

Physics. — *Line spectrum of samarium ion in crystals and its variation with the temperature.* By SIMON FREED and J. G. HARWELL. (Communicated by Prof. W. J. DE HAAS.)

(Communicated at the meeting of September 24, 1932.)

The magnetic behaviour of Sm^{+++1}) showed that there was an equilibrium distribution of the ions between different electronic configurations and as anticipated, the absorption spectra ²⁾ consisted of lines varying in their relative intensities with changing temperature. The present work was instituted with the view of obtaining quantitative data concerning the differences in energy between the various configurations. These differences have been looked upon as originating through the action of the electric fields about Sm^{+++} in the lattice. They are a measure of their symmetry and intensity. Recently, Miss AMELIA FRANK ³⁾ obtained rough agreement with the magnetic susceptibility at higher temperatures by taking into account the presence of the activated state ${}^6H_{7/2}$, presumably about 1000 cm^{-1} higher in energy than the basic state ${}^6H_{5/2}$. The agreement is rather surprising since both the basic state, ${}^6H_{5/2}$ and activated states, ${}^6H_{7/2}$ are probably decomposed into sub-levels of wide separation by the electric fields of the lattice. The specific heat of Sm^{+++4}) at low temperature has given a measure of these separations. It appeared that energy of about 160 cm^{-1} (450 cal/mole) had to be supplied to activate a mole of Sm^{+++} . Even greater intervals may have resulted in the decomposition of the ${}^6H_{5/2}$ term but they must be so great that relatively few ions exist in the upper level.

The present work is mainly concerned with the effect of the electric fields upon the state ${}^6H_{5/2}$ that is, with levels which are sufficiently occupied at ordinary temperatures to have their presence recorded in the absorption spectrum. They are identified by the change in the relative intensity of the lines as the temperature changes, more especially by those instances when a line increases in intensity apparently at the expense of a neighbouring line. When this line is of higher frequency than the one whose intensity is decreasing, there is considerable probability that the lines arise at two levels slightly different in energy and end in a common energy level. And the recurrence of the same interval in different regions of the spectrum practically establishes the existence and separation of the lower energy levels.

¹⁾ S. FREED, Journ. Am. Chem. Soc. **52**, 2702 (1930).

²⁾ S. FREED and F. H. SPEDDING, Nature **123**, 525 (1929).

³⁾ A. FRANK, Phys. Rev. **39**, 119 (1932).

⁴⁾ J. E. AHLBERG and S. FREED, Phys. Rev. **39**, 540 (1932).

The experimental method has been described¹⁾ in another connection. A hydrogen discharge tube served as the source of the continuous radiation and the spectra extended from 4200 Å to about 2200 Å. A Hilger spectrograph of the type *E 2* was employed. The radiation was passed parallel to the optic axis of the hexagonal crystal²⁾ $\text{Sm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ which was about 0.5 mm. thick. For the purpose of lowering the temperature of the crystal, liquid hydrogen (20° K), liquid nitrogen (77° K), and liquid ethylene (169° K) were used, all boiling at atmospheric pressure. The average absolute error in the measurement of the lines is about 5 cm^{-1} . Some of the lines were faint or diffuse and there has been listed next to each line in the table, the number of times it was measured and the reproducibility of the measurement. The recorded intensities are visual estimates and should be trusted only as a measure of relative intensity within a restricted region of the spectrum and in spectra originating at the same temperature.

The groups of lines assigned to energy levels have undergone such changes in intensity that the increase or decrease in intensity of one line with respect to another could be told at a glance on an enlargement of the spectrogram.

For convenience, the groups have been numbered on the reproductions of the spectra. Below each diagram is given a list of the frequencies derived from the energy levels and these are compared with the observed frequencies for each group of lines. All the deviations are well within the errors of measurement. Groups 4, 7, 8 and 10 under low dispersion appear as doublets having the same energy difference at each temperature. Under higher dispersion, each line is found to be doubled and with the data in hand it is impossible to prove rigorously whether the "fine-structure" energy level belongs to the basic term system or not. More data, we are informed, will be available soon in a more extensive paper by SPEDDING and BEAR from Berkeley. If the "fine-structure" level is assigned to the basic multiplet, it becomes possible to include the quartet 5 and also the sextet 3 and 6. This arrangement of levels has a considerable degree of probability and by its aid all the multiplets in which marked intensity changes occur can be interrelated.

Below is a typical example of an energy level pattern which the quartets 4, 7, 8 and 10 accord with and also the basic separations which are valid for all of them. The intensities, too, agree with these assignments.

