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The Line Absorption Spectrum of Gadolinium Ion in Crystals

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With a view to determining the dependence upon crystal symmetry and chemical composition of the energy levels in a solid, the absorption spectrum of Gd^{+++} in a number of different synthetic crystals has been photographed at temperatures between 300° and 20°K. Using the external crystallographic symmetry as an indication of the probable degree of symmetry about the gadolinium ion in the lattice, it is established that the important factor in determining the splitting of the multiplets or the excited levels is the lattice symmetry and not the negative ion except insofar as the negative ion influences the crystal structure, for the spectra of monoclinic gadolinium chloride, bromide, sulfate and selenate are almost identical, but are very different from the spectra of the hexagonal formate, bromate and ethylsulfate. Gadolinium propionate and butyrate evidently have somewhat different internal symmetry from that of the other monoclinic crystals since their spectra resemble much more the spectrum of triclinic gadolinium acetate. The group of compounds including gadolinium trichloracetate, propionate, butyrate, isobutyrate and trichlorbutyrate is similar in that the spectra of all are weak, diffuse, and little resolved even at the temperature of liquid hydrogen. The presence or absence of water of crystallization affects the spectra only slightly. The positions of the multiplets, and the positions of the lines within the multiplets of anhydrous gadolinium formate are much the same as in the ethylsulfate and bromate enneahydrates. The phenomenon of highly discrete selective reflection in the ultraviolet region by three compounds has been observed. A discussion of the nature of the excited states of the gadolinium ion in crystals is presented.


IN a previous paper[3] the absorption spectrum of gadolinium ion in six compounds was reported on. It was shown that through studies of the discrete absorption of salts of the rare earth elements intimate knowledge of the energy states arising from various configurations of electrons in the outer regions of atoms in crystals (hence of most immediate interest to chemists) can most readily be gained. Compounds of gadolinium are especially suitable for this purpose for their spectra are simple, and, since the basic states are single, the absorption lines present in effect energy level diagrams of the excited states. Changes attending alteration of lattice structure and changes of chemical composition are easily followed and may be exactly measured. There are three major difficulties in using gadolinium for such a study. In seeking to interpret the spectra of ions in the solid state analyses of the spectra of the gaseous ions are of immense value, and such analyses are lacking for all but one of the triply ionized rare earth atoms. That one is cerium. Gadolinium is also unfortunate in that its spectrum lies in the ultraviolet,

with the chief multiplets near 2700A. A regrettably large number of anions absorb in this region, so salts of gadolinium with them, although they may be interesting chemically and crystallographically, cannot be studied. There is, furthermore, no powerful source of ultraviolet light, and thus spectrograms obtained by transmission through conglomerates of small crystals or by diffuse reflection from powders of microcrystalline substances cannot be obtained with an instrument of high dispersion in a reasonable length of time. It seems to be a fact, moreover, that the rare earth compounds which crystallize in the tetragonal and isometric systems, and are of most theoretical interest, are uniformly insoluble, and hence may be obtained with an ordinary expenditure of effort only as powders.

In the present paper new data are given on the absorption spectra of the Gd^{+++} ion in hexagonal crystals of $Gd(COOH)_3$, $Gd(BrO_3)_3 \cdot 9H_2O$ and $Gd(C_2H_5SO_4)_3 \cdot 9H_2O$; in monoclinic crystals of

$$Gd_2(SO_4)_3 \cdot 8H_2O, \quad Gd_2(SeO_4)_3 \cdot 8H_2O,$$
$$Gd(C_2H_5COO)_3 \cdot 3H_2O$$
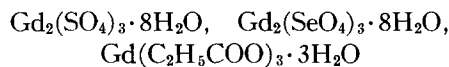
and $Gd(C_3H_7COO)_3 \cdot 2H_2O$; in triclinic crystals of $Gd(CH_3COO)_3 \cdot 4H_2O$; and in

$$Gd(CCl_3COO)_3 \cdot 3H_2O;$$
$$Gd(CCl_3CH_2CH_2COO)_3 \cdot 10H_2O$$
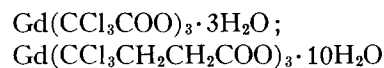
and $Gd(iso\ C_3H_7COO)_3 \cdot 6H_2O$. Crystallographic

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[3] F. H. Spedding and G. C. Nutting, J. Am. Chem. Soc. **55**, 496 (1933).

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measurements on most of the compounds have been made for us by Professor Adolf Pabst[4] of the geology department of the University of California, and we are glad to acknowledge his aid. There are no crystallographic data on gadolinium chloracetate, chlorbutyrate and isobutyrate.

EXPERIMENTAL PART

With the exceptions of the bromate and ethylsulfate, which were obtained by double decomposition between barium bromate and ethylsulfate and gadolinium sulfate, the compounds were prepared by dissolving gadolinium oxide in the appropriate acids. When it was possible to obtain them, only perfect single crystals were photographed, but in the case of the formate, selenate, chlorbutyrate and isobutyrate conglomerate pictures were found necessary. The thickness of the crystals ranged from 0.4 to 2.5 mm. In establishing the composition of the compounds, molecular weight determinations, carried out by converting weighed quantities of salts into gadolinium oxide, were made. Wolff[5] has reported only three molecules of water of crystallization in cerous isobutyrate while we have found six molecules in the gadolinium compound.

In order to take advantage of the increased sharpness and increased resolution of the absorption lines obtained at low temperatures, whenever feasible the spectra were photographed at 78°K, and in several instances at 20°K. The crystals were immersed directly in the cooling bath of liquid air, liquid nitrogen or liquid hydrogen contained in a large Dewar flask with a quartz extension at the bottom. The background of continuous ultraviolet light was provided by a hydrogen discharge tube. Photographs were made with a quartz three meter Littrow spectrograph (Hilger E185) giving dispersion of 3A per mm at 3100A, 2.1A per mm at 2750A and 1.5A per mm at 2500A. Since many exposures were long (the times varied from three minutes to a week) the temperature of the room was kept constant within 0.1°C. Positions of the absorption lines were measured with reference to the iron spectrum.

Repeated attempts to secure satisfactory spectra of gadolinium nitrate and bromate in the 2700A region failed. Regardless of the purity of the salts, the ultraviolet light brought about decomposition whose products showed continuous absorption, although potassium nitrate and potassium bromate (both anhydrous salts, incidentally) transmit well as far as 2700A, particularly at low temperatures. The difficulty was partially overcome in the case of gadolinium bromate by using very thin crystals, but no spectra of the hydrated nitrate below 3100A were ever obtained.

