Absorption Spectra of the Samarium Ion in Solids. V. The Absorption Spectrum and Energy Levels of the Sm⁺⁺⁺ Ion as It Exists in Monoclinic Crystals of $Sm_2(SO_4)_3 \cdot 8H_2O$

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The absorption spectrum and energy levels indicated therein for the samarium ion in crystalline monoclinic $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ are shown to be similar to those of $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, which is also a monoclinic salt. Absorption lines of the sulfate at temperatures between 20°K and room temperature are used to prove the existence of several low-lying levels separated from the basic one by 160, 188 and 225 cm⁻¹. These levels are of particular interest in view of heat capacity and magnetic studies of this salt.

N previous papers of this series' we have described the absorption spectra of the samarium ion for monoclinic crystals of SmCl₃.6H₂O and for hexagonal ones of $Sm(BrO_3)_3 \cdot 9H_2O_3$ $Sm(C_2H_5SO_4)_3 \cdot 9H_2O$ and $SmI_3 \cdot 9H_2O$. The chloride spectrum was found to be distinctly different from those of the hexagonal group in that its individual multiplets were spread out somewhat more and frequently contained more lines. These results were in agreement with those of Spedding and Nutting² for the corresponding gadolinium compounds, i.e., the extension within multiplets and the number of components of each of the multiplets of the rare earth ions seem to depend more on the positions of surrounding atoms or ions in the crystal and less on the chemical composition of the compound, except insofar as the composition affects the crystal structure.

This paper describes the spectrum of a second monoclinic salt, $Sm_2(SO_4)_3 \cdot 8H_2O$. The magnetic susceptibility³ and heat capacity⁴ of this solid have already been measured over a wide temperature range, and a spectroscopic determination of the energy levels will be useful in attempting to understand the results of these other investigations. Here we present only the experimental facts. In a later paper we shall introduce a discussion of the relation between the physical and chemical properties of samarium salts and their energy levels.

EXPERIMENTAL PART

Because of the difficulty of obtaining the moderately soluble sulfate as large single crystals, conglomerate absorption has been used exclusively. However, the constituent crystals were of sufficient size to escape the description "powdered" and were of approximately the same individual dimensions as the material used in preparing the former conglomerates. Groth⁵ states that the crystals are monoclinic in external symmetry, with axial ratios a : b : c $=3.0030:1:2.0022, \beta=118^{\circ} 16'.$

Two different preparations (however, from the same ultimate source) gave identical results. One was secured by recrystallization of sulfate of high degree of purity as originally supplied by the Wellsbach Company; the other was obtained from the same material after precipitation of the samarium as the oxalate, ignition to the oxide, solution in HCl, evaporation and reconversion to the sulfate by the method described by Freed⁴ (double decomposition between H_2SO_4 and the chloride in alcoholic solution and digestion of the solid sulfate with water). Crystals finally used were grown by slow evaporation of saturated solutions.

Even more than in the chloride investigation was it difficult to choose the proper thickness of absorbing layer. Because of the magnitude of the separation between the basic state and the excited lower levels, rather thick conglomerates are required to bring out the high-temperature lines, i.e. those increasing in intensity as the temperature is raised. The extreme thickness

¹Spedding and Bear, Phys. Rev. **42**, 58, 76 (1932); **44**, 287 (1933); **46**, 308 (1934). ²Spedding and Nutting, Phys. Rev. **38**, 2294 (1931); J. Am. Chem. Soc. **55**, 496 (1933). ³Freed, J. Am. Chem. Soc. **52**, 2702 (1930). ⁴Ahlberg and Freed, Phys. Rev. **39**, 540 (1932).

⁵ Groth, Crystallography, Vol. 2, p. 458.

in turn offers trouble with increased complexity of spectra and makes longer exposures necessary. The sulfate has the additional inconvenience of showing rather diffuse lines. In obtaining the photographs with the sulfate, however, the same thicknesses, from 5 to 10 mm, have been found most satisfactory.

Investigation of only the visible region of the spectrum has been done. The equipment described before was used to obtain the photographs at low temperatures.

Results

In Fig. 1 are shown the spectra of the sulfate as transmitted at 20°, 78°, 169° and 298°K by a conglomerate of 5 mm thickness. In addition is shown a 10 mm layer photograph as it appears at 78°. Table I gives measurements and roughly estimated intensities of the absorption lines and bands observed at those temperatures.

Close examination of the photographs at low

temperatures of the thin- and thick-layer spectra shows a marked tendency for the thicker layer to produce doublets from lines which are apparently single in the thin-layer case. In some instances the lines can be observed to be double for both thin and thick layers and then the effect is noticed as a widening of the separation between the two peaks of intensity.

This behavior suggests that the double lines themselves are not completely resolved. If they were composed of very fine lines of varying intensities, with the strongest located on the inner side (with respect to the doublet) of each component, one would understand how the widening occurred. Increase in layer thickness would enlarge the apparent separation of the doublet components by increasing the number of fine lines that are able to absorb strongly the light. The fine unresolved lines composing the doublet components could possibly be results of Stark splitting of the resolvable lines by the crystal field, but one is more inclined to suppose



FIG. 1. Conglomerate absorption of $Sm_2(SO_4)_3 \cdot 8H_2O$. The substances at whose boiling points the spectra were photographed are indicated on the right, the corresponding temperatures on the left. *H* is placed above regions wherein the most prominent high-temperature lines are located.

TABLE I. Conglomerate absorption lines and bands of $Sm_2(SO_4)_3 \cdot 8H_2O$.

H (type) = high-temperature line; L (type) = low-temperature line; HL (type) = probably both types overlap; R.T., E.T., N.T. and H.T. = columns for measurements at room, ethylene, nitrogen and hydrogen temperatures, respectively; Int. = columns of intensity and character of the lines, completely filled only for hydrogen temperature. Intensity is estimated very roughly on a scale of 10, with very faint lines given as 0; *s*, *w* indicate degrees of increasing sharpness; *ws* signifies that a line is somewhat broader than a single one would be expected to be but has fairly sharp edges; *md*, *d*, *wd* indicate degrees of increasing diffuseness; *b* = broad line or band, used most frequently with bands; "2," "3" possibly double or triple, respectively. Primed values represent band edges, *s*, centers where otherwise the figure might be mistaken for a band edge, \ddagger stands before lines or bands that have required extremely thirk conglomerates to bring them out, *x* before lines or bands that are quoted from plates obtained with the same thick conglomerate but are also visible distinctly on plates of thinner conglomerates. The last type of line is given as it appears for thick conglomerates because of widening or greater complexity made evident therein and may be roughly compared in many cases with its appearance in a thin conglomerate by looking at the figures given to rhyloca temperature. All of which are for a thin 5 mm conglomerates.

