The Effect of Crystal Symmetry and Chemical Composition on the Energy Levels of Solids

By F. H. Spedding[1] and G. C. Nutting

In the past few years energy level diagrams have been constructed for most of the gaseous atoms and the more simple gaseous molecules and many relations have been established between the physical and chemical properties of the substances investigated and their energy levels.

As a large part of chemistry deals with solids and solutions it would be very desirable to extend these relations so as to apply to them. Unfortunately, however, very little at present is known about energy levels in solids.

So far the two most promising methods of attack on this problem have been by means of the double crystal x-ray spectrograph and the Raman effect. Both these methods have serious disadvantages. The former deals with spectra in the x-ray region where the energies involved are very large and differences due to chemical causes are hard to measure with any great accuracy as they are only a small percentage of the total energies concerned. In the part of the spectrum ordinarily investigated 15,000 calories correspond to a shift of only 0.1 to 0.01 x-units or about 0.0001 to 0.00001 of the total energies involved. On the other hand, while the Raman effect is free from this objection, it gives only a few lines at most and an energy level diagram without additional help is out of the question.

Another method of investigation[2] which gives great promise but which so far has not produced many quantitative results is the study of the absorption spectra of solids and solutions or glasses particularly at low temperatures. This method is free from the objections raised but unfortunately most of the lines arising from the energy levels are blurred into broad diffuse bands in most of the solids and solutions investigated due to the temperature agitation. The energy levels are non-degenerate due to the electric fields of the neighboring atoms or ions and the amount these levels are split apart depends on the strength of the fields, which at room temperatures are fluctuating very rapidly as the nearby atoms approach and recede from the atoms in question. Since the photographic plate indicates the differences between sets of levels over an interval of time the net effect is the blurred bands observed.

It is probably true also that many of the higher excited states in the free atom tend to become unstable upon the close approach of another atom

(1) National Research Fellow in Chemistry.

(2) This subject has received a great deal of attention but usually with the emphasis on other phases than the energy levels. A few investigators who have done considerable work in the field are J. Becquerel, *Leiden Communications;* R. Brunetti, *Il Nuovo Cimento;* P. F. Ephrain, *Berichte;* Jones and Strong, *Carnegie Pub.;* Freed and Spedding, *Physical Review.*

and an electron which ordinarily would jump to a well-defined level giving rise to a sharp line will move into the unstable region and a continuum will result.   This is not true for all states so by cooling the solids or glasses to very low temperatures it is possible to resolve into sharp lines the bands from a large number of compounds.

The absorption spectra of the rare earths offer the most encouraging points of attack upon the problem of the energy levels of solids.   The reason for this becomes evident upon examination of their electronic structures.

	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p
La^{+++}	2	2	6	2	6	10	2	6	10	..	2	6
Ce^{+++}	2	2	6	2	6	10	2	6	10	1	2	6
Pr^{+++}	2	2	6	2	6	10	2	6	10	2	2	6
Gd^{+++}	2	2	6	2	6	10	2	6	10	7	2	6
Lu^{+++}	2	2	6	2	6	10	2	6	10	14	2	6

It is seen that the "active"[3] electrons are in the 4f shell and that they are partially shielded from the effects of the neighboring atoms by the completed 5s and 5p shells.   These electrons, then, are not nearly so much disturbed as are the active electrons in iron or chromium, where they are not so shielded.

One might expect that the energy levels in a solid would be intermediate in type between those of a gaseous atom and those of a gaseous molecule. To a first approximation, in a gaseous atom the electric field is spherically symmetrical about the nucleus.   In a diatomic molecule it is cylindrically symmetrical around the line joining the nuclei.   In a polyatomic molecule the symmetry varies widely, but it is apt to be very low.[4,5]

Because of the regularity of the crystal lattice the electric symmetry in a solid is probably higher and in the case of the cubic lattice the levels are much more likely to be similar to atomic than molecular levels.   It is to be expected that the fields are of various strengths, some of which make the atomic levels non-degenerate as would weak Stark fields, while others destroy the coupling between the electrons and correspond to strong Stark fields.[6]

The basic levels of the rare earths are atomic, for Hund[7] has shown that the measured magnetic susceptibilities of the rare earth ions in the solid state are those to be anticipated if the lowest levels in the solid and the gas

(3) An "active" electron is one which is excited by the light absorbed. The electrons in the completed shells are firmly coupled to give a ^1S term in which the resultant orbital and spin moments are zero. A considerable amount of energy is required to break this coupling.