OBSERVATIONS

The Gd IV absorption spectrum consists of nine principal multiplets, which, since they arise from a single lower level, constitute an energy level diagram of the excited states. Besides these multiplets there are scattered through the spectrum numbers of much fainter lines, sometimes sharp, sometimes diffuse, sometimes gathered into groups, sometimes appearing as widely separated individuals. Slight overexposure frequently masks them altogether. Their intensity is greatly enhanced at low temperatures and they appear most prominently in the sulfate, chloride and acetate spectra. Since it may be that many of them are due to other rare earths than gadolinium, we shall not consider them further.[6]

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[4] A. Pabst, Am. J. Sci. **22**, 426 (1931); **26**, 73 (1933).
[5] H. Wolff, Zeits. f. anorg. allgem. Chemie **45**, 89 (1905).

[6] These lines are of the same general type as the faint lines reported in the visible by S. Freed and F. H. Spedding, (Phys. Rev. **34**, 945 (1929), and J. Am. Chem. Soc. **52**, 3747 (1930)). While the Gd salt was some of atomic weight purity, kindly sent us by Professor Hopkins, this does not mean that it was entirely free from traces of other rare earths. These traces will have a negligible effect on any atomic weight determinations since the differences in the atomic weights of the rare earths are small but in absorption spectra they may become important. Since the above papers were published we have definitely found that some of those weak lines were due to other rare earths. We therefore think it advisable in this paper to omit all lines below a certain level of intensity as at present we have no way of knowing which of the lines (if any) come from the gadolinium and which from traces of other rare earth impurities. If these lines should prove to be due to impurities it would appear that the hexagonal lattice is less tolerant of other rare earth ions than the monoclinic. Therefore in the fractional crystallization of the rare earths, if one picked out large single crystals free from mother liquor a more rapid separation might be effected. It is interesting in this connection to observe that the bromate and ethylsulphate, both hexagonal crystals, are two of the best salts for rapid fractionation of the Gd group of rare earths.

It is found that the gross features of the spectra are independent of the nature of the negative radical and the presence or absence of water of crystallization. Dilution through hydration brings shifts of the multiplets a few angstroms toward shorter wave-lengths, and the multiplets of the metal organic compounds lie almost invariably slightly to the red of the multiplets of wholly inorganic compounds. Much greater differences are noted in the spectra of compounds having different crystallographic symmetry. It appears that the multiplets would in gaseous ions degenerate into single levels, or at any rate into simpler structures, and that the complicated patterns actually observed have arisen from the various action on the simple levels of the force fields existing between the gadolinium ions and their definitely and regularly oriented neighbors in the crystal lattice. If this is true, since vibrational coupling between the positive and negative constituents of the compound in most cases is clearly absent, it might be expected that the structure of the multiplets is largely determined by the symmetry of the lattice, and the higher the symmetry type the simpler the spectrum. Just what the symmetry is, is to be decided from x-ray patterns, and x-ray data on rare earth compounds are at present and probably will be for some time to come very meager. At least it is likely that the internal symmetry is reflected in some measure in the external form of the crystal, and that it is probably of higher order in a hexagonal than in a monoclinic or triclinic crystal. The gadolinium spectra support this view, for spectra of varied compounds which crystallize in the monoclinic system are very similar, yet unlike the spectra of hexagonal crystals, which among themselves are also similar.

The usual result of cooling the crystals is marked sharpening of the absorption lines. Lessening the thermal motion in the lattice decreases the Doppler broadening and in addition doubtless decreases the natural width of the lines. A third reason is perhaps most important of all. The approach and recession of an ion or a dipole adjacent to a gadolinium ion is attended by a continuously varying Stark field which shifts the position of the gadolinium energy levels by a small amount. The total effect produced upon the multitude of atoms contributing to the absorption is the pronounced widening of the absorption lines. At low temperatures the shift of the levels is small and the absorption lines are correspondingly sharp. It is also true that the multiplets widen slightly with decreasing temperature and the lines in general shift to the red. The shift is small and takes place principally between room and liquid-air temperatures. Sometimes on further cooling to 20°, a few of the lines are displaced once more to the violet, but only by about 1 cm^{-1} from the position they occupy at 78°. The amount of the shift appears to depend largely upon the symmetry of the crystal, being greatest (from 8 to 10 cm^{-1}) in the spectra of the hexagonal bromate and ethylsulfate, intermediate (4 to 7 cm^{-1}) in the monoclinic chloride and sulfate, and least (1 to 3 cm^{-1}) in the triclinic acetate. The shifts are probably to be accounted for in the main by the contraction of the lattice. This brings the adjacent atoms closer to the gadolinium, thus increases the strength of the electric fields acting on the gadolinium and increases the amount of the splitting of its energy levels.

Gadolinium propionate, butyrate, isobutyrate, trichloracetate and trichlorbutyrate show strange behavior, for the lines in their spectra are always very wide and very fuzzy, in decided contradistinction to the lines of gadolinium sulfate and bromate, and even formate and acetate. The apparent intensity of absorption is very low, too, but this is understandable in view of the unusual width of the lines. Lowering the temperature brings some narrowing and resolution, but even at the temperature of liquid hydrogen the absorption lines are much wider than those of an inorganic gadolinium compound at room temperature.

The phenomenon of strong selective reflection in the λ3100 multiplet found by Spedding and Bear[7] in gadolinium chloride has been observed also in gadolinium ethylsulfate and isobutyrate. Although a reflection phenomenon, we have usually observed it in spectra photographed by transmission through either a badly cracked single crystal or a conglomerate of small crystals, in which the surfaces necessary for multiple

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[7] F. H. Spedding and R. S. Bear, Phys. Rev. **39**, 948 (1932).

reflection are abundant. Absorption spectra of conglomerates of gadolinium fluoride, sulfite, selenate, iodate, trichloracetate, formate, propionate, butyrate and malonate have been photographed and all showed the normal absorption lines. It is to be regarded as a chance occurrence that in a mass of tiny crystals the facets should be so oriented that on the average the light of wave-lengths represented in the λ3100 band is reflected from them instead of passing through the surfaces and being absorbed in the body of the crystals. It seems likely that if it were possible to obtain large single crystals of these gadolinium salts, successive reflection from certain of their surfaces would in all cases bring about isolation of the frequencies of the λ3100 lines. Selective reflection from crystals is common enough, but gadolinium is absolutely unique in the narrowness of its reflection bands, which at 20° in the ethylsulfate are considerably less than one angstrom in width, and are quite comparable with the selective reflection of the 2537A line of mercury in the vapor state described by Wood.[8] Since the reflectivity of a substance for a given wave-length depends on both the index of refraction and the extinction coefficient, it is probably fortuitous that it should reach the observed high value in the λ3100 multiplet rather than in any of the others. The relative intensities of the lines are usually very different from the intensities of the corresponding absorption lines. One chloride plate showed λ3118, 3115 and 3112 in reflection and λ3110 faintly in absorption. Another chloride conglomerate, photographed by reflection, showed the four 3110A lines strongly in reflection, the 3050A lines entirely absent and the 2700A lines extremely faintly in absorption. An ethylsulfate spectrum showed the 3110 and 3109 lines in reflection and 3108 in absorption. Careful comparison of plates made at 300°K has demonstrated that for both gadolinium chloride and ethylsulfate the positions of the lines absorbed and selectively reflected are identical. It is noteworthy that the λ3050 and 3110 multiplets were never obtained from sulfate conglomerates at 300°, despite many attempts to do so, yet they invariably showed up perfectly in the photographs of single crystals at all temperatures and of conglomerates at 85°. It was presumably because the sulfate crystals were

