *F*, against the silvered side of the tube. A thermocouple *H*, so arranged that its junction came in contact with the crystal was wrapped about a similar cylinder and led out through a side arm at *L*.

When liquid hydrogen was in the Dewar we found that the temperature of the crystal remained constant to within 0.1° for seven hours and changed only when the liquid dropped below the tube *B*. The direct radiation from a 500-watt tungsten lamp raised the temperature about 4°, although the the heat from the lamp was sufficient to melt the deKhotinsky seals at the windows. (Hence they had to be protected.)

REPORT OF RESULTS

No previous investigations on the absorption spectra of crystals of the salts of gadolinium have been published. A few bands have been reported for the solutions.[7]

$GdCl_3 \cdot 6H_2O$ crystallizes in beautiful colorless plates in the tetragonal system. The spectra were taken along the principal axis, that is perpendicular to the faces. We also obtained a photograph perpendicular to the principal axis. Both directions yielded spectra which were identical within our limits of measurement.

We also grew a crystal of the chloride which had been prepared from gadolinium oxalate bought from the Welsbach Company. The spectrum from this crystal was practically the same as the one obtained with gadolinium purified under the direction of Professor Hopkins.

Spectra in general. The spectrum consisted of about ninety lines mostly in the ultra-voilet. These lines were clustered in groups or multiplets with rather large intervals between them. Many constant frequency differences were observed and groups allowed themselves to be readily arranged into multiplets of the type,

39196.0	36262.5		
			$\Delta\nu = 59.0$
36136.5	36204.0	36220.0	
			$\Delta\nu = 39.5$
	36164.5	36180.5	
$\Delta\nu = 67.0$	$\Delta\nu = 16.0$		

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[7] Urbain Compt Rend., Compt. Rend., **140,** 1233 (1905); J. Chem. Physique **4,** 328 (1906); Jones and Strong, Carnegie Inst. Wash. Pub. 110 (1909); 130 (1911); 160 (1916).

However as several other multplets involving the same lines could also be tabulated any allotment of energy values was considered arbitrary until Zeeman effects now in progress will have been completed. Constant frequency differences were also observed between the groups as a whole.

Effect of change in temperature. Lowering the temperature to that of liquid air caused the multiplets to spread out and their center of gravity to shift slightly to the red. This spreading out continued as the temperature was reduced to that of liquid hydrogen and was sufficient in some cases to cause the violet components of the multiplets to shift back to shorter wavelengths. The average change in the frequency of a line between room temperature and that of liquid hydrogen was about four wave-numbers.

Width of lines. All the lines (except a few in the visible) were exceedingly sharp even at room temperature and they compared in fineness with the emission lines of iron which were used for comparison. A very few faint diffuse bands in the visible seemed to sharpen at lower temperatures. The uneven intensities of these bands suggested that they may be close multiplets which might be resolved into separate lines under higher dispersion and at lower temperatures. We intend to photometer these lines in our next work.

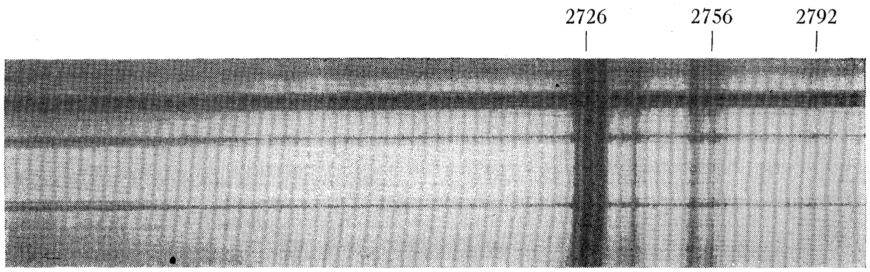

Fig. 2. Absorption spectrum of $GdCl_3 \cdot 6H_2O$ taken at room temperature.

The lines in group IV were resolved only at the temperature of liquid air when the hydrogen discharge tube was our source of continuous radiation. The under-water spark gave some structure in this region of the spectrum which blurred the absorption lines of the crystal with those of the background.