(4) The effect of the electric fields is to make the atomic levels non-degenerate, just as an externally applied electric field produces Stark splitting. When the field is weak it couples with the j of an atomic term, thus splitting the level into a number of components. When it becomes strong it breaks down the coupling between spin and orbital moments themselves. In fields of the higher degrees of symmetry there is partial balancing of forces which tends to diminish the splitting.

(5) Robert S. Mulliken gives an excellent account of this effect in his "Interpretation of Band Spectra," *Rev. Modern Phys.*, **4**, 1 (1932).

(6) This effect has been discussed by H. Bethe, *Ann. Physik*, **3**, 133 (1929), from the standpoint of wave mechauics and group theory.

(7) Hund, *Z. Physik*, **33**, 855 (1926).

are the same. The rare earths offer the further advantage that they give an unusually large number of lines in the photographic region of the spectrum. This is probably due to the fact that while the orbits just outside the completed shells are greatly influenced by the neighboring atoms, they are less influenced than those orbits further out, and electronic states arising from them will have more of their levels potentially stable. Thus in the rare earths electronic transitions occur to levels which in other atoms would correspond to the basic levels.[8]

It is possible also that in strong electric fields of the crystal quadripole radiation may be permitted and jumps take place by a recoupling of the 4f electrons.

This is the first of a series of papers on a systematic investigation of the energy levels of solids and gives in detail the results reported briefly in a letter to the *Physical Review* of December 15, 1931.

Experimental

Gadolinium salts are the most desirable for this sort of work. Gd^{+++} ion gives sharp lines at room temperature; it shows the simplest absorption spectra of all the rare earth ions, its lines and multiplets being well separated from one another, and its basic level $^8S_{7/2}$ is known to be single. Its chief disadvantage is that most of its lines occur in the ultraviolet. The gadolinium material used was from two sources. One, of almost atomic weight purity, was furnished us by Professor B. S. Hopkins of the University of Illinois. The other was from the Welsbach Company and contained about 1% Tb and 0.5% Sm.

Crystallographic measurements were made for us by Professor Adolph Pabst of the Mineralogy Department of the University of California and we wish to express our thanks for this assistance.

$GdCl_3·6H_2O$.—The spectrum of gadolinium chloride has been reported elsewhere.[9] The crystals belong to the normal class of the monoclinic system,[10] although Benedicks[11] has classified them as tetragonal. The constants are $a:b:c = 1.4725:1:1.2185$; $\beta = 86°20'$. The frequencies of the lines of seven of the most intense multiplets are given in Table I. Spectra from crystals prepared from both sources of gadolinium were photographed and the positions of the lines were found to be identical.

$GdBr_3·6H_2O$.—The spectrum of this compound has also been described elsewhere.[12] The crystals are of the normal class of the monoclinic system. They have a notably

(8) Freed [*Phys. Rev.*, **38**, 2122 (1931)] photographed the spectra of Ce^{+++} compounds and found only broad, diffuse bands in the ultraviolet. He reasoned that as Ce^{+++} ion has only one 4f electron it must jump to the outside orbits in giving rise to these bands, and as they are diffuse all such jumps must be of this type. He attributed them to a 4f-5d jump. This, however, does not seem reasonable, for as Gibbs and White [*Phys. Rev.*, **33**, 157 (1929)] have shown, if one plots the known gaseous energy levels of the isoelectric sequence Cs I, Ba II, La III and Ce IV, the curves are lines of small curvature which cross, and while the 6s orbit is lowest in Cs I, the 5d is probably so in Ce IV. From magnetic researches in solids it is known that for La III the 5d level is lowest, while for Ce IV (Ce^{+++}) it is the 4f. Between these two elements the curves must cross and unless they do so at a steep angle, which is not known to occur in any other case, the 4f-5d jump should be found in the far infra-red. The diffuse bands in the ultraviolet are probably due to electronic jumps to higher orbits which are slightly unstable.