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[8] R. W. Wood, *Physical Optics*, third edition, p. 534.

immersed in liquid air (a medium of very different refractive index from gaseous air) that the absorption lines appeared in this last case. Perhaps it should be mentioned that selective reflection was observed when the interfaces through which the incident light entered the various crystals were of quartz, air, liquid air, liquid nitrogen and liquid hydrogen. For a given substance the intensity of reflection in each of these cases would probably be different because of the differences in indices of refraction, but we have not attempted to secure data on this point.

In the paragraphs which follow are set forth some of the details of the spectra. We shall consider the multiplets in turn.

3110 and 3050A multiplets

The spectra of the chloride, bromide and sulfate single crystals are practically identical—the position, width and intensity of the lines for a given temperature are the same. The spacing of the lines in the spectrum of the selenate conglomerate is much like that of the other wholly inorganic monoclinic crystals, but the multiplet spreads are distinctly greater. The lines are unusually wide, unusually intense and unusually fuzzy.

Monoclinic crystals of gadolinium propionate and butyrate give lines which are wide and very much blurred. The 3110A lines in both are practically not resolved at all at room temperature. The 3050A group is somewhat better, distinctly so in the case of the butyrate. The 3118 line of the propionate is missing at 300° but shows up faintly at 78°. At 78° the propionate spectrum at 3110A sharpens markedly, but still the lines are very much less sharp than in one of the inorganic compounds. At 78° the 3050A lines of the propionate are stronger but about as fuzzy as at 300°, and are spread out over about one and one-half times the distance. Upon cooling propionate crystals to 20°, it is found that the absorption lines are about as diffuse as they are at 78°. There is no resolution, no change in relative intensities and no change in relative position. On the other hand the butyrate lines are appreciably narrower at 20° than at 78°, and one line resolves into two components. The multiplets of gadolinium isobutyrate are at room temperature two very faint, ill-defined, structureless, unmeasurable bands. At the temperature of liquid air the absorption is more intense and the bands become narrower and resolve, showing five lines in the λ3110 and four lines in the λ3050 multiplets. The lines are wider and the multiplets are wider and situated farther toward the red than in the butyrate spectrum.

The lines of the nitrate are stronger and wider than those of the chloride and are less spread out, but have about the same limit on the violet side. They do not become narrower or less diffuse at the temperature of liquid air. The lines of the acetate resemble the lines of the chloride very much in width, spacing and intensity. They are, however, displaced somewhat to the red, and the multiplet spread is two-thirds

or less that of the chloride. In the spectrum of the trichloracetate the lines are faint, diffuse and unresolved. The multiplets are slightly wider than the multiplets of the acetate and are shifted several angstroms to the violet. At 85° the 3110A multiplet which, for most salts, is composed of either three or four lines shows ten, distributed irregularly, all of them fuzzy and faint and spread over twice the distance of the acetate multiplet. The 3050A group has the normal number of three lines.

The spectra of the bromate, formate and ethylsulfate resemble one another closely and are radically different from the spectra of salts crystallizing in other systems. The resemblance between the ethylsulfate and formate is particularly close. There are only three λ3110 lines in the ethylsulfate at room temperature, and no resolution takes place on cooling. At room temperature there are two 3050A lines in the ethylsulfate, the violet one of which splits at 78°. At 20° the absorption lines of gadolinium ethylsulfate and bromate are as sharp as the finest of the emission lines of gaseous iron which served as the comparison spectrum. The 3110A lines of the bromate are four in number at 300°, the violet two being a close doublet. At 78° the multiplet is spread somewhat, and the separation of the two violet lines is quite noticeably increased. In addition, the red components increase their intensity markedly. At 20° the λ3110 lines of the bromate become six, spreading toward the red but beginning at about the same wave-length on the violet side. There are three lines in the 3050A group at all temperatures. The violet two are by themselves and appear to be the close doublet of the ethylsulfate enormously separated. The overall multiplet spreads of the hexagonal crystals are about one-third those of the monoclinic. The ethylsulfate spectrum is shifted farthest to the violet of any salt, while the bromate is next, and the centers of gravity of the formate multiplets are slightly to the violet of those of the chloride.

2700A multiplets

The bromide and chloride spectra are practically completely identical, even to distribution of intensities. The sulfate spectrum also resembles that of the chloride very closely, but shows somewhat more resolution, and the intensities are a bit different. All the sulfate multiplets are shifted slightly to the violet, but within the multiplets the position of corresponding lines is nearly the same. The selenate spectrum resembles that of the sulfate closely in its gross appearance. All the 2700A multiplets have the same overall spread as the sulfate multiplets, thus contrasting them with the λ3100 bands. Owing to the continuous absorption by the selenate ion and to the fact that a conglomerate of crystals were used, detail, especially in the violet groups, is lacking. Within the 2720–2760A multiplets the general appearance of the fine structure resembles that of the sulfate multiplets, but the resemblance is not nearly so close as in the case of the sulfate, bromide and chloride.

The 2700A groups of the propionate and butyrate are so pulled in that the spectra mirror that of the triclinic acetate more than they do the spectra of the other monoclinic salts. As in the 3100A multiplets, the lines are extremely hazy and the resolution extremely bad. The widths of the multiplets of the propionate and butyrate are nearly identical at room temperature. The grouping of the lines within the multiplets appears to be somewhat closer in the butyrate, and in the butyrate the lines are slightly narrower. At 78° the spectra of gadolinium propionate and butyrate are alike. The multiplets are wider than at room temperature and the lines are fuzzier and broader. It looks as if, without exception, each of the 2700A lines is about to split into two lines. This seeming resolution does not proceed further, however, and the spectra of both salts appear much the same at 20° as at 78°. A few lines sharpen, while the majority remain as diffuse as at the higher temperature. The gadolinium isobutyrate spectrum is distinguished by possessing a few sharp lines at room temperature, while most are very diffuse and all are very faint. All the multiplets are much wider than those of the butyrate and lie several angstroms to the red, in fact farthest to the red of any of the salts investigated. A single photograph of gadolinium trichlorbutyrate made at room temperature with a Hilger E3 spectrograph indicates that the line groups are intermediate in position between those of the isobutyrate and trichloracetate, and are wider and slightly better defined than the butyrate multiplets.