Intensity of lines. The relative intensity values listed are very rough and can only be compared at the same temperature and in the same regions of the spectrum. The relative intensities of the lines within a multiplet changed somewhat with the temperature. In the visible, however, the faint diffuse lines or bands contracted and increased markedly in intensity as the temperature was lowered. There were several lines especially in the region between 3000A and 4000A whose intensities were so low that their wave-lengths could not be measured with any precision.

Fluorescence spectra. A very weak fluorescence spectrum appeared to exist in the visible, more pronouncedly at lower temperatures and in the neighborhood of absorption bonds. We are planning to investigate these spectra more closely under more favorable conditions.

TABLE I. *Wave-lengths and wave-numbers in the line absorption spectrum of* $GdCl_3 \cdot 6H_2O$.

Room temperature			Liquid air temperature			Liquid hydrogen temperature		
λ(A)	ν(cm⁻¹)	*I*	λ(A)	ν(cm⁻¹)	*I*	λ(A)	ν(cm⁻¹)	*I*
2441.26	40,950.0	4	2441.35	40,948.0	4	The continuous radiation used at this temperature contained so much structure in this region that the lines were hidden by it.		
2443.96	40,905.0	1	2444.84	40,890.0	1			
2446.10	40,868.0	4	2446.49	40,862.5	4			
(2451.2)	40,783.	0	2451.52	40,778.5	0			
(2451.6)	40,778.	0						
(2454.6)	40,727.	0	2454.53	40,728.5	2			
(2454.9)	40,722.	0						
2462.30	40,600.0	8	2462.36	40,599.0	8			
2463.15	40,586.0	8	2463.24	40,584.5	8			
(2469)	40,491.	0	2469.61	40,480.0	2			
2522.49	39,631.5	6	2522.68	39,628.5	6			
2524.66	39,597.5	6	2524.84	39,594.5	6			
2526.40	39,570.0	6	2526.60	39,567.0	6			
2528.74	39,533.0	4	2529.09	39,528.0	4			
2529.91	39,515.5	4	2530.31	39,509.0	4			
2726.85	36,661.5	7	2727.07	36,658.5	6	2727.00	36,659.5	5
2727.48	36,653.0	7	2727.82	36,648.5	6	2727.79	36,649.0	5
2726.84[1]	36,637.5	7	2729.31[2]	36,628.5	6	2728.78[1]	36,635.5	5
			2730.24	36,616.0	6			
			2731.17[2]	36,603.5	7	Unresolved band due to structure in source.		
2731.73	36,596.0	7	2732.18	36,590.0	6			
2732.70[1]	36,583.0	7	2733.11	36,577.5	5			
	band		2733.75	36,569.0	5			
2734.12	36,564.0	7	2734.38	36,560.5	5			
2734.68	36,556.5	4	2735.06	36,551.5	4	2734.95	36,553.0	4
						2735.36	36,547.5	0
2735.80	36,541.5	4	2736.33	36,534.5	4	2736.26	36,535.5	4
2737.12	36,524.0	1	2737.83	36,514.5	1	2737.94	36,513.0	1
2738.69	36,503.0	4	2738.95	36,499.5	4	2738.76	36,502.0	4
						2739.48	36,492.5	1
2739.85	36,487.5	4	2740.19	36,483.0	4	2740.08	36,484.5	4
						2740.45	36,479.5	1
			2741.02	36,472.0	1	2741.05	36,471.5	1
2741.81[3]	36,461.5	8	2742.03[4]	36,458.5	6	2742.00	36,459.0	6
			2742.45	36,453.0	6	2742.37	36,454.0	6
2743.09	36,444.5	5	2743.54	36,438.5	4	2743.31	36,441.5	4
			2744.71	36,423.0	1	2744.33	36,428.0	1
2745.05	36,418.5	4	2745.57	36,411.5	4	2745.46	36,413.0	4
2756.59	36,266.0	4	2756.93	36,261.5	6	2756.86	36,262.5	4
2757.20	36,258.0	2	2757.62	36,252.5	2	2757.62	36,252.5	2
2757.66	36,252.0	2	2758.03	36,247.0	2	2758.00	36,247.5	2
2758.11	36,246.0	2	2758.46	36,241.5	2	2758.42	36,242.0	2
2758.53	36,240.5	2	2758.87	36,236.0	2	2758.83	36,236.5	2
2759.08	36,234.5	2	2759.37	36,229.5	2	2759.40	36,229.0	2
2759.86	36,223.0	4	2760.17	36,219.0	5	2760.09	36,220.0	4
2760.93	36,209.0	2	2761.23	36,205.0	2	2761.31	36,204.0	2
2761.62	36,200.0	3	2761.88	36,196.5	4	2761.92	36,196.0	4
2762.65	36,186.5	6	2763.07	36,181.0	8	2763.10	36,180.5	6
2763.86	36,170.5	4	2764.29	36,165.0	4	2764.33	36,164.5	4
2765.06	36,155.0	1	2765.63	36,147.5	1	2765.63	36,147.5	1
2765.90	36,144.0	3	2766.47	36,136.5	4	2766.47	36,136.5	4
			2767.77	36,119.5	0	2767.66	36,121.0	1
2786.52	35,876.5	3	2786.68	35,874.5	2	2786.83	35,872.5	3
			2787.86	35,859.5	0			