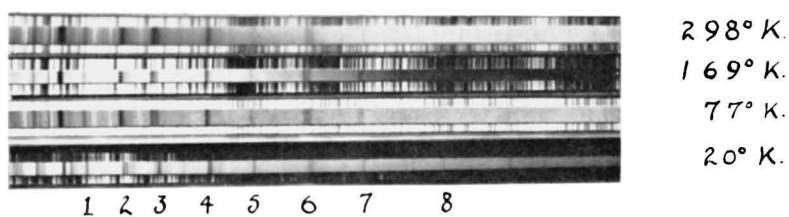
Some of the lines which one would normally expect from these levels were too faint to be measured. At higher temperatures, some of the lines were so diffuse that the average between two unresolved lines is given.

There can be no doubt concerning the existence of an interval of 60 cm^{-1} (at 20° K, 65 cm^{-1} at 77° K, and 60 cm^{-1} at 169° K) between

¹⁾ S. FREED, *Phys. Rev.* **38**, 2122 (1931).

²⁾ F. M. JAEGER, *Rec. des Trav. Chem. Pays Bas* **33**, 362 (1914).

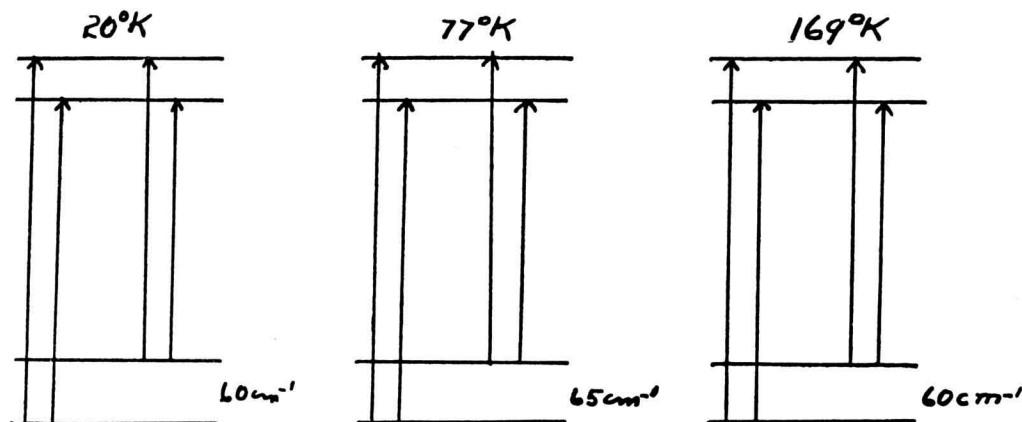
SIMON FREED AND J. G. HARWELL: LINE SPECTRUM OF SAMARIUM
ION IN CRYSTALS AND ITS VARIATION WITH THE TEMPERATURE.



Absorption Spectrum of Sm^{+++} in $\text{Sm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$.

Group	Temp. °K	Seperation of Upper Level, cm^{-1}	Calc. Line cm^{-1}	Observed Line cm^{-1}	Deviation cm^{-1}
4	20°	12		29.008 (accepted)	
			28,996	$28,996 \pm 3$	0
			28,948	$28,949 \pm 1$	1
			28,936	$28,936 \pm 1$	0
	77°	12		29,010 (accepted)	
			28,998	$28,996 \pm ?$	2
			28,945	$28,945 \pm 3$	0
			28,933	$28,936 \pm ?$	3
	169°	12		29,016 (accepted)	
			28,956	$28,955 \pm 0$	1
7	20°	12		32,721 (accepted)	
			32,708 too faint		
	77°	12		$32,723 \pm 1$ (accepted)	
			32,658	$32,655 \pm 2$	3
	169°	12		$32,728 \pm 1$ (accepted)	
			32,668	$32,666 \pm 1$	2
8	20°	23		35,857 (accepted)	
			35,834	$35,834 \pm 2$	0
	77°	12		$35,846 \pm 2$ (accepted)	
			35,834	$35,833 \pm 0$	1
			35,781	$35,777 \pm 3$	4
	169°	12		$35,838 \pm 0$	
			35,778	$35,777 \pm 0$	1
10	20°	23		$42,321 \pm 1$ (accepted)	
			42,261	$42,260 \pm 2$	1
	77°	12		$42,319 \pm 1$ (accepted)	
			42,254	$42,251 \pm 1$	3

two energy levels in the basic multiplet. Also, there is little doubt but that this interval can be related to the influence of the electric fields of the lattice upon ${}^6H_{5/2}$. It may be predicted at this point that a close study of



the specific heat measurements at low temperatures will confirm the existence of this interval.