In the acetate spectrum the red edges of the multiplets lie at nearly the same positions as those of the chloride, but the spread of the multiplets is only three-fourths as great. The consequent crowding of the lines gives an impression of haziness at room temperature, while actually the lines are only slightly less sharp than the lines of the chloride. There is practically line for line correspondence within the multiplets. The trichloracetate lines are even fuzzier and less resolved than those of gadolinium butyrate; the detail is scarcely better than in spectra of solutions containing gadolinium ion, where, owing to the relatively great freedom of motion and the indefinite composition of the clouds of water molecules surrounding the positive ions, blurring is to be expected .Except in their extreme haziness, the spectra of solutions and chloracetate crystals have little in common. The 2790A multiplet of the chloracetate, which at 300° consists of two very wide lines, becomes at 85° nine lines of which two are almost surely double. The rest of the multiplets both at 85° and at 20° show little resolution and are wider and are spaced differently from the propionate multiplets at the same temperatures.

The multiplets of the hexagonal crystals are only one-fourth to one-half as wide as those of the chloride, and there are fewer lines within the multiplets. All are displaced to the violet, the ethylsulfate and bromate appearing at about the same places, the farthest to the violet of any of the compounds used. The formate lines are wide and blurred and resolution is incomplete. The ethylsulfate and bromate spectra resemble one another more than they do the formate spectrum. At liquid nitrogen temperature the lines and multiplets of the bromate widen and give evidence of impending further resolution. Spedding and Bear[9] have observed the same phenomenon in the spectrum of samarium bromate.

[9] F. H. Spedding and R. S. Bear, Phys. Rev. **44**, 287 (1933).

TABLE I. *Frequencies of the absorption lines of gadolinium compounds.* Intensities (Int.) have been visually estimated on the scale 0–10. D indicates a double line, T a triple line, M a multiple line of unknown number of components. The letters w, d and vd indicate lines which are wide, diffuse and very diffuse. Primed frequency numbers represent band edges; c, band centers.

| Gd$_2$(SO$_4$)$_3$·8H$_2$O | | | | | | | Gd$_2$(SeO$_4$)$_3$·8H$_2$O | |
| 20° | | | 78° | | 300° | | 300° | |
λ	ν	Int.	ν	Int.	ν	Int.	ν	Int.
3116.47	32078.3	5	32078.6	6	32083.8	5	32061	10wd
3113.64	32107.5	5	32106.2	7	32110.6	7	32101	10wd
3110.87	32136.1	6	32135.8	9	32136.4	9	32131	10wd
3108.27	32162.9	5	32162.2	8	32159.9	9	32166	10wd
3065.2	32615	0						
3059.24	32678.4	7	32678.7	7	32683.3	7	32665	10wd
3055.60	32717.3	7	32717.0	7	32719.0	7	32709	10wd
3052.44	32751.2	7	32750.6	8	32748.8	7	32752	10wd
3049.1	32787	0						
3029.8	32996	0						
2792.35	35801.6	5	35801.2	5	35808.0	4	35797	8wd
2789.63	35836.5	5	35836.5	5	35839.3	3	35832	10wd
2788.13	35855.8	7	35856.4	7	35858.5	7	35851	10wd
2786.13	35881.5	5	35880.9	4	35883.2	1	35873	4wd
2765.63	36148.8	10	36149.4	10	36155.6	10	36141	10d
2763.33	36177.6	10	36178.0	8	36181.6	8	36170	10w
2762.07	36194.1	10	36194.1	9	36195.6	9	36198	10dD?
2761.10	36206.8	10	36207.0	9	36209.4	8	36215	6d
2759.92	36222.3	6	36222.5	7	36227.8	9	36225	6d
2759.48	36228.0	6	36227.9	7	36236.8	6	36236	6d
2759.08	36233.3	5	36233.4	5				
2758.56	36240.1	5	36240.3	5	36243.3	6	36242	6d
2757.99	36247.6	6	36247.7	6	36250.4	6	36248'	
2757.60	36252.7	6	36254.4	10D	36254.3	6		
2757.36	36255.9	6						
2757.02	36260.4	5	36260.3	6	36258.8	10M	36259c	10
2756.43	36268.2	9	36268.4	8				
2756.11	36272.3	7	36272.5	8	36271.5	10M	36271'	
2744.68	36423.4	10	36423.9	10	36430.3	9D	36417	8dD
2742.59	36451.1	10	36451.7	8	36455.5	8	36443	7wd
2741.41	36466.8	10	36467.1	10	36471.4	10D	36462	7dD
2741.05	36471.6	10	36472.4	10			36482	7dM
2739.42	36493.3	9	36493.4	8	36495.4	8	36503	6wd
2738.38	36507.2	8	36506.9	7	36507.8	8	36542	7wd
2735.52	36545.3	9	36545.9	9	36551.2	10	36556	5wd
2734.32	36561.4	8	36561.6	7	36567.0	7	36567'	
2733.42	36573.4	9						
2732.97	36579.4	9D	36578.0	10D	36581.0	10M		
2732.17	36590.1	9	36590.1	9	36593.6	8		
2731.28	36602.1	8D	36599.9	7	36605.1	10	36607c	5
			36604.1	7	36621.2	10M		
2730.01	36619.1	10M	36618.9	8T				
2728.81	36635.2	10	36635.2	10	36638.9	10D	36649'	
2728.37	36641.1	10D	36640.8	10				
2727.24	36656.3	10	36656.4	10	36661.7	10D	36664	5dD
2726.52	36666.0	10	36665.7	10				
2725.6	36678	1						
2725.2	36684	0						
2528.85	39531.8	8	39532.9	6	39523	5		
2528.11	39543.4	8	39544.8	6	39546.5	6		
2525.54	39583.6	9	39584.5	5	39585.9	5		
2523.52	39615.3	10	39616.5	7	39619.2	6		
2521.62	39645.1	10d	39645.6	6d	39645.4	5		
2462.44	40597.8	4	40608.7	10				
2462.1	40604	4	40604.9	10	40602	8D		
2461.60	40611.7	7D	40610.9	10	40613	8D		
			40613.6	10				
2453.3	40748	0	40747	2d				
2452.8	40757	0						
2445.6	40878	0	40879	3d	40884	1d		
2443.4	40914	0	40916	3d	40921	1d		
2440.7	40959	0	40963	3d	40968	1d		