Int.	0 1d 3d	19 19 19 19 19		1d 2nd 10s	10ws	0 1s 2nd	1s	05 25	$0 \\ 2d$			15
Γ. ν(cm ⁻¹)	$\begin{array}{c} 18109\\ 181196\\ 18132\\ 18142'\\ 18115'\\ 18153\\ 18153\\ 18153\\ \end{array}$	18166' 18179 18189 18223 18223 18223 18263		18890 18915.8 18943.1	$\begin{bmatrix} 10940 \\ 18951.3 \\ 18954' \\ 18981' \end{bmatrix}$	18991'∫ 18998.9 19015.8	19029.6	19098.0	19127 19163		X	19547.0
.н. Х(А)	5520.6 5517.6 5513.6 5510.6 5507.9 5507.1	(5503.1' 5499.5 5496.2 5481.6 5481.6 5474.0		5292.4 5285.10 5277.50	5275.25 5274.4' 5266.9'	\5264.1' 5262.00 5257.35	5253.50	5234.70	5226.7 5216.8			5114.45
Int.	1		1d ''2'' 1d 1d									
$\underset{\nu(\mathrm{cm}^{-1})}{\mathrm{N.T.}}$	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \\ 1\\ \\ 1\\ \\ 1\\ \\ 1\\ \\ 1\\ \\ 1\\ \\ 1\\ \\ $	(18167) 18178 18178 18206 18222 18238 18263	$ \begin{array}{c} \pm 18291 \\ 18718' \\ 18726' \\ 18755' \\ 18769' \\ 18780' \end{array} $	(18795/ 18890 18917 18943.9	$ \begin{array}{c} x \\ 18955 \\ 18960' \\ 18984' \end{array} $	18993' 19000.5 19009 119016.5 c	$\ddagger 19019.0c$ $\ddagger 19031.0$ 19055	$ \begin{array}{c} 19006.3 \\ 19100 \\ 19100 \\ 10131 \\ \end{array} $	‡ 19132 19165	${}^{+}_{+}$ 19188' 19208' 19233'	(19263) (19293) (19325) (19521)	19550 † 19559
Type	רר ררר	ЧЧЧЧЧЧ	а н нС	1 HHH	IJ.	പപ്പ	പപപം	าว่า-	111	2 2	222	цц
E.T. $\nu(\mathrm{cm}^{-1})$	‡ [18151'	18176'	$\{ \begin{array}{c} 18720' \\ 18723' \\ 18763' \\ + \end{array} \} 18779' \\ 18779' \\ 18786' \\ \end{array}$	+(18798' 18918 18941' 18051'	x 10901	± 18993 ‡ 19002.8	<pre># 19021.3 # 19034.0 # 10034.0</pre>	+ 19070.4 + 19098 + 10118	+ 19158' ‡{19158'			
R.T. $\nu(\mathrm{cm}^{-1})$			{ 18720' { 18735' } 18784'	(18805' [18943'	18960							
Int.	5 as 3 d 5 d	3d			106	100 10 <i>ws</i> "2"	3d 3d	19	00	0 1 0 0 0 0	0	00
$T.$ $\nu(cm^{-1})$ Int.	17127 5 ^{ns} 17205 3 <i>d</i> 17256 5 <i>d</i>	17481 3 <i>d</i>			17889' 17890.4	$\begin{array}{c} 17892'\\ 17917'\\ 17919.9\\ 17919.9\\ \end{array}$	17922'] · · · · · · · · · · · · · · · · · ·	17956 1d 17956 1d 17955 1d	179926 0 18002 0	$\begin{array}{c} 18010c\\ 18020c\\ 18027'\\ 18027'\\ 0 \end{array}$	$18043' \\ 18048' \\ 18056' \\ 18068' \\ 1$	18095 0 18095 0
$\lambda(A)$ H.T. $\mu(cm^{-1})$ Int.	5837.1 17127 5es 5810.6 17205 3d 5793.3 17256 5d	5718.9 17481 3 <i>d</i>			[5588.6' 17889'] [5588.05 17890.4] 10.	5587.5' 17892' 5579.7' 17917' 5578.85 17919.9 10ws "2"	[5578.1' 17922'] · · [5574.9 17933 3d	5561.6 17956 1d 5564.2 17956 1d 5561.8 17955 1d	[5555.66 179926] 0 [5553.5 18002] 0	$ \begin{array}{c} \left(\begin{array}{c} 5551.0c \\ 5557.0c \\ 5547.8 \\ 5547.8 \\ 5545.7' \\ 18020' \\ 0 \end{array} \right) \begin{array}{c} 0 \\ 1d \\ 0 \\ 0 \end{array} \right) $	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5524.9 18095 0 5524.9 18095 0
Int. $\lambda(A)$ H.T. $\mu(\text{cm}^{-1})$ Int.	5837.1 17127 545 545 5793.3 17205 3d 0 0	0 5718.9 17481 3 <i>d</i> 1 <i>d</i> 1 <i>d</i> 1 <i>d</i>	2d 1d 0	00 0	0 5588.6' 17889' 5588.05 17890.4 10	5587.5' 17892' 108 5587.5' 17917' 5579.7' 17917' 5578.85' 17919.9' 10ws "2"	[5578.1' 17922'] 5574.9 17933 3d 5570.7 17933 3d	5564.2 17956 14 5564.2 17956 14 5564.8 17975 14	[5556.66 17992c] 0 [5553.5 18002] 0	$\begin{cases} 5551.0c & 18010c \\ 5547.8 & 18020c \\ 5545.7' & 18027' \\ 0 \end{cases}$	$\begin{cases} 5540.7' 18043' \\ 5539.3' 18048' \\ 55536.9' 18056' \\ 55533.6' 18056' \\ \end{array}$	5530.0 18080 0 5524.9 18095 0
N.T. $\nu(\text{cm}^{-1})$ Int. $\lambda(\text{A})$ H.T. $\mu(\text{cm}^{-1})$ Int.	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	* 112836 112834 112837 * 112857 * 12857	$\begin{array}{c} 11378 \\ 11386' \\ 117886' \\ 1178887 \\ 5588.6' \\ 5588.05 \\ 17890.4 \\ 106 $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	* 117923.4 (5578.1' 17922') 117928.4 5574.9 17933 3d 17037 5774.9 17933 3d	11957 5567.6 17956 14 17967 5564.2 17957 14 17967 5564.2 17957 14 17076 5564.8 17075 14	117989/ 17995 17905 15553 55553 18002 17902 17902 0	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	18080 5530.0 18080 0 ‡ 18096 5524.9 18095 0
Type $\nu(\text{cm}^{-1})$ Int. $\lambda(A) \xrightarrow{\mu(\text{cm}^{-1})}$ Int. Int.	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{ccccccc} \mathrm{H}^{2} & 11404 & 0 & 5718.9 & 17481 & 3d \\ \mathrm{H} & 17667 & 1d & 5718.9 & 17481 & 3d \\ \mathrm{H} & \left\{ 17692c & 1d \\ \mathrm{H} & \left\{ 17702c & 1d \\ \end{array} \right\} \end{array} $	H 17732 2 d H $\left\{ 17763, 1d$ H $\left\{ 17764, 0 \right\}$ H $\left\{ 17764, 0 \right\}$ H $\left\{ 178104, 0 \right\}$	H 1178326 H 1178346 H 117847 h 117857 h 117856 h 1178566 h 1178566 h 1178566 h 1178566 h 1178566 h 1178566 h 11785666 h 1178566666666666666666666666666666666666	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	L # 17894.3 [5587.5' 17892' [103 [17898' [5587.5' 17992'] L # [17915.0 [5578.85 17919.9] [0ws ''2''	L #117923.4 [5578.1' 17922'] L 17928' 5574.9 17933 3d	L 11957 5567.6 17956 14 L 11957 5564.2 17956 14 L 117976 5564.2 17967 14 5564.2 17975 14	L [17989' L [17995 [5555.6c 17992c] 0 L [18003 [5553.5c 18002] 0	[18009' [5551.0c 18010c 0 L 180201 55547.3 18020' 1d L 180281 55545.7' 18027' 0	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	L 18080 55300 18080 0 L ‡ 18096 5524.9 18095 0
E.T. N.T. N.T. H.T. $\nu^{(\mathrm{cm}^{-1})}$ Type $\nu^{(\mathrm{cm}^{-1})}$ Int. $\lambda(A)$ $\mu^{(\mathrm{cm}^{-1})}$ Int.	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{cases} 17887' & ? & ? & 17878 & 0 \\ 17887' & 17886' & 5588.6' & 17889' \\ L & x \\ 17888.7 & 5588.05 & 17890.4 \\ 17888.7 & 5588.05 & 17890.4 \\ 10.6 & 10.6 \\ 17888.7 & 5588.05 & 17890.4 \\ 10.6 & 10.6 \\ 1$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	L 117957 5567.6 117956 1d L 117957 5567.6 117956 1d L 117967 5564.2 117967 1d 1.77076 5564.8 177057 1d	+{ 17996' L 177995 5555.66 179926 0 +{ 18003 5555.66 179926 0	[18009' [18009' [5551.0c 18010c] 0 L 18021 [5547.8 18020 1d 18028' [5545.7' 18027' 0	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	[18092' L 18080 5524.9 18080' 0 5524.9 18095 0