(9) Freed and Spedding. *Phys. Rev.*, **34**, 945 (1929).

(10) Adolf Pabst, *Am. J. Sci.*, **22**, 426 (1931).

(11) Benedicks, *Z. anorg. Chem.*, **22**, 403 (1900).

(12) Freed and Spedding, THIS JOURNAL, **52**, 3747 (1930).

different habit from the chloride crystals, but the axial ratios for the two are almost identical.[10] Because of its extreme deliquescence, only rough measurements were made.

$Gd_2(SO_4)_3 \cdot 8H_2O$.—On account of its small solubility, no large crystals were grown. Instead we have used conglomerates of small crystals fixed to quartz plates by means of a lacquer of pyroxylin dissolved in amyl acetate. The crystals are monoclinic, and although we have made no accurate measurements to confirm them, the data given in Groth, "Chemische Krystallographie" certainly cannot be far from correct By a re-orientation of $Gd_2(SO_4)_3$ $8H_2O$ crystals so that 101 becomes 001, 111 becomes 011 and 100 becomes 101, the new axial elements $83°26^1/_2'$ $a:b:c$ $1.4250:1:1.2224$, may be obtained.

$$a:b:c = 3.0086:1:2.0068 \quad \beta = 118°2'$$

$Gd(C_2H_5SO_4)_3 \cdot 9H_2O$.—The salt was prepared by double decomposition between equivalent quantities of barium ethyl sulfate and gadolinium sulfate and was twice crystallized from solution in conductivity water. The crystals are hexagonal, showing the forms $(1\,0\,\bar{1}\,0)$ $(1\,1\,\bar{2}\,0)$ $(1\,0\,\bar{1}\,1)$ and $(1\,1\,\bar{2}\,1)$. They probably belong to the normal class. The ratio $c:a$ was found to be 0.5075, although Benedicks has stated that it is 0.5014.
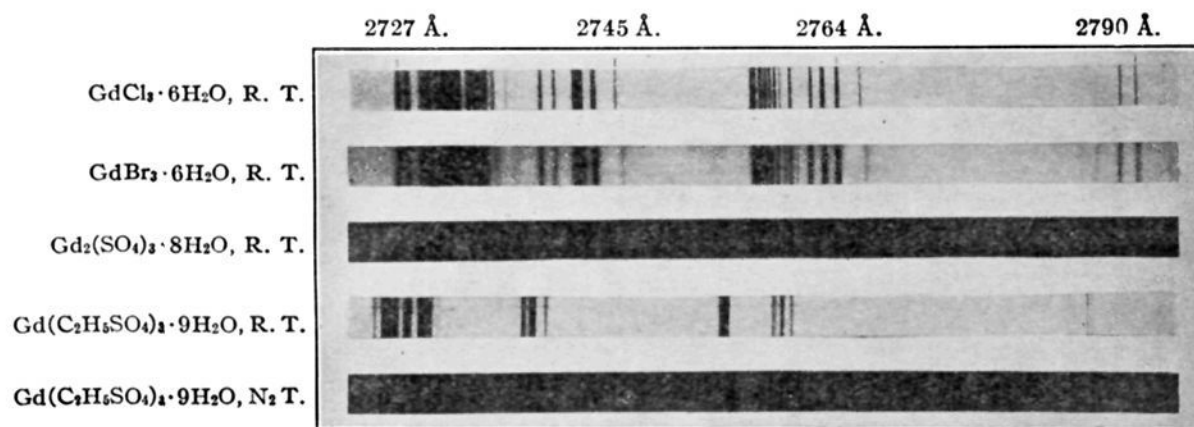

| | 2727 Å. | 2745 Å. | 2764 Å. | 2790 Å. |
GdCl₃·6H₂O, R. T. ... GdBr₃·6H₂O, R. T. ... Gd₂(SO₄)₃·8H₂O, R. T. ... Gd(C₂H₅SO₄)₃·9H₂O, R. T. ... Gd(C₂H₅SO₄)₃·9H₂O, N₂ T.