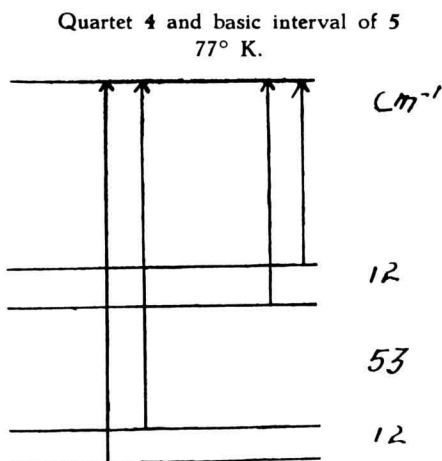
Based upon the same pattern of levels as those given above, the quartet 5 will have the following basic intervals:

60 cm⁻¹ at 20° K, 54 cm⁻¹ at 77° K, and 43 cm⁻¹ at 169° K.

Temp. °K	Calc. Line cm ⁻¹	Observed Line cm ⁻¹	Deviation
20		30,115 ± 2 (accepted)	
	30,130	30,133 ± ?	3
	30,070	30,071 ± 2	1
	30,055	30,058 ± 1	3
77		30,121 ± 2 (accepted)	
	30,067	30,067 ± 1	0
169		30,118 ± 1	
	30,075	30,072 ± 2	3

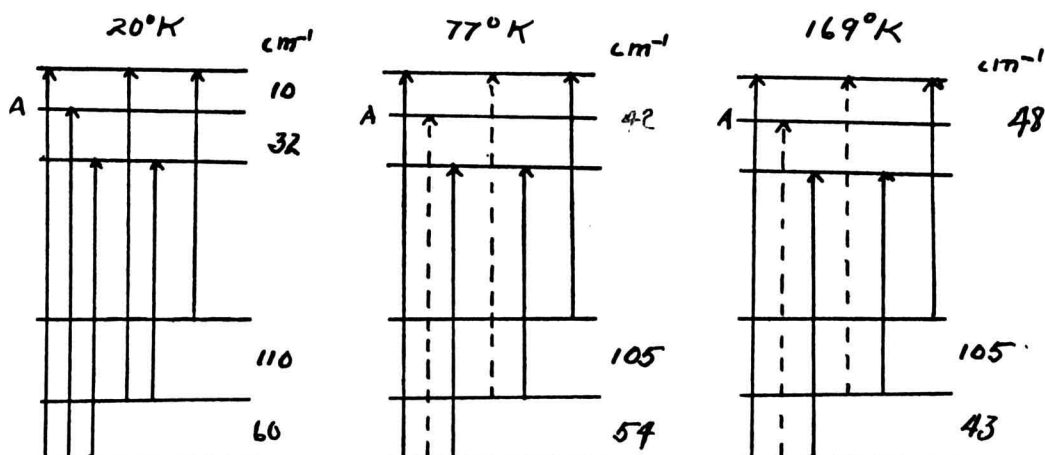
Now, it is clear that if the 12 cm⁻¹ interval (the "fine-structure" interval) is inserted in the basic multiplet of 4, 7, 8, 10, the group 5 fits into the same scheme as groups 4, 7, 8, 10 and we shall see later the sextets 3 and 6 will also be associated with the same levels. As an example we shall give the energy levels of group 4 and 5 at 77° K employing the same basic multiplet for both.

The fact that the "fine-structure" interval is of the same magnitude in all groups (with the possible exception of 8) is evidence for including it



in the basic multiplet. Its inclusion results naturally in any attempt to superpose the levels of the groups for the purpose of obtaining all the components which ${}^6H_{5/2}$ has been split into. The total number can not exceed six. It must be stated again that more data are necessary for this purpose, especially spectra at the temperature of liquid helium.

Since the spectrum of Sm^{+++} consists of rather isolated groups, one would expect the lines within a group to originate and end at neighbouring levels. The intensities justify this point of view as the components of greater frequency always become more intense as the temperature is reduced. The sextets 3 and 6 contain the same energy interval as the quartet 5 and the intensities of corresponding lines behave in the same way with regard to temperature. We shall therefore associate 3 and 6 with the same basic states as 5. Below is the energy level pattern of 3 based upon that of 5.



A is the "fine structure level" which can be inserted in the basic multiplet so that the interval 10 cm^{-1} (or 12 cm^{-1}) would be produced there (See page 982).