SPECTRA OF Sm ION IN SOLIDS

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	Int.	$\begin{array}{c} 1d \\ 10 tws \end{array}$	1s 1s 2s	10d 10d	$\begin{array}{c} 9d \\ 2d \end{array}$	10db	10db $10db$	10db	10db		8db	INGO	10db		10db	8db	14	1d	0 0	15 15	2vs 2d 1vs.	8db 2d	qp6	8db
	T. $\nu(\mathrm{cm}^{-1})$	$20544 \\ 20568.7$	20586.9 20594.4 20605.2	20613/ 20616 20624	20639	$20657' \\ 20677' \\ 20691' \\ 2$	20714' 20734' 20755'	20769' 20793' 20808'		21034/	21033' () 21033' () 21048' () 21077' ()	21099'		21181' 21199'	21240	21289'	21327c 21344'	$21387' \\ 21404' \\ 21424' \end{cases}$	$21439' \\ 21452' \\ 21452' \\ 21477' \\ 2$	21494.3	21506.1 21517 21526.9	21554 21565/ 21588	21628	21642'
	, у(А) У(А)	$\frac{4866.2}{4860.40}$	4856.10 4854.35 4851.80	4850.1 4849.2 4847.5 4846.5	4841.0 4841.0	$ \{ 4839.7' \\ 4835.0' \\ 4831.7' \\ $	4826.2' 4821.6' 4816.8'	4813.57 4808.07 4804.47		1755 21	4749.8' 4749.8' 4743.2'	$\left \begin{array}{c} 4738.2' \\ 4732.1' \end{array} \right $		4719.9' 4716.0'	4706 87	4695.9	4687.6 <i>c</i> 4683.9′	46/4.5/ 4670.7/ 4666.4/	4663.0' 4660.3' 4656.0'	4651.10	4648.55 4646.2 4644.05	$\{ 4635.8' \\ 4635.8' \\ 4631.0 \\ $	4625.4' 4622.4'	4619.3′ 4616.8′
	Int.																3d	30	8db		8db			
	$_{\nu(\mathrm{cm}^{-1})}^{\mathrm{N.T.}}$	<pre>‡ 20544 20569</pre>	20598	20615/ 20621 20626/	20640	20655 20673 20689	20708/ 20733/ 20756/	20776/ 20789/ 20817	20842/ 20878/ 20924/	20955/ 20983/ 21010/	21039 21050 21084	21196' 21140' 21147	21149' 21165' 21173	21181/ 21206/	21227	21201	21328' 21341'	21404'	[{21454' 21466'		$\left \left\{ \begin{array}{c} 21513' \\ 21523' \end{array} \right. \right.$	21563	$ \left\{ \begin{array}{c} 21620' \\ 21625 \\ 21629' \end{array} \right. $	$\binom{21645}{21649}$
	Type	LГ	нц	ЦЦ	니니,	ц	Ц	Ч	н н	ב	ЧГ	F	ב, ג	· -	ц Ц	L	H(L)	Н(L)	L H(L)	<u>-</u> ,	L L L	71	L I	Ľ
	$\mathbf{E}.\mathbf{\hat{T}}.$ $\nu(\mathrm{cm}^{-1})$	{20562' ?0573'		20621		20659 20672 20689	20707' 20738' 20753'	20771 20789 20820	$\{20851'$ 20882' 20917'	20944' 20983' 21010'	21041	$\binom{21101'}{21141'}$	$\left\{ \begin{array}{c} 21154'\\ 21165' \end{array} \right\}$	$\left \left \begin{array}{c} 21179' \\ 21209' \end{array} \right $	21227'	21293	$\binom{21331'}{21348'}$	21405	{21450' {21471'		21500 21532	21566	21628	21648
ontinued.)	$\mathrm{R.T.}_{\nu(\mathrm{cm}^{-1})}$	20555	20602'				20698		20852' 20880' 20919'	20942	07017)	21138		21178/ 21210'	21232/	20212))	$\binom{21332'}{21362'}$	21400' 21429'	21451'	21487	21508 21548		21622'	21649′
2																								
ABLE I-(C	Int.			-			1d 1d	10 <i>nd</i> 10 <i>nd</i>	10ws 3d	000	<i>b</i> 6	0	2nd 2nd 2nd	6d 8d	<i>p</i> 0	2	104	ŝo	0	00	1d 1d	0		10 <i>s</i>
TABLE I(C	Γ . $\nu(cm^{-1})$ Int.						20009 1d 20018 1d	$\left. \begin{array}{c} \overline{20025'} \\ 20038.3c \\ 20043.3c \\ 10nd \\ 10nd \end{array} \right\}$	20054.8 10 <i>ws</i> 20067 3 <i>d</i>	20085 0 20096 0 20107 00	$20117' \\ 20124' \\ 20133' \\ 9d$	20145') . 20154 0	20171.3 2nd 20182.5 2nd 20192.3 2nd	20204 6d 20214 8d	20225 94	20236'\\	20243' 10d $20250'$	20201.1 0.5 20271' 0.5 20282' 0 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0	20294' 0 0 0	20328 0 20337 0 0	20357 1d 20386 1d 20398 1d	20415 0 20427.5 $10s$		20521.1 10 <i>s</i>
TABLE I(C	$\begin{array}{c} \mathrm{H.T.} \\ \lambda(\mathrm{A}) & \mathrm{H.T.} \\ \nu(\mathrm{cm}^{-1}) & \mathrm{Int.} \end{array}$						$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\left\{ \left\{ \begin{array}{ccc} 4992.3' & 20025' \\ \left\{ 44989.05c & 20038.3c_{1} \\ 4987.80c & 20043.3c_{1} \\ \end{array} \right\} \begin{array}{c} 10nd \\ 10nd \\ 10nd \end{array} \right\}$	$\begin{array}{rrrr} 4984.95 & 20054.8 & 10ws \\ 4981.9 & 20067 & 3d \end{array}$	4977.4 20085 0 4974.7 20096 0 4972.0 20107 00	$\left\{\begin{array}{cccccccccccccccccccccccccccccccccccc$	(4962.7' 20145') . 4960.4 20154 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4948.1 20204 6d 4045.7 20714 8d	4943.0 20225 9d	[[4940.3' 20236']]	$\left\{ \begin{array}{ccc} \left\{ 14938.5' & 20243' \right\} & 10d \\ \left\{ 4936.8' & 20250' \\ 10000000000000000000000000000000000$	$\begin{pmatrix} 4934.20 & 20201.1 & 05 \\ 4931.7' & 20271' & 0 \\ 4929.2' & 20282' \end{pmatrix}$	$\left\{\begin{array}{cccc} 4926.1' & 20294' \\ 4922.2' & 20310' \\ \end{array}\right\} 0$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\frac{4891.0}{4894.00}$ $\frac{2041.5}{20427.5}$ $\frac{10.5}{10.5}$		4871.70 20521.1 10s
TABLE I(C	Int. $\lambda(A)$ H.T. $\nu(\text{cm}^{-1})$ Int.	14	3a 2d	3d 2d	0	1d 1d	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \left\{ \begin{array}{ccc} 4992.3' & 20025' \\ (4989.05c & 20038.3c) \\ (4987.80c & 20043.3c) \\ \end{array} \right\} \begin{array}{c} 10nd \\ 10nd \\ \end{array} $	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4974.7 20085 0 4974.7 20096 0 4972.0 20107 00	$\left\{\begin{array}{cccc} 4969.6' & 20117' \\ 4967.7' & 20124' \\ 4965.5' & 20133' \\ 4965.5' & 20133' \\ \end{array}\right\} \qquad 9d$	$\left[\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4948.1 20204 6d 4045.7 20214 8d	4943.0 20225 9d	[[4940.3' 20236']]	$\left\{ \begin{array}{c} \left\{ 4938.5' & 20243' \right\} \\ \left\{ 4936.8' & 20250' \right\} \\ \end{array} \right\}$	$\begin{cases} 493.4.20 & 20201.1 & 05 \\ 493.1.7 & 20271.1 & 0 \\ 4929.2 & 20282.7 \end{cases}$	$\begin{cases} 4926.1' & 20294' \\ 4922.2' & 20310' \\ \end{cases} 0$	4915.97 20328 0 (4915.97 203377) 0	(4910.9' 20386 1d 4901.1 20386 1d 4901.1 20398 1d	4394.00 20413 0 4894.00 20427.5 $10s$		4871.70 20521.1 10s