Fig. 1.

$Gd(BrO_3)_3 \cdot 9H_2O$.—A very dilute solution of $Gd_2(SO_4)_3 \cdot 8H_2O$ was added with vigorous stirring to an aqueous suspension of $Ba(BrO_3)_2 \cdot H_2O$. The mixture was kept on a steam-bath for several hours and then filtered. $Gd(BrO_3)_3 \cdot 9H_2O$ crystallized from the filtrate was obtained as large crystals on slow evaporation of a solution in conductivity water. The crystals belong to the hexagonal system, and probably to the normal class, although the possibility of pseudo-symmetry exists. Since the bromate ion begins to absorb near 3000 Å., only two multiplets were observed.

$Gd(NO_3)_3 \cdot 6H_2O$.—Gd_2O_3 prepared from the oxalate was dissolved in 3 N nitric acid and the excess acid removed by boiling. The salt was crystallized from a conductivity water solution. The crystals are triclinic with $a:b:c = 0.5571:1:0.7615$; $\alpha = 90°6'$, $\beta = 109°55'$; $\gamma = 109°48'$.

A Hilger E 185 spectrograph was used in all the work. The dispersion in the photographs of the bromate, bromide and chloride was about 3.0 Å. per mm. at 3000 Å. and 2.0 Å. per mm. at 2700 Å. The spectra of the sulfate and ethyl sulfate were photographed with an additional prism in the train and the dispersion was increased to 1.95 Å. per mm. at 3000 Å. and 1.35 Å. per mm. at 2700 Å.

Discussion of Results

In a previous letter[13] experimental evidence was presented which showed

(13) Spedding, Phys. Rev., 38, 2080 (1931).

TABLE I
POSITIONS OF THE ABSORPTION LINES

GdCl₃·6H₂O, R. T.ᵃ Å	GdCl₃·6H₂O, R. T.ᵃ cm⁻¹	GdBr₃·6H₂O, R. T. cm⁻¹	Gd₂(SO₄)₃·8H₂O, R. T. cm⁻¹	Gd(C₂H₅SO₄)₃·9H₂O, R. T. Å	Gd(C₂H₅SO₄)₃·9H₂O, R. T. cm⁻¹	Gd(C₂H₅SO₄)₃·9H₂O, N₂ T. Å	Gd(C₂H₅SO₄)₃·9H₂O, N₂ T. cm⁻¹	Gd(BrO₃)₃·9H₂O, R. T. cm⁻¹	Gd(NO₃)₃·6H₂O, R. T. cm⁻¹
3117.04	32072.5	32061.5	.....	3110.07	32144.3	3110.96	32135.1	32132.2	32067.1
3114.87	32094.0	32095.1	.....	3108.55	32160.0	3109.21	32153.2	32145.7	32092.3
3112.14	32123.0	32123.3	.....	3107.78	32168.0	3108.26	32163.1	32152.6	32110.8
3109.86	32146.5	32146.5	.....					32157.3	32127.0
3060.54	32664.5	32656.8	.....	3053.87	32735.6	3054.64	32727.6	32708.7	
3057.08	32701.5	32698.6	.....			3051.83	32757.7	32749.1	
3053.61	32738.5	32738.7	.....	3051.32	32763.2	3051.66	32759.5	32761.0	
2792.67	35796.5	35792.3	35810.0	2786.12	35881.6	2786.81	35872.8		
2790.10	35830.5	35829.2	35840.7	2785.73	35887.7	2786.27	35879.7		
2788.70	35848.5	35850.5	35860.0	2784.40	35903.8	2784.99	35896.3		
2786.52	35876.5	35876.7	35884.0	2784.11	35907.6	2784.70	35899.9		
2765.90	36144.0	36137.1	36156.7	2759.73	36224.8	2760.40	36216.0		
2763.86	36170.5	36169.2D	36182.8	2758.85	36235.7	2759.46	36228.3		
2762.65	36186.5	36184.2D	36196.7	2758.30	36243.5	2758.89	36235.8		
2761.62	36200.0	36200.4D	36210.6	2758.07	36246.6	2758.68	36238.5		
2760.93	36209.0	36214.9	36228.7	2757.42	36255.1	2757.91	36248.6		
2759.86	36223.0	36221.1	36238.2						
2759.08	36234.5	36229.1	36244.5						
2758.53	36240.5	36236.8	36251.2			2754.81	36289.5		
				2754.11	36297.6T	2754.66	36291.4		
2758.11	36246.0	36243.3	36255.0						
						2754.49	36293.7		
2757.66	36252.0	36249.1	36259.0						
				2753.71	36304.0D	2754.26	36296.8D		
2757.20	36258.0	36255.4	36263.5						
			36271.5						
2756.59	36266.0D	36262.9D							
			36274.7						