Temp. K	Calc. Line cm^{-1}	Obs. Line cm^{-1}	Deviation cm^{-1}
20°		27,639 \pm 1 (accepted)	
	27,629	27,629 \pm 1	0
	27,597	27,597 \pm 0	0
	27,579	27,585 \pm 6	6
	27,537	27,537 \pm 0	0
	27,469	27,469 \pm 1	0
77°		27,637 \pm 1 (accepted)	
	27,595	27,595 \pm 2	0
	27,541	27,540 \pm 1	1
	27,478	27,478 \pm 1	0
169°		27,639 \pm 0	
	27,591	27,591 \pm 1	0
	27,548	27,549 \pm 0	0
	27,491	27,491 \pm 0	0

The sextet 6 follows a similar pattern, its first interval being identical at each temperature with that of 3 but the over-all separation of the basic multiplet is slightly different. This difference can probably be ascribed to another "fine-structure" interval in the basic term system. The over-all separation of 170 cm^{-1} agrees with the interval evaluated from the specific heat measurements ^{1) 2)}.

The lines which have been studied here because of the variation in their intensities constitute about one half the prominent lines of the spectrum.

A part of this experimental work was done by one of us (S. F.) during his stay in the laboratory of Professor DE HAAS Leyden, Holland while he was a fellow of the JOHN SIMON GUGGENHEIM Memorial Foundation. He wishes to express his gratitude to Professor DE HAAS for the generous hospitality of his laboratory.

¹⁾ J. E. AHLBERG and S. FREED, Phys. Rev. **39**, 540 (1932).

²⁾ Dr. SPEDDING has kindly called my attention to some unpublished spectra of $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ which he and Mr. BEAR have taken. It appears that the interval of about 165 cm^{-1} in this salt corresponds to the 60 cm^{-1} interval recorded here for the ethylsulfate and hence the interval 170 cm^{-1} found in the ethylsulfate is not to be identified with the interval found in the specific heat measurements.

Absorption Lines Obtained at 20° K.			
Intensity ¹⁾	Wave Length	Wave Number	Measured
2 D	2328.1 \pm ?	42,940 \pm ?	1
2 D	2329.4 \pm .05	42,915 \pm 1	2
3 S	2332.1 \pm .10	42,867 \pm 2	4
3 B	2333.9 \pm .05	42,834 \pm 1	4
5 S	2349.9 \pm .13	42,542 \pm 3	3
5 S	2351.5 \pm .20	42,513 \pm 3	3
5 B	2354.6 \pm .03	42,457 \pm 1	4
5 B	2362.2 \pm .05	42,321 \pm 1	4
1 S	2365.6 \pm .10	42,260 \pm 2	4
2 S	2378.8 \pm .10	42,025 \pm 1	4
Faint	2380.1 \pm ?	42,002 \pm ?	1
3 B	2383.1 \pm .03	41,949 \pm 1	4
Faint	2604.7 \pm ?	38,381 \pm ?	1
2 S	2665.3 \pm .05	37,508 \pm 1	2
Faint	2666.9 \pm ?	37,486 \pm ?	1
2 S	2667.7 \pm .10	37,474 \pm 2	2
Faint	2735.9 \pm ?	36,540 \pm ?	1
Faint	2737.2 \pm ?	36,523 \pm ?	1
3 S	2788.0 \pm .05	35,857 \pm 1	2
3 B	2789.8 \pm .20	35,834 \pm 2	4
3 D	2900.7 \pm .50	34,464 \pm 6	4
Faint	2957.7 \pm ?	33,800 \pm ?	1
2 S	2970.4 \pm .10	33,656 \pm 1	2
2 D	2971.7 \pm .05	33,641 \pm 1	2
Faint	2978.1 \pm .05	33,569 \pm 1	2
Faint	2982.9 \pm ?	33,515 \pm ?	1
Faint	2985.1 \pm .20	33,490 \pm 2	2
1 S	3020.0 \pm ?	33,103 \pm ?	1
1 S	3022.6 \pm ?	33,074 \pm ?	1
3 S	3055.3 \pm 0	32,721 \pm 0	2

¹⁾ D = diffuse. S = sharp. B = broad.