TABLE I(C	N.T. $\nu(\mathrm{cm}^{-1})$ Int. $\lambda(\mathrm{A})$ $\mu(\mathrm{cm}^{-1})$ Int.	[1981] [1981] [1981] 1d	(19835/ 5a (19858/ (19868 2d	198187 19818 19885 34 1985 34	(19897) 19911 0 19911 0	19942 1d 19963' 1d 19973' 1d	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	20083 4977.4 20085 0 20097 4974.7 20096 0 4973.0 70107 00	$ \begin{array}{c} 20115' \\ (20124' \\ (20137' \\$	20154 (4962.7' 20145') 20155 20156 4960.4 20154 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	20201' 20204 6d 20204 4948.1 20204 6d 20214 4045.7 20714 8d	20223 20223 20226 4943.0 20225 9d	[20228' [[4940.3' 20236']]	$ \left\{ \begin{array}{ccc} \left\{ 14938.5' & 20243' \right\} & 10d \\ 10248' & \left\{ 1936.8' & 20250' \right\} & 10d \\ 10260' & 0000' & 0000' \\ 1000' & 0000' & 000' \\ 1000' & 000' & 000' \\$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	20293' 4926.1' 20294' 202299' 203299' 203299' 203299' 20302' 20300' 20302'' 20302'' 20302''''''''''	(1011) (1	20301 (4910) 2035/ 20397 4901.1 20398 1d 20397 4901.1 20398 1d	$\left\{\begin{array}{cccccccccccccccccccccccccccccccccccc$	(20431' 20456	20479 20522.2 4871.70 20521.1 10s
TABLE I(C	Type $\underset{\nu(\mathrm{cm}^{-1})}{\mathrm{N.T.}}$ Int. $\lambda(\mathrm{A})$ H.T. Int. Int.	H + 19815 1d H + 19815 1d H 219815 1d	H	H 19857 H 19883 10805 H 19805 10805	HP ± 19917 HP ± 19918	H 19942 1d $H = \begin{cases} 19953' & 1d \\ 19963' & 1d \end{cases}$	$\begin{array}{c c} L \\ L $	$ \begin{bmatrix} \\ 20037' \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	$ \begin{bmatrix} L & x \\ 20060' & 4984.95 & 20054.8 & 10ws \\ L & 120072' & 4981.9 & 20067' & 3d \\ \end{bmatrix} $	L # 20083 4977.4 20085 0 L # 20097 4974.7 20096 0 L # 20097 4972.0 70107	$ \begin{array}{c} L \\ L \\ x \left\{ \begin{array}{c} 20115' \\ 20124' \\ (20137' \\ 20137' \\ \end{array} \right\} \left\{ \begin{array}{c} 4969.6' \\ 4966.5' \\ 20137' \\ \end{array} \right\} \left\} \begin{array}{c} 0.0117' \\ 9d \\ 9d \\ 9d \\ 9d \\ \end{array} \right\} $	L 20154 (4962.7' 20145') . L 20154 4960.4 20154 0	L ± 20171 4956.15 20171.3 2nd L ± 20182 4955.40 20182.5 2nd L 20193 4951.00 20192.3 2nd 4951.00 20192.3 2nd	L 20201' 4948.1 20204 6d 1 20204 4945.7 20204 6d 1 4045.7 20714 8d	L {20223' 4943.0 2025 9d	20238' [[4940.3' 20236']]	$ \begin{bmatrix} L \\ 20248' \\ 20248' \\ 20268' \\ 20268' \\ 20250' \\ 202$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccc} HL & \left\{ \begin{array}{ccc} 20293' \\ 20299 \\ 20290 \\ 20290 \\ 4922.2' \\ 20310' \\ \end{array} \right\} & 0 \\ \end{array}$	L (4918.0 20328 0 HL 20343 (4918.0 20327 0 HL 20343 (4918.0 20337 0	L 20301 (4910) 20367 (100) 20367 (100) 100 (10	L $\left\{ \begin{array}{cccccccccccccccccccccccccccccccccccc$	H ‡ 20431'	H? ‡ 20479 L 20522.2 4871.70 20521.1 10s
TABLE I(C	E.T. N.T. N.T. $\mu(\mathrm{cm}^{-1})$ Type $\mu(\mathrm{cm}^{-1})$ Int. $\lambda(\mathrm{A})$ $\mu(\mathrm{cm}^{-1})$ Int.	$\begin{cases} 19822' H \\ + 108315 \\ + 108315 \\ - 108315 \\ - 108315 \\ - 10831$	$ \begin{bmatrix} 19840' & 19835' & 3a \\ 19867' & H & 19868' & 2d \\ 19868 & 2d \end{bmatrix} $	H 119833 3d H 119883 3d H 119883 3d	19904' [19887'	$\begin{cases} 19942 & H & 19942 & Id \\ 19074' & H & (19973' & Id \\ 19974' & 10975' & 1d \end{cases}$	$\begin{bmatrix} L & \pm \\ L & \pm \\ 20009 & 4996.2 & 20009 & 1d \\ L & 10000 & 140000 & 1d \\ L & 10000 & 10000 & $		$x = 20058$ L $x (20050' + 4984.95 = 20054.8 = 10 m s^{-1} + 20072' + 4981.9 = 20057 = 3d$	L # 20083 4977.4 20085 0 L # 20097 4974.7 20096 0 L # 4075 00107 00	$ \left\{ \begin{array}{cccc} 20124' & L & x \\ 20124' & L & x \\ 20136' & \\ 120137' & \\ 120137' & \\ 120137' & \\ 14967.7' & 20133' \\ 14965.5' & 20133' \\ 14965.5' & 20133' \\ 20133' \\ 9d \\ 9$	L 20154 (4962.7' 20145') C 20154 (20145') C 20154 (20154) C 20154 (20154) C 20154 (20156) C 20156 (201566) C 20156 (2015666) C 201566 (20156666) C 201566 (201566666) C 201566 (201566666) C 201566 (2015666666) C 201566 (201566666) C 201566 (2015666666) C 2015666666 (2015666666) C 2015666666666666666666666666666666666666	$t_{20177}^{(20177)}$ L $t_{20177}^{(20177)}$ 4956.15 20171.3 2 <i>nd</i> t_{201927}^{(20182)} 4955.40 20182.5 2 <i>nd</i> 4951.00 20192.3 2 <i>nd</i> 4951.00 20192.3 2 <i>nd</i>	$\begin{bmatrix} 20206' & L \\ 1 & 20204 & 4948.1 & 20204 & 6d \\ 1 & 20704 & 4948.7 & 20204 & 6d \\ 1 & 20714 & 8d \\ 20714 & 8d & 8d \\ $		20233' [20238' [4940.3' 20236']	$ \left[\left[20250' \frac{L}{202} \right] \left[\left[\left[20248' \right] + \left[\frac{4936.8}{202} + \frac{20243'}{202} \right] \right] 0 \right] \right] \right] $	$\ddagger \{20268' HL \\ \ddagger \{20280' HL \\ 120280' \\ 4931.7' \\ 20281' \\ 0 \\ 4929.2' \\ 20282' \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ $	20295' 20293' 4926.1' 20294' 0 20306' HL 20399' 4926.1' 20294' 0 20306' 4922.2' 20310' 0	x^2 20339' L $(4915, 0, 20328') = 0$ x^2 20355' HL 20343 $(4915, 9, 20337') = 0$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	20431 L {20423' 4997.0 20413 0 20431 L {20429' 4894.00 20427.5 108	(20451'H 20431' 20455'H 20456	(20512' H? ‡ 20479 (20512' L 20522.2 4871.70 20521.1 10s (20527'