TABLE I (*Concluded*)

GdCl₃·6H₂O, R. T.[a] Å.	cm⁻¹	GdBr₃·6H₂O, R. T. cm⁻¹	Gd₂(SO₄)₃·8H₂O, R. T. cm⁻¹	Gd(C₂H₅SO₄)₃·9H₂O, R. T. Å.	cm⁻¹	Gd(C₂H₅SO₄)₃·9H₂O, N₂ T. Å.	cm⁻¹	Gd(BrO₃)₃·9H₂O R. T. cm⁻¹	Gd(NO₃)₃·6H₂O, R. T. cm⁻¹
2745.05	36418.5	36410.7	36431.5	2738.92	36499.9	2739.59	36491.0		
2743.09	36444.5	36441.4	36457	2737.95	36512.8	2738.42	36506.6		
		36455.7	36470.5						
2741.81	36461.5D			2737.63	36517.2	2738.28	36508.5		
		36463.5	36475						
						2737.70	36516.2		
2739.85	36487.5	36486.5	36497	2737.05	36524.9				
						2737.49	36519.0		
2738.69	36503.0	36502.1	36509	2736.35	36534.3	2736.84	36527.8		
2737.12	36524.0								
2735.80	36541.5	36528.8	.....						
2734.68	36556.5	36550.9	36552.5						
2734.12	36564.0D	36561.2	36568.5	2730.04	36618.4	2730.81	36608.4		
.....	.....	36570.3D	36580	2729.39	36627.4	2730.05	36618.6		
2732.70	36583.0	36580.7	36585			2729.5	36626.0D		
				2728.76	36635.8T				
2731.73	36595.0D	36593.1	36594.7			2729.09	36631.4		
		36603.5	36604	2727.73	36649.6	2728.36	36641.2		
2730.8	36608 T			2727.43	36653.7	2727.99	36646.3D		
		36609.0	36608.5	2726.62	36664.7	2727.18	36657.1		
2730.09	36618.0	36616.8	36618	2725.98	36673.2	2726.57	36665.3D		
			36624.3	2725.56	36678.9	2726.11	36671.5		
2729.27	36629.0	26623.8							
			36626			2725.50	36679.7		
				2724.84	36688.7D				
2728.64	36637.5	36631.6	36640.5			2725.26	36682.9		
2727.48	36653.0	36649.3	36658.9						
2726.85	36661.5	36659.8	36667.5						

[a] R. T. signifies room temperature; N₂ T., liquid nitrogen temperature. D indicates a double line; T, a triple line.