[1] Unresolved band.
[2] 3/2 width.
[3] Double width.
[4] Double line.

TABLE I (*Continued*)

Room temperature			Liquid air temperature			Liquid hydrogen temperature		
λ(A)	ν(cm⁻¹)	I	λ(A)	ν(cm⁻¹)	I	λ(A)	ν(cm⁻¹)	I
2788.70	35,848.5	4	2788.90	35,845.5	3	2789.08	35,843.5	3
			2789.71	35,835.5	0			
2790.10	35,830.5	4	2790.49	35,825.5	3	2790.72	35,822.5	2
			2791.66	35,810.5	0			
2792.67	35,796.5	3	2793.07	35,792.5	2	2793.22	35,790.5	2
3053.61	32,738.5	3	3053.53	32,739.5	3	3053.53	32,739.5	3
3057.08	32,701.5	3	3057.27	32,699.5	3	3057.17	32,700.5	3
3060.54	32,664.5	3	3061.00	32,659.5	3	3060.82	32,661.5	3
3109.86	32,146.5	2	3109.91	32,146.0	2	3110.10	32,144.0	2
3112.14	32,123.0	2	3112.13	32,123.0	2	3112.33	32,121.0	2
3114.87	32,094.0	2	3114.95	32,094.0	2	3115.19	32,091.5	2
3117.04	32,072.5	2	3117.52	32,067.5	2	3117.67	32,066.0	2
			3940.5[5]	25,360	0	Beyond limits of plate		
			3942.0	25,370				
3941.5[6]	25,365	0	3946.0[5]	25,335	0			
3943.0	25,355		3947.5	25,325				
4011.4[6]	24,922	2	4011.9[6]	24,919	3	4012.61[7]	24,914.5	4
			4012.8[8]	24,913	3			
			4013.6[8]	24,908				
4016.4	24,891		4014.1[8]	24,905		4014.10	24,905.0	4
4024.5[6]	24,841	2	4024.8[8]	24,839	3	4025.75	24,833.0	4
4026.6	24,026	2	4026.2	24,830	3			
			4072.7[6]	24,547		4074.11	24,536.5	
			4073.7[9]	24,541				
			4152.3[6]	24,076	00	4153.28	24,070.5	1
			4152.7[9]	24,074				
						4156.84	24,036.5	1
			4157.2[6]	24,048	00			
			4157.9[9]	24,044				
4644.9	21,523.0	0	4646.62	21,515.0	0	4647.05	21,513.0	1
				?		4650.74	21,496.0	00
						4840.80	20,652.0	0
						4843.61	20,640.0	0
						4857.94	20,579.0	
						4860.80	20,567.0	
						4863.40	20,556.0	
						4865.90	20,545.5	0
						4868.28	20,536.0	0
						5803.24	17,227.0	1
						5829.00	17,151.0	1

[5] Diffuse band. Appears to be made up of several lines.
[6] Diffuse band.
[7] Narrow bands. Appear to be made up of lines.
[8] Appear to be unresolved lines.
[9] Possibly two lines.