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	Int.	10db 10db 10db	04b 94b 94b	9 <i>db</i> 9 <i>db</i> 8 <i>db</i>	$\begin{array}{c}10db\\9d\\0\\10d\\9d\\9d\end{array}$	9d 7d 8db 3vs		10 <i>vs</i>	$\begin{array}{c} 10d \\ 0 \\ 10s \\ 10s \end{array}$	10db	р6 1 д
	T. ^ν (cm ⁻¹)	22609' 22616' 22630' 22652' 22652'	22667' 22679' 22745' 22761' 22761'	22855' 22855' 22894' 22946'	22959' 22974' 22998 23018 23041 23074	23086 23103 23122 23151' 23164' 23299.3		23898.7 23961'] 23968	$23982 \\ 23988' \\ 23995 \\ 24015 \\ 24045' \\ 2405' $		24289') 24321 24350
) (H.	4421.7' 4420.4' 4417.7' 4414.7' 4413.5' 4412.6'	$\left(\begin{array}{c} 4410.4\\ 4408.2\\ 4398.2\\ 4395.4\\ 4395.3\\ 4387.$	$\begin{cases} 4378.1 \\ 4378.1 \\ 4371.4 \\ 436.7 \\ 4359.9 \\ 4356.9 \\ \end{cases}$	$\begin{cases} 4354.3' \\ 4351.5' \\ 4347.0 \\ 4343.1 \\ 4338.8 \\ 4338.8 \\ 4332.7$			4183.15 [4172.37 [4171.1	$\left(\begin{array}{c} 4168.6\\ 4167.5'\\ 4166.4\\ 4160.8\\ 4160.52\\ 4157.8'\\ \end{array}\right)$		(4110.0 ⁷ 4110.4 4105.7
	Int.						0 1 <i>d</i> 9 <i>d</i>	<i>p</i> 6			1 <i>d</i> 6 <i>d</i> 4 <i>d</i>
	$\underset{\nu(\mathrm{cm}^{-1})}{\mathrm{N.T.}}$	{22616' 22625' 22646'	(22663' 22731' 227765' 227765'	{22855 22855 22894 222894 222932	$\begin{array}{c} (222949' \\ (222962' \\ 23001 \\ 23043 \\ 23075 \\ 23075 \\ \end{array}$	23086 23104 23124 23154 23300.6 23300.6	$ \left\{ \begin{array}{c} 1 \\ 23680' \\ 23690 \\ 23747' \\ 23753' \\ 23782' \\ 23796' \\ \end{array} \right. $	{{23808' 23820' 23846' 23900 [23964'	23986' 24031 24050' 24075'	24098' 24182' 24213' 24257' 24257'	24299 24319 24333 24333
	Type	ц	н н н н	ר ר נ	പപപപപ	- - - - - - - - - - - - - - - - - - -	ан на н	ш ц	нын н	ччч	~ しまし
	E.T. $\nu(\mathrm{cm}^{-1})$	22609' 22628' 22642' 22656'	$\begin{array}{c} \begin{array}{c} 1 \\ 22732' \\ 22744' \\ 22766' \\ \end{array} \end{array}$	\$ 22945	# 22971 # 23003 23045 (23079 <i>c</i>	(23088c 23107 23160 23305.7	23720' 23747' 23758' 23785' (23800'	$\begin{cases} 23812' \\ 23826' \\ 23850' \\ 23883' \\ 23907' \\ (23969' \end{cases}$	(23985' 24056' ()(24056'	{24152' 24152' 24186'	24337
ontinued.)	R.T. $\nu(\mathrm{cm}^{-1})$	∳{22650' 22650'	22722' 22776'	•	(23015' 23055' 23072'	23113' 23152' 23175' 23645'	23712' 23759'	23812' 23853' 23918' 23918' 23965'	23990' 24040' 24067'	(24194' 24137' 24196'	24325'
ге I—(С	Int.	db db	ר פי כי כי	e e e	db nd		gg	<u>২</u> ১১		2 _ S S	ads a
TAB	-1						26) 10	3.8 10		22, 24, 24, 24, 24, 24, 24, 24,	33.38 8 33.38 8 33.38 8 8 3.38 8 8 8 8 8
	I.T. ^ν (cm	21668 21688 21698 21715 21715	21756 21776 21778 21778 21778	21820 21820 218340 218540 218560 218710 218710	21921 21943 21971 21989 21989		22183	22238		22419 2243 2243 22445 22445 22445 22445 22465	22549 22584 22584
	۱ (A) ۸	$\left \begin{array}{c} 4614.2'\\ 4610.7'\\ 4607.5'\\ 4603.8'\\ 4603.8'\\ 4601.6'\\ \end{array}\right $	4598.97 4598.97 4593.87 4591.57 4589.47	4579.57 4579.57 4576.87 4574.57 4572.77 4569.87	$\begin{cases} 4560.6' \\ 4556.1' \\ 4550.1' \\ 4546.4' \\ 4538.55 \end{cases}$		$\left\{ \begin{array}{c} 4505.9c\\ 4504.9c \end{array} \right\}$	4495.40 4492.30		$\left\{\begin{array}{c} 4459.3'\\ 4457.9'\\ 4456.1'\\ 4453.7\\ 44453.7\\ 4443.15\\ 4443.15\end{array}\right.$	4433.5 4430.05 4426.7 4424.0
	Int.			•	0 1 <i>d</i> 1 <i>d</i>	11 11 0	0	1d 2d	1d 1d "2" 1d "2"		
	N.T. ^{<i>p</i>(cm⁻¹)}	21668' 21674 21692' 21717' 21717'	21737 21759 21779	21873 21873 21873	± 21906 21931 ± 21966 ± 22014 ± 22014	*(22039) + 22052 + 22068 + 22082 + 22094 + 221127	$\begin{array}{c} \begin{array}{c} & \pm \\ & 22149' \\ & 22181' \\ & & 22186 \\ & & 222196 \\ & & 22234' \end{array}$	x22237 x22241 222244 22254.6 22254.6 222281 222281 222281 222300	22341 $1^{22360'}$ $x^{22379'}$ $x^{22392'}$	$\begin{array}{c} x \\ 22420 \\ x \\ 22437' \\ 22437' \\ 22468.3 \\ 22500.0 \end{array}$	22549 22566.5 22583
	Type	чч	ц ц ц ц ц ц ц ц ц ч ч	1111	~⊐ ¤⊐¤́⊐	~н нн	Н 2"L	ор Одда	ннн	니니 니니니	ЧЧЧЧ
	E.T. $\nu(\text{cm}^{-1})$	{21682' 21682' 21693' 21693' 21706'	± 21777	$\begin{array}{c} + & 21802 \\ + & 21828 \\ + & 1 \\ 21862' \\ + & 1 \\ 21879' \end{array}$	x{21915' 21950' 21970 {22014'	(22036' (22088' (22088'	*{22185' ''	22240 22255 ‡{22303' 27374'	t{22334' 22348' t{22348' 22385' 22397'	$x \begin{cases} 22420' \\ 22435' \\ 22470 \\ 22501 \end{cases}$	x{22539' ‡ 22554' ‡ 22566
	R.T. $\nu(\mathrm{cm}^{-1})$	21677' 21708'			21951' 21983' 22007'	(22033' (22072' (22101'	22186' 22202' 22236'	22258'	(22342'	22421' 22448' 22446' 22501'	22531'