Absorption Lines Obtained at 20° K. (Continued).			
Intensity	Wave Length	Wave Number	Measured
4 B	3056.5 \pm .10	32,708 \pm 1	2
2 S	3058.1 \pm .10	32,691 \pm 1	2
Faint	3063.6 \pm ?	32,632 \pm ?	1
3 D	3170.7 \pm .10	31,530 \pm 1	2
2 B	3172.6 \pm .05	31,511 \pm 1	2
5 S	3177.4 \pm 0	31,463 \pm 0	2
4 B	3179.0 \pm ?	31,448 \pm ?	1
2 D	3183.7 \pm .10	31,401 \pm 1	3
1 D	3188.6 \pm .4	31,353 \pm 4	4
Faint	3308.3 \pm ?	30,218 \pm ?	1
2 S	3309.1 \pm .15	30,211 \pm 1.5	2
2 S	3317.7 \pm ?	30,133 \pm ?	1
3 D	3319.6 \pm .20	30,115 \pm 1.5	2
Faint	3320.6 \pm .20	30,106 \pm 1.5	2
1 D	3324.5 \pm .15	30,071 \pm 1.5	2
2 D	3326.0 \pm .10	30,058 \pm 1	2
Faint	3335.7 \pm 0	29,970 \pm 0	2
2 S	3337.6 \pm .35	29,953 \pm 2.5	2
Faint	3332.4 \pm ?	30,000 \pm ?	1
1 D	3339.4 \pm ?	29,937 \pm ?	1
1 D	3417.3 \pm .10	29,255 \pm .50	2
1 D	3426.8 \pm 0	29,173 \pm 0	2
Faint	3437.3 \pm ?	29,084 \pm ?	1
5 B	3446.3 \pm 0	29,008 \pm 0	2
7 S	3447.8 \pm .30	28,996 \pm 3	2
4 S	3451.6 \pm .20	28,964 \pm 1.5	2
4 D	3453.4 \pm .15	28,949 \pm 1	2
5 S	3454.9 \pm .15	28,936 \pm 1	2
5 D	3456.3 \pm .10	28,924 \pm 1	2
Faint	3538.7 \pm .30	28,251 \pm 2	2

Absorption Lines Obtained at 20° K. (*Continued*).

Intensity	Wave Length	Wave Number	Measured
2 D	3540.0 \pm .25	28,241 \pm 1	2
1 S	3547.1 \pm ?	28,184 \pm ?	1
3 D	3551.5 \pm 0	28,149 \pm 0	2
2 D	3552.9 \pm .40	28,138 \pm 3.5	2
7 D	3617.1 \pm .15	27,639 \pm 1	2
10 B	3618.3 \pm .15	27,629 \pm 1	2
7 B	3622.6 \pm 0	27,597 \pm 0	2
5 B	3624.0 \pm .40	27,585 \pm 3.5	2
5 B	3630.5 \pm 0	27,537 \pm 0	2
2 D	3639.4 \pm .15	27,469 \pm 1	2
Faint	3648.2 \pm ?	27,403 \pm ?	1
Faint	3711.7 \pm ?	26,934 \pm ?	1
Faint	3718.5 \pm ?	26,885 \pm ?	1
3 D	3739.3 \pm .20	26,735 \pm 2	3
1 S	3743.2 \pm ?	26,708 \pm ?	1
5 B	3748.4 \pm .20	26,670 \pm 1.5	4
4 B	3751.3 \pm 0	26,650 \pm 0	2
4 S	3755.4 \pm 0	26,621 \pm 0	2
10 B	3758.8 \pm .30	26,597 \pm 2	2
Faint	3763.2 \pm ?	26,566 \pm ?	1
Faint	3770.5 \pm ?	26,514 \pm ?	1
Faint	3774.4 \pm ?	26,487 \pm ?	1
Faint	3779.8 \pm ?	26,449 \pm ?	1
Faint	3785.6 \pm ?	26,408 \pm ?	1
Faint	3790.8 \pm ?	26,372 \pm ?	1
2 D	3801.8 \pm ?	26,296 \pm ?	1
2 S	3806.9 \pm ?	26,261 \pm ?	1
2 S	3811.4 \pm ?	26,230 \pm ?	1
2 S	3853.5 \pm ?	25,943 \pm ?	1
2 S	3857.7 \pm ?	25,915 \pm ?	1

Absorption Lines Obtained at 20° K. (Continued).			
Intensity	Wave Length	Wave Number	Measured
2 S	3875.9 ± ?	25,793 ± ?	1
2 S	3878.7 ± .15	25,775 ± 1	2
2 S	3884.1 ± .60	25,739 ± 4	3
2 S	3887.9 ± ?	25,714 ± ?	1
Faint	3903.0 ± ?	25,614 ± ?	1
5 B	3907.3 ± .50	25,586 ± 3	4
5 B	3913.9 ± .20	25,543 ± 1.5	2
5 S	3915.0 ± .15	25,536 ± 2	2
1 S	3923.4 ± .80	25,485 ± 5	2
2 D	3969.3 ± 0	25,186 ± 0	2
1 S	3974.9 ± ?	25,151 ± ?	1
4 D	3981.8 ± 0	25,107 ± 0	2
2 S	3985.6 ± .40	25,083 ± 3	2
1 S	4001.0 ± ?	24,987 ± ?	1
1 S	4004.5 ± ?	24,965 ± ?	1
10 B	4011.8 ± 0	24,919 ± 0	3
10 B	4019.9 ± .50	24,869 ± 4	4
1 S	4042.5 ± .60	24,730 ± 4	3
1 S	4049.3 ± ?	24,681 ± ?	1
1 S	4052.6 ± .20	24,669 ± 1.5	2
5 B	4076.8 ± .20	24,522 ± 1	2
1 S	4082.6 ± ?	24,487 ± ?	1
1 S	4086.2 ± .60	24,466 ± 3	2
1 S	4088.6 ± ?	24,451 ± ?	1
3 D	4094.3 ± .60	24,417 ± 4	3
2 S	4101.2 ± .30	24,376 ± 2	3
2 D	4108.4 ± .30	24,334 ± 2	2
1 S	4151.3 ± .80	24,082 ± 5	2
1 S	4156.1 ± ?	24,054 ± ?	1
7 S	4162.7 ± 0	24,016 ± 0	4