TABLE I.—*Continued.*

| Gd(C$_2$H$_5$COO)$_3$·3H$_2$O | | | | | | GdCl$_3$·6H$_2$O solution. 300° | |
| 20° | | 78° | | 300° | | | |
ν	Int.	ν	Int.	ν	Int.	ν	Int.
32054	0d	32057.6	4wd	32067	4wvd	32088'	
32079	0d	32081.2	6wd	32082	4wvd	32092c	3
32096	0d	32094.3	6wd	32098	4wvd	32097'	
32104	0d	32105.0	6wd			32111'	
						32116c	3
32655	0d	32654.5	5wd	32660.7	6wd	32121'	
32678	0d	32681.3	6wd	32676	6wd	32138'	
						32157c	6D
32697	0d	32696.6	6wd	32686	6wd	32174'	
35782	1wd	35783.7	10wd	35785.3	4d	32684'	
						32689c	4
35809	1wd	35810.8	5wd	35810	2d	32696'	
35823	1d	35823.4	6wd	35823	1d		
						32721'	
35843	1dD	35843.2	7dD	35841.3	3wd	32726c	6
						32732'	
36136	2dM	36141.9	10dM	36136.8	7d		
						32750'	
36148	2d			36146.6	7d	32757c	6
36161	1d	36162	7wd	36161	3d	32762'	
36171	1d	36174.2	7wd	36171	3d		
36184	1wd	36182.4	7wd	36183.2	4d		
		36189.2	4wd				
		36203'		36208	6dM?	35819'	
36211	2d	36219c	8	36219	5	35823c	0
36228	3wd	36236'		36227.8	10D?	35826'	
36247	2dD	36248.1	10D	36244	10	35841'	
36410	1wd	36407'		36417	8d	35849c	2
		36420c	10			35852'	
36427	3wd	36434'		36426.8	10dD?	35860'	
36439'						35866c	2
36446c	1d	36448	8dM	36446	7wd	35874'	
36452'		36464	7dD	36462	7d	35889'	
36464	1wd					35895c	1
36527	1wd	36523'		36529.7	7wd	35904'	
36538	1wd			36540.8	9wd	36167'	
36551	2wd			36552.4	9wd	36173c	1
36562'		36570c	6d	36566'		36178'	
36572c	3d			36574.5c	10d	36187'	
36583'				36584'		36195c	10
36592	2d			36594.0	8wd	36205'	
36599'				36607	8wd	36219'	
36606c	1d						
36614'		36617'				36224c	1
36630	1dM	36630	7dM	36625	9wd	36229'	
				39501	7	36245'	
				39515	6	36270c	10
				39536	9	36294'	
				39567	6	36303'	
				39580.8	7	36309c	10
				40552'		36316'	
				40566c	7d	36442'	
				40584'		36446c	1
				40844	1wd	36449'	
				40884	1wd		
						36460'	
						36475c	10
						36490'	
						36510'	
						36519c	8
						36529'	
						36577'	
						36628c	10
						36692'	

TABLE I.—*Continued.*

Gd(C₃H₇COO)₃·2H₂O				Gd(iso C₃H₇COO)₃·6H₂O			
78°		300°		78°		300°	
ν	Int.	ν	Int.	ν	Int.	ν	Int.
32066	1d	32069	5vd	32041	1wd		
32079	3d	32080	5vd	32069	1wd		
32092	2d	32090	5vd	32089	1d	Too faint	
32103	2d	32103	5vd	32124	0d	to	
32662	2d	32661	5wd	32139	0d	measure	
32678	3d	32678	5wd	32650	1wd		
32697	3d	32691	5wd	32672	1wd		
35789	5d	35788	4d	32703	1wd		
35809	2d	35813	1vd	32768	0d		
35820	2d	35824	1vd	35757	2d	35757	1d
35842	3d	35841	2d	35777	0d	35788	0d
36137′		36144	8dD?	35801	1d	35802	0d
36144c	8d			35830	1d	35820	0d
36152′		36158	2d	35856	0d		
36160	3d			35869	0d		
36171	4wd	36170	3d	36110	2dM	36111	1d
36186	5wd	36181	4d	36126	2wd	36123	1d
36203′		36207	6wvd M?	36169	2wd		
36219c	8d	36219	4d	36181′		36192	2d
36233′		36228	10w	36203c	2d	36213	2d
				36224′			
36244	7wd	36241	9w	36245	0wd	36247	1d
36414′		36417′		36259	0wd		
36423c	8d	36424c	10d	36272	2wd	36272	1d
36432′		36431′		36379′		36390	1d
36443	3d	36442	3d	36398c	2d	36399′	
36452	2d	36450	1d	36418′		36407c	1wd
36464	4wd	36460	5d			36414′	
36528′		36528′		36431′		36438′	
36544c	6d	36543c	7d	36442c	1d	36443c	2wd
36559′		36558′		36451′		36450′	
36564′		36567′		36468	1d	36468	0d
		36575c	10d	36490′		36536	1wd
36584c	6d	36583′		36548c	1d	36554′	
		36590′				36562c	1d
		36596c	8d			36570′	
36606′		36602′				36590′	
36613	1d	36625	7w	36606′		36598c	1d
36621′		39501	2d	36626	0wd	36607′	
36627c	5d	39515	2d	36661	1d	36627	1d
36634′		39534	2d			36658	1d
		39564	2d				
		39580	2d				
		40561′					
		40567c	7vd				
		40575′					

Gd(CH₃COO)₃·4H₂O				Gd(CCl₃COO)₃·3H₂O			
78°		300°		78°		300°	
ν	Int.	ν	Int.	ν	Int.	ν	Int.
32059.8	10	32062.5	7	32077	0wd		
32070.9	10	32073.6	7	32088	0d		
32087.4	10	32087.9	7	32096	2d	32093	0d
32099.7	10	32098.2	7	32106′			
32643.9	10	32648.7	7	32112c	1d	32115	0d
32673.2	10	32673.6	7	32118′			
32698.4	10	32696.1	7	32124	0d		
35788.3	8	35792.0	8	32135	1d	32134	0d
35810.4	3	35813.4	3	32147	1d		
35824.4	8	35826.7	8	32152	1d		
35839.3	4	35840.5	4	32671	2d	32683	0d
36139.6	10	36143.4	10	32699	2d	32699	0d
36148.0	10	36151.1	10	32738	1d	32721	0d
36160.7	7	36162.8	7	35773	0d		
36171.8	9	36174.9	9	35797	1d		
36183.8	8	36185.0	7	35805	1d	35802′	
36205.5	7	36208.0	8	35812	4d	35810c	3d
36209.4	7	36212.2	8	35818	3d	35819′	
36215.2	7D	36217.3	8M	35828	1d	35837′	