TABLE II

SEPARATIONS OF THE LINES IN THE MULTIPLETS[14]

| | Hexagonal | | | Monoclinic | | | | Triclinic | |
| | Gd(C₂H₅SO₄)₃·9H₂O $\Delta\nu$ (cm.$^{-1}$) | | Gd(BrO₃)₃·9H₂O $\Delta\nu$ (cm.$^{-1}$) | GdCl₃·6H₂O $\Delta\nu$ (cm.$^{-1}$) | | GdBr₃·6H₂O $\Delta\nu$ (cm.$^{-1}$) | | Gd₂(SO₄)₃·8H₂O $\Delta\nu$ (cm.$^{-1}$) | Gd(NO₂)₃·6H₂O $\Delta\nu$ (cm.$^{-1}$) |
Multiplet	Room temp.	Liquid nitrogen temp.	Room temp.	Room temp.	Liquid nitrogen temp.	Room temp.	Liquid nitrogen temp.	Room temp.	Room temp.
3110 Å.	15.7	18.1	13.5	21.5	26.5	33.6	36.0	Too faint	25.2
			6.9	29.0	29.0	28.2	29.5	to measure,	18.5
	8.0	9.9						but about	
			4.7	23.5	23.0	23.2	23.5	the same.	16.2
		30.1	40.4	37.0	40.0	41.8	43.0	See note	
3050 Å.	27.6							below	NO₃⁻
		1.8	11.9	37.0	40.0	40.1	42.0		Absorption
	6.1	6.9	BrO₃⁻	34.0	33.0	36.9	37.5	30.7	
2790 Å.	16.1	16.6	Absorption	18.0	20.0	21.3	22.5	19.3	
	3.8	3.6		28.0	29.0	26.2	27.5	24.0	
	10.9	12.3		26.5	28.0	32.1	26.0	26.1	
2765 Å.	7.8	7.5		16.0	17.5	15.0	19.0	13.9	
	3.1	3.7		13.5	16.0	16.2	14.5	13.9	
	8.5	10.1		9.0	15.5	14.5	17.0	18.1	
	12.9	15.6		26.0	27.0	30.7	34.5	35.5	
2740 Å.	14.4	1.9		17.0	20.0	14.3	15.0	13.5	
		7.7				7.8	6.0	4.5	
	7.7			26.0	24.5				
		2.8				23.0	25.0	22.0	
	9.4	8.8		15.5	16.6	15.6	15.0	12.0	

The multiplets at 2755 Å. and 2730 Å. are not included in this table since they are not completely resolved.

---

[14] There may be two causes for the faintness of these lines. In the first place a conglomerate of many small crystals was photographed, and since these particular lines show strong selective reflection [Spedding and Bear. *Phys. Rev*. 39, 948 1932)], there is a tendency toward masking of the absorption. In the second place, at higher temperatures where the field fluctuations become large enough to cause a Paschen–Back effect, the excited levels become partially unstable and the lines blur and fade. At −190° all but one of the lines appear as do also the faint multiplets at 2990, 3180, 3250, 3500, 3920 and 3980 Å.

that all the lines arise from a single basic level, $^8S_{7/2}$, which is almost undisturbed by the crystal fields.[15] For this reason the positions of the lines and multiplets constitute effectively an energy level diagram of the excited levels. From Table I it is seen that the negative radicals have very little effect on the number and position of the multiplets which must therefore arise from electronic transitions of the Gd^{+++} ion. On the other hand, the number of lines and their positions within the multiplets are very much dependent on the nature of the chemical compound and evidently have their origin in the forces brought into play by the atoms surrounding the Gd^{+++}. The important factor in determining the splitting of the multiplet or excited level seems to be the crystal symmetry and not the negative radical, except in so far as the negative radical influences the crystal structure. The spectrum of the monoclinic $Gd_2(SO_4)_3 \cdot 8H_2O$ is almost identical with that of the monoclinic $GdCl_3 \cdot 6H_2O$, but very different from the hexagonal $Gd(C_2H_5SO_4)_3 \cdot 9H_2O$.