Absorption Lines Obtained at 77° K.			
Intensity	Wave Length	Wave Number	Measured
Faint	2332.3 \pm .05	42,862 \pm 1	2
3 B	2333.9 \pm .05	42,834 \pm 1	4
2 S	2350.1 \pm .05	42,538 \pm 1	2
2 S	2351.5 \pm ?	42,513 \pm ?	1
3 B	2354.6 \pm .20	42,457 \pm 3	4
3 B	2356.1 \pm .05	42,430 \pm 1	2
3 D	2356.5 \pm .05	42,423 \pm 1	2
2 S	2359.2 \pm ?	42,374 \pm ?	1
2 S	2360.5 \pm ?	42,351 \pm ?	1
3 B	2362.3 \pm .03	42,319 \pm 1	4
2 S	2364.3 \pm ?	42,283 \pm ?	1
2 B	2366.1 \pm .03	42,251 \pm 1	4
Faint	2378.9 \pm .10	42,023 \pm 2	2
1 S	2381.6 \pm ?	41,976 \pm ?	1
3 B	2383.1 \pm .05	41,949 \pm 1	4
1 S	2660.3 \pm ?	37,579 \pm ?	1
1 S	2661.3 \pm ?	37,564 \pm ?	1
1 S	2663.3 \pm .30	37,536 \pm 3	2
1 S	2665.3 \pm .30	37,508 \pm 4	2
1 S	2667.2 \pm ?	37,481 \pm ?	1
2 D	2669.4 \pm .05	37,450 \pm 1	4
Faint	2672.7 \pm ?	37,404 \pm ?	1
Faint	2679.7 \pm ?	37,306 \pm ?	1
Faint	2681.1 \pm ?	37,287 \pm ?	1
Faint	2682.0 \pm ?	37,275 \pm ?	1
1 S	2701.9 \pm .05	37,000 \pm 1	2
2 D	2788.9 \pm .20	35,846 \pm 2	4
2 D	2789.9 \pm 0	35,833 \pm 0	2
2 D	2794.3 \pm .30	35,777 \pm 3	4
Faint	2879.8 \pm ?	34,714 \pm ?	1

Absorption Lines Obtained at 77° K. (<i>Continued</i>).			
Intensity	Wave Length	Wave Number	Measured
Faint	2887.0 \pm ?	34,628 \pm ?	1
2 D	2900.5 \pm .15	34,467 \pm 2	4
1 S	2904.9 \pm 0	34,415 \pm 0	2
1 S	2905.4 \pm .06	34,409 \pm 1	3
1 S	2907.5 \pm ?	34,384 \pm ?	1
1 S	2908.7 \pm ?	34,370 \pm ?	1
1 S	2910.3 \pm .20	34,351 \pm 2	4
3 B	3055.1 \pm .10	32,723 \pm 1	4
1 S	3058.5 \pm .20	32,686 \pm 2	4
2 D	3061.4 \pm .20	32,655 \pm 2	4
2 D	3170.4 \pm .10	31,533 \pm 1	2
3 D	3172.6 \pm ?	31,511 \pm ?	1
2 D	3173.5 \pm .10	31,502 \pm 1	3
3 D	3174.0 \pm ?	31,497 \pm ?	1
3 D	3177.6 \pm .10	31,461 \pm 1	4
2 D	3183.0 \pm .15	31,408 \pm 2	4
3 D	3187.4 \pm .15	31,364 \pm 1	4
3 D	3319.0 \pm .20	30,121 \pm 2	2
1 B	3325.0 \pm .20	30,067 \pm 1	4
5 B	3446.0 \pm .20	29,010 \pm 2	4
5 S	3447.8 \pm ?	28,996 \pm ?	1
Faint	3449.9 \pm ?	28,978 \pm ?	1
5 B	3453.8 \pm .30	28,945 \pm 3	4
3 S	3454.9 \pm ?	28,936 \pm ?	1
Faint	3538.7 \pm ?	28,251 \pm ?	1
5 B	3617.3 \pm .10	27,647 \pm 1	4
2 D	3622.8 \pm .30	27,595 \pm 2	4
5 B	3630.0 \pm .15	27,540 \pm 1	4
5 B	3638.3 \pm .15	27,478 \pm 1	4
1 S	3739.1 \pm .20	26,737 \pm 1	3