TABLE I.—*Continued.*

Gd(CH₃COO)₃·4H₂O				Gd(CCl₃COO)₃·3H₂O			
78°		300°		78°		300°	
ν	Int.	ν	Int.	ν	Int.	ν	Int.
36220.0	7			35833	1d	35842'	3d
36223.7	7	36223.0	8	35842	4wd	35846'	
36228.8	7	36230.7	8	35868	1d		
36233.9	8	36237.4	8D	36133	1d		
36238.9	8			36148	3d	36148'	
36415.8	10w			36157	3wd	36153c	4d
36425.5	10w	36419.9	10wd	36165	3wd	36160'	
36432.3	10w	36431.7	10D	36173	3wd	36173	3wd
36440.9	10	36443.3	8	36182	1d		
36454.3	10	36456.6	9	36188	1d		
36464.2	10	36465.0	9d	36195	6wd.	36192	3wd
36536.1	10D?	36539.4	8wD?	36208	1d		
36546.8	10D?	36549.9	8wD?	36212	1d		
36554.2	10	36559.0	8	36215'		36220'	
36566.4	10	36565.6'		36240c	6d	36241c	5d
36569.7'				36263'		36262'	
36582.8c	9	36582.2c	10	36407	1d		
36596.4'		36597.8'		36422	4wd	36420'	
36604.9	8	36605.5	8	36432'			
36616.7	8w			36440c	6d	36441c	3d
36623.1	8w	36620.8	10D	36448'			
39504.9	10w	39507.0	8	36458	6wd	36462'	
39517.3	10w	39518.2	8	36467	0d	36474'	
39538.4	10w	39538.2	8	36478	3wd	36486c	1d
39561.3	10w	39562.3	7d	36496	1wd	36496'	
39590.2	10w	39589.6	7d	36535	4d	36535'	
40468	3D	40562'		36544'			
40573	3	40573c	5d	36587c	5d	36595c	4d
		40580'		36630'			
40848	1wd	40851	3wd	36638	3d		
40874	1wd	40877	3wd	36646	3d		
40895	1wd	40898	3wd	36654	3d	36655'	
				36659	3d		

Gd(COOH)₃				Gd(BrO₃)₃·9H₂O			
78°		300°		78°		300°	
ν	Int.	ν	Int.	ν	Int.	ν	Int.
32108.6	4	32106.4	7	32126.1	10	32132.2	5
32121.6	4	32119.7	4	32140.1	10	32145.7	6
32133.9	5	32133.5	8	32146.0	7	32152.6	8
32704.3	4	32702.6	5	32153.7	6	32157.3	8
32725.0	5	32723.1	6	32702.4	8	32708.7	8
35841.4	4	35843.3	3	32743.9	8	32749.1	7
35858.9	3	35861.3	3	32757.8	9	32761.0	7
35873.7	6	35873.0	4	35878.8	10D	35883.7	10
36186.3	4	36187.5	4	35888.2	4	35892	2
36200.1	3	36203.0	4	35898.8	6	35899.8	3
36215.7	7wD?	36216.2	6wdD?	36222.3'		36227.8	6
36259.0	6w	36261.1	7	36229.3c	10	36232.1	10
36264.7	1			36236.6'		36237.1	6
36269.3	1	36270.3	1	36244.2	6	36246.8	4
36278.6	4	36279.0	5	36284.4'		36290.2	7
36282.9	4	36283.0	5	36292.5c	5	36296.6	8
36463.0	3	36465.2	4	36300.4'		36300.2	7
36472.5	4	36475.9	5	36306.4	5	36305.9	5
36491.3	5w	36492.0	6wD?	36498'			
36500.2	1w	36500.7	1	36505c	3	36502	6
36583.7	4	36587.3	6	36511'		36511	7D?
36601.0	2	36603.5	3	36516	2	36519	7D?
36609.4	7D	36611.8	8M	36526	2	36527	3
36625.6	3	36627.5	6	36612'		36619'	
36643.8	7D	36645.4	8D	36621c	1	36627c	5
36653.6	1			36630'		36635'	
36656.8	1			36640	1M	36643	3D?
				36650'		36655	2
				36667c	1	36660'	
				36685'		36666c	3
						36672'	
						36681	1D?

TABLE I.—*Continued.*

Gd(BrO₃)₃·9H₂O 20°		Gd(C₂H₅SO₄)₃·9H₂O 20°					
ν	Int.	ν	Int.	ν	Int.	ν	Int.
32119.6	3	32135.3	1	35900.7	3	36516.5	5
32128.0	4	32153.2	3	36216.1	8	36519.8	5
32137.9	6	32163.0	8	36229.0	10	36528.5	4
32145.1	4	32714	0	36236.4	5	36608.8	7
32151.5	1	32727.2	4	36238.8	5	36618.9	7
32155.4	3	32758.5	4	36249.3	4	36628.2	7 *M*
32702.8	6	32761.0	4	36291.7	10*wD?*	36641.5	7
32743.4	4	35873.9	4	36297.4	9	36646.9	8*wD?*
32758.5	4	35881.0	4	36491.0	8	36657.5	7
		35897.4	3	36508.2	10*wD?*	36668	6*wD?*
						36671.9	6
						36679.7	6
						36682.9	5

2500A multiplets

The lines of the chloride and sulfate are almost identical in spacing, spread, intensity and width, while the lines of the propionate and butyrate, though fuzzy, are nevertheless far sharper than the lines at 2700 and 3100A. The multiplet spread in the propionate and butyrate spectra is the same as that of the acetate—about three-fourths that of the chloride. The acetate lines are wider and more blurred than the lines of the chloride. Numerous attempts to obtain absorption bands in this region from gadolinium ethylsulfate have resulted in finding a single weak, wide, blurred line, which appears at 300° at 2458A.

Table I presents new data on the positions and intensities of the absorption lines and bands in the spectra of the various gadolinium compounds discussed, while in Figs. 1, 2 and 3, a number of the spectra are reproduced.

DISCUSSION

While the normal state of the Gd⁺⁺⁺ ion in crystals is indubitably the virtually unperturbed $^8S_{7/2}$ term[10] the nature of the excited states is not known. They may arise through transitions in which all the $4f$ electrons remain within the completed $5s$, $5p$ shells. In other words all the electrons are $4f$ electrons both in the initial and final states, and in any transitions between the states there is violation of Laporte's rule ($\Delta\Sigma l = 0$) which holds rather rigorously for dipole radiation by gaseous atoms. The rule can be violated if the atoms are strongly perturbed by an electric field not possessing a center of symmetry. Violation in the case of Gd⁺⁺⁺ is unlikely because in a number of its salts, whose spectra have all the multiplets we are considering, there is definitely octahedral arrangement of the atoms closest to the Gd⁺⁺⁺ ion, and with such an arrangement

[10] W. F. Giauque, J. Am. Chem. Soc. **49**, 1870 (1927).