Absorption spectrum in aqueous solution. The absorption spectrum of gadolinium chloride dissolved in water resembled that of the crystal, especially as regards the position of the muliplets. However in solution the multiplets tended to blur into narrow bands.

Discussion of Results

The magnetic susceptibility of a hydrated salt of gadolinium has been measured by Kammerlingh-Onnes and his associates[8] from room temperature to 1.3°K. Its magnetic behavior is identical with that expected of a perfect magnetic gas having ^8S for its basic electronic level.[9] It was this very level that Hund arrived at in an unforced manner from the electronic configurations of the rare earths. And it is this level which must be assumed for the absorption spectrum of gladolinium ion.

The fact that the basic level is single (since all S levels are single) would lead us to anticipate that gadolinium ion has a simpler absorption spectrum than the other rare earths. An S term implies that the vector sum of the orbital moments of the electrons is zero. Such a neutralization of the orbital moments would be expected to result in an arrangement of unusual stability. It requires more energy to disrupt the stable arrangement possessing the zero orbital moment of gadolinium than to activate the less symmetrical arrangement of most of the other rare earths. Hence it is not surprising that the salts of gadolinium are colorless, that is, that ultra-violet light is necessary to activate them, while the other rare earths that do not have S levels for their basic terms are colored.

The shift in position of the lines as the temperature is reduced is primarily due to the contraction of the crystal, that is, the mutual approach of its constituents. Such an approach causes a decrease in the difference in energy between the various energy levels as is shown by the general displacement of the lines toward the red as the temperature is reduced. (That is the inner and outer energy levels are affected to different degrees.) Also, the intervals between the lines of the same group increase. Such a behavior suggests that these intervals are due to the fields external to the positive ion which increase in intensity as the ions approach each other. (Experiments are now in progress to test this point.)

The narrowing of the lines as the temperature is reduced is due to the thermal agitation of the substances in the crystal lattice. In addition to the slight Doppler Effect there is the continuous variation in the intensity of the electric fields to which the positive ions are exposed. As the constituents of the crystal exterior to the positive ion approach and recede from it, its energy levels vary. And although at any particular instant the line from a single ion is extremely narrow, the line observed spectroscopically is the superposition of the lines emanating from all the ions which the light traverses and no two of these at any particular instant are exposed to a field of the same magnitude and direction. Hence the effect is a greater blurring or widening of the lines at the higher temperature when the thermal agitation is greater.

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[8] Woltjer and Kamerlingh-Onnes, Leiden Comm. 167C.

[9] Giauque, J. Am. Chem. Soc. **49**, 1870 (1927).

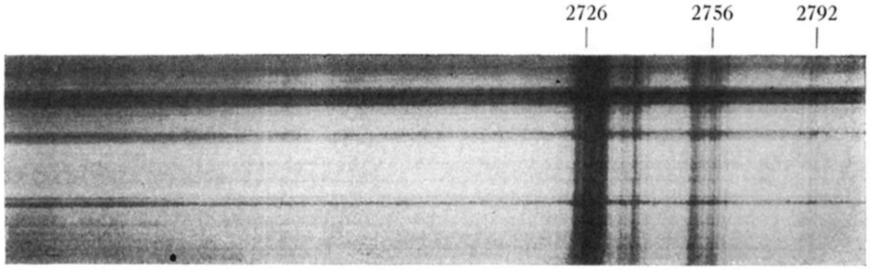

Fig. 2. Absorption spectrum of $GdCl_3 \cdot 6H_2O$ taken at room temperature.