TABLE III

SHIFTS OF THE POSITIONS OF THE CENTERS OF THE MULTIPLETS FROM THOSE OF $GdCl_3 \cdot 6H_2O$ AT ROOM TEMPERATURE

	Hexagonal			Monoclinic				Triclinic
	Gd(C₂H₅SO₄)₃·9H₂O Δν (cm.⁻¹)		Gd(BrO₃)₃·9H₂O Δν (cm.⁻¹)	GdBr₃·6H₂O Δν (cm⁻¹)		Gd₂(SO₄)₃·8H₂O Δν (cm.⁻¹)	GdCl₃·6H₂O Δν(cm.⁻¹)	Gd(NO₃)₃·6H₂O Δν (cm.⁻¹)
Multiplet	Room temp.	Liquid nitrogen temp.	Room temp.	Room temp.	Liquid nitrogen temp.	Room temp.	Liquid nitrogen temp.	Room temp.
3110 Å.	+48.4	+41.5	+38.0	-2.4	-7.9	....	-1.4	-9.7
3050 Å.	+52.5	+46.8	+38.1	-3.5	-8.8	....	-2.0	...
2790 Å.	+57.2	+49.2	....	-0.8	-6.2	+10.7	-3.5	...
2765 Å.	+59.1	+51.4	....	-0.8	-8.3	+13.1	-5.4	...
2755 Å.	+53.5	+47.2	....	-3.2	...	+11.5	-4.1	...
2740 Å.	+56.2	+51.0	....	-2.8	-7.7	+10.5	-2.3	...
2730 Å.	+56.8	+48.9	....	-0.7	-7.2	+10.7	-9.9	...

The symmetry and separation of the ions in the lattice determine the magnitudes and directions of the fields on the electrons of the Gd^{+++} ion and thus the amount and type of splitting of the levels. The lines are so slightly affected by the mass of the negative ions that it is unreasonable to assign their origin to vibrational effects.

While we do not wish to generalize widely from so few examples we shall nevertheless call attention to some of the regularities we have observed in the data. The spectra of the monoclinic crystals are similar, with the lines appearing at nearly the same frequencies in the several cases. The shift in position of the lines between room temperature and that of liquid nitrogen is almost as great as the shift in position of lines from compound to compound.

(15) The basic ⁸S level is only very slightly affected by the electric fields since its orbital moment is zero. As Kramers has pointed out, there should be small splitting due to second-order terms, and that this exists is clearly shown by the Zeeman patterns. In the accompanying pictures made at room temperature it can be observed only as a slight widening of the lines.

On the other hand, the spectra of the hexagonal crystals are distinctly different from those of the monoclinic, the multiplets being much narrower and shifted toward higher frequencies (Table III). The spacings are also different and in some cases fewer lines are observed.[16] Since only one band from a triclinic crystal has been measured, no conclusions can be drawn, but preliminary observations on gadolinium acetate, which is triclinic, indicate that its spectrum is different from that of both the hexagonal and monoclinic types.

These results are in qualitative agreement with predictions made by Bethe[6] on theoretical grounds. Quantitative results, however, are not to be expected as he made many simplifying assumptions which do not apply here.

Summary

Absorption spectra of gadolinium ion in crystals consist of lines which arise from electronic transitions from a single basic level $4f^7$, $^8S_{7/2}$, to excited levels which are non-degenerate through the influence of the electric fields of the neighboring ions. The amount and nature of the splitting depend upon the symmetry and separation of the ions in the lattice with higher symmetry corresponding to smaller separations of the levels.

We are continuing this work, extending the number of compounds in each crystal system and including anhydrous as well as hydrated compounds.

(16) While hexagonal crystallographic symmetry does not necessarily mean that there is hexagonal symmetry about the gadolinium ion, it is likely that the symmetry in the hexagonal crystals is much higher than that in the monoclinic.

The Recording of Pressure and Time in Gas Explosions[1]

BY BERNARD LEWIS[2] AND GUENTHER VON ELBE[3]

Numerous investigations have been made of the increase in pressure during gas explosions in closed vessels. Generally, the instrument for indicating the pressure has been a thin metal diaphragm whose deflection is measured by a suitable optical arrangement. These diaphragms are, on the whole, very satisfactory for following rapid pressure changes. As they have been used, however, they possess at least two serious disadvantages. First, the tension of the diaphragm is dependent on the strength with which it is clamped into position. This clamping strength may be