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	Int.		
	$r_{\nu(\mathrm{cm}^{-1})}$	25803'} 25803'} 25820 25859 25859 25820'] ag.	
-	.н (А)	(3874.44 3871.7 3868.8 3866.1 (3857 to stro	
	Int.		
	$\underset{\nu(\mathrm{cm}^{-1})}{\mathrm{N.T.}}$	255192 25531 25533	
	$\mathbf{T}_{\mathbf{y}\mathbf{p}\mathbf{e}}$	ы ың ым ылып м ын н ндараа	
	E.T. $\nu(\mathrm{cm}^{-1})$	255797 25797 25797 25797 25797 25797 25797 255997 255997 255997 255997 255997 255997 255997 255997 266937 266937 266937 266937 266937 266937 266937 266937 266937 266937 266937 2669367 2669367 2669367 2669367 2669367 2669367 2669367 2669367 2669367 2669367 2669367 2669367 2669367 2669367 2669367 2669367 2669367 277387000 2669367 2773870000 277387000 277387000 2773870000 277387000 277387000 2773870000 277387000 2773870000 277387000 2773870000 2773870000 2773870000 27738700000 27738700000 277387000000 2773870000000000000000000000000000000000	
Continued.)	R.T. $\nu(\mathrm{cm}^{-1})$	255816 255816 255816 255816 255820 256026 26026 26026 26026 26026 26026 26026 26026 26026 277165 277175 27775	
TABLE I-(Int.	7d 2d 9d 7d 7d 7d 10d 9d 10d 10d 10d 10d 10d 10d 10d 10d 10d 10	
	T. $\nu^{(\mathrm{cm}^{-1})}$	24369 24398 24412 24438 244412 24438 24566 24566 24566 24566 24566 24566 24566 225373 255373 225573 225566 225546 2255482 2255482 2255552 2255552 225552 2255552 2255552 2255552 2255552 2255552 2255552 2255552 2255552 22555552 22555552 22555555	25764']
	H A(A)	4102.5 40957.5 40957.5 4095.2 4090.9 4087.2 4066.9 4066.9 4066.9 4055.4 4055.4 4055.4 4055.1 3937.1 3937.1 3937.1 3929.6	(3880.3'
	Int.	22 22 22 23 23 24 24 25 25 25 26 26 27 27 26 27 27 26 27 27 27 27 27 27 27 27 27 27 27 27 27	
	$v(\mathrm{cm}^{-1})$	24357 24356 244306 2244366 2244366 2244366 224530 245494 245570 245513 245513 2551357 2551357 2551357 2551357 2551357 2551357 2551357 2551357 2551357 2551357 255526 255556 2555666 2555666 2555666 2555666 2555666 2555666 2555666 2555666 2555666 2555666 2555666 2555666 2555666 2555666 2555666 2555666 2555666 2555666 2555666666666 25556666666666	25749
	$\mathbf{T}_{\mathbf{ype}}$	жыждылылылылы с соссос с с с с с соссериение с соссериение с с с с с с с с с с с с с с с с с с с	
	E.T. $\nu(\mathrm{cm}^{-1})$	24362 24362 244101 24415 244101 24415 244101 24415 24456 24554 24556 24551 24550 24551 24551 24551 24551 24551 25516 255	
	$\operatorname{R.T.}_{\nu(\operatorname{cm}^{-1})}$	24387' 24386' 24486' 24580' 24580' 24550' 25377 25377 25377 25574' 25574' 25574' 25574' 25574' 25574' 25574' 25574' 25574' 25574' 25574' 25574'	(25764'