Absorption Lines Obtained at 77° K. (Continued).			
Intensity	Wave Length	Wave Number	Measured
1 S	3743.2 \pm .15	26,708 \pm 1	4
5 S	3749.4 \pm .30	26,664 \pm 2	3
5 S	3752.3 \pm .30	26,643 \pm 2	3
5 S	3755.1 \pm .30	26,623 \pm 2	3
10 B	3757.7 \pm .10	26,604 \pm 1	3
5 S	3761.0 \pm .15	26,581 \pm 1	2
Faint	3782.2 \pm ?	26,432 \pm ?	1
Faint	3790.0 \pm ?	26,378 \pm ?	1
1 S	3807.5 \pm 0	26,257 \pm 0	2
Faint	3848.6 \pm .30	25,976 \pm 2	2
Faint	3855.3 \pm .15	25,931 \pm 1	2
1 S	3877.0 \pm .15	25,786 \pm 1	2
1 S	3883.0 \pm .15	25,746 \pm 1	2
1 S	3895.4 \pm ?	25,664 \pm ?	1
2 S	3907.0 \pm .40	25,588 \pm 2.5	4
1 S	3913.7 \pm ?	25,544 \pm ?	1
2 S	3914.4 \pm .20	25,532 \pm 1	3
1 S	3920.0 \pm .20	25,503 \pm 1	2
2 D	3969.3 \pm .80	25,186 \pm 5	3
1 S	3974.5 \pm 0	25,153 \pm 0	3
2 D	3981.7 \pm .40	25,108 \pm 2	3
2 B	3986.6 \pm 0	25,077 \pm 0	2
1 S	3997.6 \pm .50	25,008 \pm 2	2
1 S	4001.9 \pm .50	24,981 \pm 3	3
1 S	4005.5 \pm ?	24,959 \pm ?	1
1 S	4009.3 \pm 0	24,935 \pm 0	2
1 S	4013.4 \pm .40	24,910 \pm 2	3
10 B	4016.9 \pm .40	24,888 \pm 2	2
10 B	4032.1 \pm .20	24,794 \pm 1	4
2 S	4043.3 \pm ?	24,725 \pm ?	1
5 B	4076.7 \pm .15	24,532 \pm 1	2
5 B	4081.7 \pm .15	24,493 \pm 1	2
2 S	4142.0 \pm ?	24,136 \pm ?	1
Faint	4157.4 \pm ?	24,047 \pm ?	1
7 S	4162.7 \pm 0	24,016 \pm 0	4

Absorption Lines Obtained at 169° K.			
Intensity	Wave Length	Wave Number	Measured
Faint	2664.9 \pm ?	37,514 \pm ?	1
2 D	2668.9 \pm .10	37,457 \pm 1	2
Faint	2789.5 \pm 0	35,838 \pm 0	2
Faint	2794.3 \pm 0	35,777 \pm 0	2
Faint	2882.7 \pm ?	34,680 \pm ?	1
Faint	2894.9 \pm ?	34,533 \pm ?	1
Faint	2900.5 \pm .05	34,467 \pm 1	2
Faint	2904.6 \pm 0	34,418 \pm 0	2
Faint	2909.5 \pm .05	34,360 \pm 1	2
3 D	3054.6 \pm .10	32,728 \pm 1	2
3 D	3060.4 \pm .10	32,666 \pm 1	2
1 D	3133.6 \pm ?	31,903 \pm ?	1
1 D	3135.6 \pm ?	31,883 \pm ?	1
Faint	3169.7 \pm ?	31,540 \pm ?	1
3 B	3172.7 \pm ?	31,510 \pm ?	1
Faint	3173.2 \pm ?	31,505 \pm ?	1
Faint	3174.3 \pm ?	31,494 \pm ?	1
2 D	3177.9 \pm .15	31,458 \pm 1.5	2
2 D	3182.2 \pm .10	31,416 \pm 1	2
3 D	3186.7 \pm .10	31,371 \pm 1	2
2 D	3194.5 \pm ?	31,295 \pm ?	1
1 D	3198.2 \pm ?	31,259 \pm ?	1
1 S	3313.7 \pm ?	30,169 \pm ?	1
Faint	3314.9 \pm ?	30,158 \pm ?	1
1 S	3319.3 \pm .10	30,118 \pm 1	2
2 D	3324.4 \pm .20	30,072 \pm 2	2
5 B	3445.4 \pm .30	29,015 \pm 2.5	2
7 B	3452.7 \pm 0	28,955 \pm 0	2
1 S	3486.6 \pm ?	28,673 \pm ?	1
1 S	3490.4 \pm ?	28,642 \pm ?	1