there is associated a cubic, centro-symmetric field.[11] By Pauli's principle the only octet term permitted Gd⁺⁺⁺, with its seven $4f$ electrons half completing the $4f$ shell, is the lowest one, $^8S_{7/2}$. All transitions involving only $4f$ electrons then require reversal of one or more of the electron spins. The possible terms resulting from such intercombination transitions are again limited by Pauli's principle to ^6P, ^6D, ^6F, ^6G, ^6H, ^6I, a larger number of quartets and a still larger
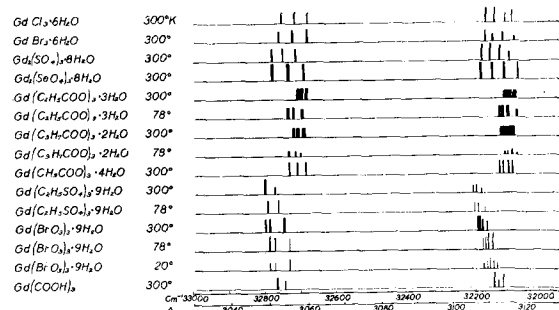

FIG. 1. The 3100A multiplets of the absorption spectra of gadolinium compounds.
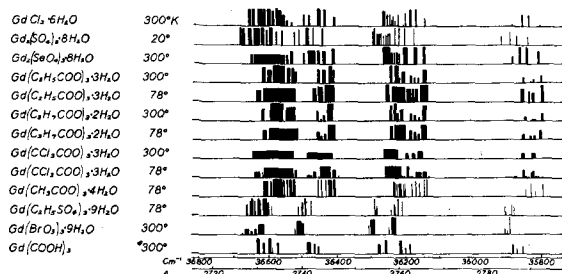

FIG. 2. The 2700A multiplets of the absorption spectra of gadolinium compounds.

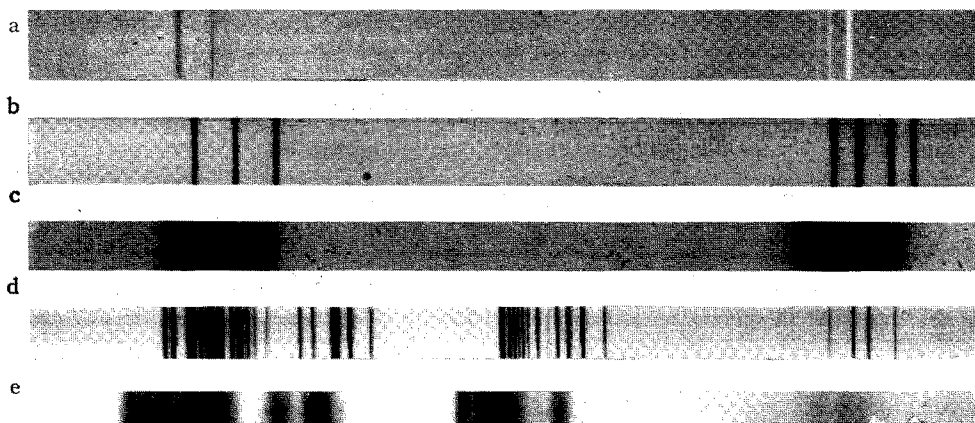[11] Phys. Rev. **50**, 574 (1936).

FIG. 3. Photographs of the spectra of gadolinium compounds. (a) Absorption and selective reflection in the 3000A multiplets of gadolinium ethylsulfate; (b) and (c) the 3000A multiplets of gadolinium chloride hexahydrate crystals and solution, respectively; (d) and (e) the 2700A multiplets of gadolinium chloride hexahydrate crystals and solution.

number of doublets. If the absorption multiplets of Gd^{+++} may be assigned to the jumps $^8S \rightarrow {}^6P$, $^8S \rightarrow {}^6D$, etc. (with the multiplet fine structure determined for the most part by the manner of crystal splitting of the upper state) then to account for the entire number of well-separated multiplets one must probably concede the likelihood of the breakdown of the selection rule $\Delta L = \pm 1$, or the reversal of two or three spins, producing octet-quartet and octet-doublet transitions, or both. Absorption in the principal multiplets is of comparable intensity and if one assumes octet-quartet jumps to explain their number one must make the unattractive premise that the frequency of occurrence of octet-sextet and octet-quartet transitions is about the same. To sum up, dipole radiation by Gd^{+++} requires violation of the three selection rules $\Delta \Sigma l = 0$, $\Delta S = 0$, $\Delta L = \pm 1$, and therefore is improbable. In quadrupole radiation the selections rules for $\Delta \Sigma l$, ΔS and ΔL are different, but the intensity of radiation is weak, perhaps too weak to account for the observed absorption by rare earth ions in crystals.

The upper states of Gd^{+++} may also arise from electron configurations in which one $4f$ electron has jumped through the complete shells to the $5d$, $5f$, $5g$ or higher orbits. The supposition often made that all the states outside $5s$, $5p$ are necessarily diffuse seems unwarranted. Sharp line spectra of a number of chromium and manganese salts have been observed.[12] The spectra arise from jumps of $3d$ electrons, which are outside completed shells and are presumably exposed to forces very similar to those acting on a $5d$ electron of a rare earth ion. Since sharp quantization is possible in both the upper and lower states of Cr^{+++} and Mn^{++}, it is reasonable that it should be possible also in the upper state of a rare earth ion, which may be closely analogous to the lower state of Cr^{+++} and Mn^{++}.

Magnetic evidence at present favors the idea that the transitions in Gd^{+++} are of the type $4f \rightarrow 5x$ for the g factors of the upper states are all either 0 or 2, again resembling Cr^{+++} and indicating that only the electron's spin moment orients in a magnetic field.[13] It is difficult to understand how the g is 0 or 2 for all the upper states if they originate in a $4f$ configuration, because the upper states should then be shielded to about the same extent as the normal state and should express their individualities by showing a

[12] F. H. Spedding and G. C. Nutting, J. Chem. Phys. 2, 421 (1934), and unpublished data; J. Gielessen, Ann. d. Physik 22, 537 (1935).

[13] In continuing the magnetic researches reported in the preliminary paper (F. H. Spedding, J. Chem. Phys. 1, 144 (1933)) we have greatly improved the experimental technique so that polarized spectra could be studied. We have found that with a light path parallel to any principal axis the g factor of the upper state is either 2 or 0 (usually 2). While the second-order Zeeman effect is small in monoclinic crystals, it is fairly large in the hexagonal ones. Thus gadolinium salts behave like chromium salts (F. H. Spedding and G. C. Nutting, J. Chem. Phys. 3, 369 (1935)) in that the orbital moments are not so tightly frozen if the crystals have a hexagonal axis of symmetry.

wide variety of g values. However, the g's of the sextet states are presumably very different from those calculated by Landé's equation for pure L–S coupling since the multiplets are very narrow. Ideally the multiplet width of the sextet terms of gadolinium would be zero since the 4f shell is just half completed.