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that they are due to magnetic interactions between samarium ions because of the extreme smallness of the effect. This phenomenon is not entirely absent in the chloride spectrum but it is interesting that this peculiarity should be most pronounced with the sulfate, whose spectrum in other ways seems to be that resulting from a crystalline field which is even stronger than that of the chloride.

It seems reasonable to assume that the easily distinguishable lines composing a multiplet group are the ones that reflect the separations between levels arising from electric splitting of a highly excited level which would be single and degenerate in the absence of the crystal field. Smaller separations between lines within a multiplet may indicate small electric separations (of the order of 10 cm^{-1} or less) of the wellshielded basic ${}^{6}H_{5/2}$ level, while the variability in apparent position of individual lines indicates that a further, possibly magnetic, perturbation affects the levels. This division of the experimentally observed effects cannot be proved at present, however, since both electric and magnetic phenomena would produce qualitatively identical results, i.e., with stronger or less homogeneous fields the magnitudes of both types of splitting would be greater. If the above explanation of the behavior of the lines is correct, one would expect that greater spectroscopic resolution, and perhaps lower temperatures, will reveal important facts concerning the nature of energy levels in solids. The longer exposures required for this procedure (they are already from 30 to 60 hours in length) would raise extreme difficulties at 20°K or lower.

In spite of the trouble in locating the exact position of the individual components of the doublets, it has been found possible to determine pretty definitely the situation of the lower levels that are most important spectroscopically. This has been done by working with centers of doublets and diffuse lines or bands. The results for the most clear multiplets (the same ones previously diagrammed for the chloride) are given in Fig. 2, though many of the less important faint *low-temperature lines* of these regions are not included. All of the most intense *high-temperature lines* in these multiplets can be explained by the use of the levels 0, 160, 188 and 225 cm⁻¹. Evidence from other more complex portions of the spectrum supports these values in general. Again *both constant energy separations* and *proper temperature behavior of intensity* have been made the requirements for the location of the lines in the diagram.

There is some evidence at higher temperatures for the existence of another level at approximately 245 cm⁻¹ from the basic one. This is most apparent at about 23,600 to 23,800 cm⁻¹, where no other simple explanation of the redmost ends of the bands observed at ethylene and room temperatures seems possible. The faint bands, which extend 300 and more cm⁻¹ from the nearest low-temperature line in the chloride spectrum and which probably require levels of corresponding separations, are not visible in the sulfate spectrum. This may be related to the general displacement of the sulfate levels to higher energy values, a shift perhaps just able to eliminate possibility of observing transitions from these levels.

In the foregoing consideration it is assumed that the basic levels of the ions of the two salts are similar (${}^{6}H_{5/2}$) and that the 145, 160, 204 and 217 levels of the chloride are related, respectively, to the 160, 188, 225 and 245 ones of the sulfate. In this connection it is interesting that though the chloride lines arising from the levels 160 and 217 seem to be most conspicuous, in the sulfate the 160 and 225 lines are most noticeable. This suggests a reversal of the relation just given within the doublets of levels.