Absorption Lines Obtained at 169° K. (Continued).			
Intensity	Wave Length	Wave Number	Measured
5 B	3617.1 \pm 0	27,639 \pm 0	2
1 S	3623.4 \pm .10	27,591 \pm 1	2
5 B	3628.8 \pm 0	27,549 \pm 0	2
5 B	3636.5 \pm 0	27,491 \pm 0	2
1 S	3643.4 \pm ?	27,439 \pm ?	1
1 S	3648.0 \pm ?	27,405 \pm ?	1
1 S	3655.4 \pm ?	27,349 \pm ?	1
1 S	3661.0 \pm ?	27,307 \pm ?	1
Faint	3723.3 \pm ?	26,850 \pm ?	1
Faint	3730.3 \pm ?	26,800 \pm ?	1
1 S	3735.6 \pm ?	26,762 \pm ?	1
1 S	3739.0 \pm 0	26,738 \pm 0	2
5 S	3750.7 \pm .15	26,654 \pm 1.5	2
5 B	3757.0 \pm .30	26,609 \pm 2.5	2
2 S	3905.7 \pm .15	25,596 \pm 2	2
1 D	3912.8 \pm 0	25,550 \pm 0	2
1 S	3967.1 \pm 0	25,200 \pm 0	2
1 D	3980.0 \pm .30	25,119 \pm 1.5	2
1 S	4009.1 \pm .15	24,936 \pm 1	2
1 S	4011.8 \pm .35	24,919 \pm 2	2
10 B	4015.7 \pm .30	24,895 \pm 2	2
10 B	4028.9 \pm 0	24,814 \pm 0	2
1 S	4040.6 \pm ?	24,742 \pm ?	1
1 S	4052.5 \pm .15	24,669 \pm 1	2
1 S	4059.5 \pm .60	24,627 \pm 3	2
3 D	4069.4 \pm ?	24,567 \pm ?	1
5 B	4075.7 \pm .30	24,529 \pm 3	2
5 B	4078.6 \pm ?	24,511 \pm ?	1
1 S	4091.4 \pm .15	24,535 \pm 1	2
1 S	4105.7 \pm 0	24,350 \pm 0	2
5 S	4159.1 \pm .20	24,037 \pm 1	2
3 S	4167.9 \pm .20	23,986 \pm 1.5	2
3 D	4175.0 \pm .20	23,941 \pm 1	2

Summary.

The absorption spectra of Sm^{+++} in the hexagonal crystal $\text{Sm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ were taken parallel to the optic axis at 20° K , 77° K , and 169° K . Absorption lines are listed in the region of the spectrum between 4200 \AA and 2200 \AA .

This paper is principally concerned with the various electronic configurations in the basic multiplet, especially as they result from the inter-action of Sm^{+++} and the electric fields of the lattice. In consequence, all the lines whose relative intensities vary with the temperature have been studied in terms of energy level diagrams.

Physics. — *The Calibration of a Pressure Balance in Absolute Units.*

(31st Communication of the VAN DER WAALS Fund). By
A. MICHELS. (Communicated by Prof. J. D. VAN DER WAALS Jr.).

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Introduction. For the measurement of pressure in absolute units, as soon as the pressure is greater than some atmospheres, the only method that need be considered is that using a mercury column. This method, however, involves considerable difficulties when the pressures to be measured become appreciable. A few examples are known of high pressure mercury manometers such as those of AMAGAT in a mine-shaft at Verpillieux near St. Etienne, and of CAILLETET in the Eifel Tower, with which it was possible to measure up to about 400 atm. In the same group can be placed the so-called "gebroken manometer" designed by KAMERLINGH ONNES, which is still in use for measurements up to 120 atm. We are unaware of any direct measurements with a mercury column besides these.

Of the secondary gauges in use the most suitable for accurate measurement is the pressure balance which also allows measurements to be made at much higher pressures. For the most accurate work it should, however, be calibrated directly. Many types of this apparatus are known (AMAGAT, WIEBE, STÜCKRATH, WAGNER, LANGE, HOLBORN, BRIDGMAN and others) all of which are designed on the same principle: a piston is ground to fit as well as possible in a cylinder; the unknown hydrostatic pressure is applied under the piston and the force is measured necessary to keep the piston in equilibrium. The pressure can then be calculated from

$$P = \frac{K}{0}$$

where K is the force applied and 0 the area of the piston. By giving the piston a rotatory or to and fro motion the friction can be kept low.