We feel that at present the evidence for the various proposals as to the nature of the absorption process is inconclusive, with some points supporting the view that absorption is to be attributed to quadrupole radiation involving only 4f electrons, while others suggest jumps outside the 5p orbit. It appears highly probable from the experimental results which we have presented that all the lines of the multiplets of the inorganic salts and most of the lines of the organic salts arise from a crystal Stark splitting of lines in the spectrum of gaseous Gd^{+++} ion. If they originate in the superposition of intramolecular or lattice frequencies on electronic frequencies, one would expect some correlation between the masses of the ions and molecules associated with the gadolinium ions and the separations in the gadolinium absorption spectrum, yet none is observed. All the compounds which we have studied are either highly hydrated or else contain carboxyl groups, so it is likely that each gadolinium ion in the crystals has as its nearest neighbors a group of oxygen atoms. It may be argued that the presence of a shell of oxygen atoms would tend to mask the mass effect, but it should be pointed out that the oxygen atoms themselves are joined to various other atoms and that in some compounds this coupling is known from chemical evidence to be stronger, even, than the gadolinium—oxygen binding.

If the separations of the multiplet lines are identified with vibrations somewhere in the lattice most of the vibrational energies are of the order of a few tens of wave numbers. Harmonics and constant frequency differences between lines of different multiplets might well be expected (but are not found) and there should almost certainly be notable intensity changes with changing temperature. New absorption lines corresponding to jumps from higher and higher vibrational states should appear as the temperature is raised and the population of molecular

groups in the higher states increases, but none are observed within the range 20° to 300°.

We have not yet been able to account satisfactorily for the excessive diffuseness of the spectra of all but the simplest of the organic compounds of gadolinium. Crystals of the substances are soft but are usually perfectly formed, and show no very obvious indication of possessing a vitreous or semivitreous structure. If they were glass-like the randomness of the atomic arrangement would presumably be expressed in the unusual breadth and lack of sharpness of the absorption lines of the rare earth ion. Diffuseness of the lines of a perfect crystal of a salt such as gadolinium butyrate would result if, as a result of oscillation or rotation somewhere in the alkyl group, the carboxyl oxygens which join the alkyl group to the gadolinium atom undergo a small, periodic displacement. The magnitude of the displacement would be much greater than that experienced by the oxygen of the water molecules in contact with the metal ion in highly solvated $GdCl_3 \cdot 6H_2O$, for example. We have shown that the fuzziness of the absorption of gadolinium propionate and butyrate persist in large measure even to temperatures as low as 20°K, so that if its origin is in motion of some part of the alkyl radical the energy producing that motion cannot be thermal. It might, however, be abstracted from the ultraviolet continuum with which the crystals were illuminated. None of the lower members of the series of fatty acids absorb in the region of the principal bands of gadolinium but all show absorption below 2500A. The intensity of absorption is greater in propionic and butyric than in formic and acetic acids. The principal part of the light energy absorbed probably goes to excite electrons of carbon, but associated with the electron jumps may be vibration of carbon against carbon, carbon against hydrogen, and so on. In a series of experiments lately completed we have photographed the absorption spectrum of perfect crystals of $Gd(C_2H_5COO)_3 \cdot 3H_2O$ using as source of light regions about 100A broad selected from the hydrogen continuum by means of a quartz monochromator. The temperature of the crystals was about 25°C. The line groups between 2700 and 2800A and at 3050 and 3100A were observed yet there was no sharpening of the lines over that

previously recorded when the light incident on the crystals contained all wave-lengths transmitted by quartz. When a Wollaston prism was placed between the crystal and the spectrograph, the lines were slightly sharper than before.

It has been known for a long time from Werner's work on complex salts and from transference experiments that the coordinated water molecules in the first shell about an ion in solution are probably fixed in number and position with respect to the central ion. Fig. 3, which shows spectra of a crystal and a solution of gadolinium chloride, gives further confirmation of this. The fact that in dilute solutions the multiplets are resolved into lines indicates that a field of definite symmetry is acting on the central ion. This means that the water molecules in the first shell about the central ion must be fixed in number and approximately in position, for if they were not and a condition of randomness existed, some atoms would have one type of splitting, other atoms another and the net result would be a blurred band, instead of discrete lines.

That the general order in solution is not as perfect as in solids is demonstrated by the fact that the lines are from two to seven times as broad as the corresponding lines in the solid crystalline salts which were used in preparing the solutions. The field about the ion in dilute solution is almost certainly determined by the closest water molecules, which probably are situated at the corners of an octahedron. This octahedron for a given atom is distorted more or less depending on the position of the water molecules in the second shell, and that considerable variation in distortion is present can be seen from the great width of the lines. Most of the distortion is probably due to the lack of order in the outer shells of the water envelope but some of it is undoubtedly due to thermal motion. At present we have no way of separating these factors.

It is interesting to note that the solution spectrum resembles the monoclinic type of crystal spectrum more than it does the hexagonal. Furthermore, in solution the negative ion does not approach very close to the gadolinium ion, since we could detect no deviation from Beer's law even for saturated solutions of the very soluble gadolinium chloride.

Carbon Dioxide. The Heat Capacity and Vapor Pressure of the Solid. The Heat of Sublimation. Thermodynamic and Spectroscopic Values of the Entropy

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An apparatus for low temperature calorimetric and vapor pressure measurements on condensed gases is described. The heat capacity of solid carbon dioxide has been measured from 15 to 195°K. The heat of vaporization at the sublimation point, 194.67°K, was found to be 6030 cal./mole. The vapor pressure has been measured and the observations are closely represented by the equation: Solid carbon dioxide, $154-196°K$; $\log_{10} P(\text{int. cm Hg}) = -(1354.210/T) + 8.69903 + 0.0015880T - 4.5107 \times 10^{-6}T^2$. The entropy of carbon dioxide gas has been calculated from the calorimetric data and the third law of thermodynamics to be 51.11 cal./deg. per mole at 298.1°K. This value is in excellent agreement with the value 51.07 cal./deg. per mole obtained from band spectrum data.

BECAUSE of the importance of carbon dioxide, it seems desirable that its thermodynamic properties should be investigated as accurately as possible. The fact that its band spectrum has been measured and very satisfactorily interpreted by several investigators offers an unusually good opportunity to compare the entropy obtained from the third law of thermodynamics with that obtained with the assistance of the spectroscopic data. The molecule is known to be of the linear symmetrical type. Thus there should be no possibility of encountering false equilibrium of the end for end random orientation type such as occurs in solid carbon monoxide, nitric oxide and nitrous oxide. Kelley[1] has shown that the available low

[1] Kelley, Bureau of Mines Bulletin, (a) **350**, 20 (1932); (b) **383**, 35 (1935).