The multiplet on the long wave-length end of the spectrum at 17,000 to 17,300 cm⁻¹ is one that offers some rather puzzling features. In the chloride, ethylsulfate and bromate spectra nothing of certainty could be gathered from it, hence it could not be used to determine the energy levels. The corresponding sulfate lines, however, do seem to indicate the presence of another level by the existence of two hightemperature satellites 78 cm⁻¹ from their respective low-temperature companions. It is not justifiable to base the existence of a level, whose Boltzmann population should allow it to be made more evident elsewhere in the spectrum, upon such isolated cases. Though the evidence at hand is inconclusive, it would not be surprising to have such a level be demonstrated eventually.



FIG. 2. Energy levels of $Sm_2(SO_4)_{3} \cdot 8H_2O$. Shaded areas represent bands. Figures in parentheses denote band edges measured at ethylene temperature. All other figures are from plates taken at 78°K. Levels which are actually probably double are indicated by "2."

It may be anticipated that the bromide spectrum also has a possible level at 58 cm^{-1} , evidence for which is based on similar scanty evidence in this region, beside the proper "monoclinic" levels somewhat higher.

Table II shows how well the lines agree with the level diagram assumed. In many other places on the plates the existence of the new lines brought into evidence at low temperatures by the lessened thermal agitation of the crystal and the higher population in the basic state makes it impossible to pick out satisfactorily the location of the high-temperature satellites. However, at ethylene temperature (169°K), when the fainter low-temperature lines have been "washed out," one is often able to locate additional confirmation of the postulated levels.

The most important relations between the sulfate and chloride spectra in other types of behavior are the following. The sulfate shows practically the same amount of displacement in the positions of lines upon changing the temperature from 298° to 20°K. At any given tempera-

ture the sulfate multiplets are shifted to shorter wave-lengths from the corresponding ones in the chloride spectrum, though only by about 10 to 20 cm⁻¹. On the other hand it will be recalled that the bromate acted in a different manner, manifesting slightly greater shifts with temperature change and possessing multiplets located 50 to 100 cm⁻¹ toward longer wave-lengths than

TABLE II. Prominent low-temperature lines and their hightemperature satellites (78°K).

Lt. line	Satelli	te A	Satelli	te B	Satellite C			
ν (cm ¹)	$\nu(\mathrm{cm}^{-1})$	$\Delta \nu_A$	ν(cm ^{−1})	$\Delta \nu_B$	$\nu(\text{cm}^{-1})$	$\Delta \nu_C$		
17891	17732	159	17702	189	17667	224		
17919	17758	161	17732	187	17692	227		
18949	18787	162	18762	187	18722	227		
20041	19882	159	Too di	ffuse	19815	226		
20056	19895	161	19868	188	19831	225		
20130	19968	163	19942	188				
20522	20361	161						
20621	20456	165						
22190	22030	160			21966	224		
22239	22074	163	22052	187	22014	225		
22255	22094	161						
23975	23814	161	23789	186	23750	225		

those of the chloride. The ethylsulfate of samarium resembled the bromate in these respects.

CONCLUSIONS

Again, this time in the sulfate spectrum, is proved the existence of more than three lower levels which are of importance in determining the absorption spectrum of the samarium ion. It seems impossible that crystal splitting of the basic ${}^{6}H_{5/2}$ level could account for them all, since only three new levels $(J+\frac{1}{2})$ can be expected when electric perturbations remove the degeneracy of such a state. A possible

explanation of these levels has been advanced by one of us.⁶

Magnetic interactions between samarium ions could increase the number of levels resulting from the ${}^{6}H_{5/2}$ one, but it is unlikely that these could be of sufficient magnitude since the magnetic moment of a samarium ion is so small. We have indicated that magnetic effects are probably responsible for the diffuseness and variability in appearance of certain of the absorption lines, an effect so small as to be unresolvable on the present plates.

⁶ Spedding, J. Am. Chem. Soc. 54, 2593 (1932).

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PHYSICAL REVIEW

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Elastic Electron Scattering in Potassium

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A method was developed for the measurement of slow electron scattering in vapors. Angular distribution curves from 25° to 160° were obtained for 5, 10, 15, 25, 50, 75, 100 and 150 volt electrons elastically scattered by potassium atoms. All curves contained a large peak near 100°. The scattering curves fell off rapidly for angles up to about 60° and rose rapidly for angles greater than about 130°. The position of the peak was found to shift to larger and then smaller angles as the energy of the colliding electrons

INTRODUCTION

`HE angular distribution curves for electrons scattered elastically by gaseous atoms generally contain a set of maxima and minima. These are referred to as diffraction patterns and are attributed to the diffraction of the associated de Broglie waves in their passage through the field of the atom.¹

If exchange effects are neglected the nature of these patterns is seen to depend almost entirely upon the electrons' distance of closest approach as taken from the classical theory and the magnitude of the field at that distance. Considerable progress has been made in our under-

was decreased. Henneberg's calculations which employ the Thomas-Fermi atomic field were found to give scattering curves whose general shapes agree quite well with the experimental curves. Best agreement occurred for the 5 and 50 volt electrons. When the potassium and argon experimental curves were compared it was found that the curves were quite similar for electron energies of 50 volts or more. For slower electrons the curves became more dissimilar.

standing of the relations between these factors by the comparison of diffraction patterns for various gases and for various energies of the scattered electrons.

So far scattering measurements have been made on several important groups of atoms, namely, the inert gases,^{2, 3} the halogens,⁴ and three elements from the third column of the periodic table, zinc,⁵ cadmium,⁶ and mercury.^{7, 8} The longest unbroken sequence of increasing

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¹ For general discussion of theory, see Mott and Massey, Theory of Atomic Collisions, Oxford Press (1933).

² F. L. Arnot, Proc. Roy. Soc. A133, 615 (1931).

⁸ Hughes, McMillen and Webb, Phys. Rev. 41, 154 (1932)

⁽¹⁹²⁾.
⁴ F. L. Arnot, Proc. Roy. Soc. A144, 360 (1934).
⁵ E. C. Childs and H. S. W. Massey, Proc. Roy. Soc. A141, 473 (1933).
⁶ E. C. Childs and H. S. W. Massey, Proc. Roy. Soc.

⁶ E. C. Churds and A. 142, 509 (1933).
⁷ F. L. Arnot, Proc. Roy. Soc. A140, 334 (1933).
⁸ E. B. Jordan and R. B. Brode, Phys. Rev. 43, 112



FIG. 1. Conglomerate absorption of $Sm_2(SO_4)_3 \cdot 8H_2O$. The substances at whose boiling points the spectra were photographed are indicated on the right, the corresponding temperatures on the left. *H* is placed above regions wherein the most prominent high-temperature lines are located.