Absorption Spectra of the Samarium Ion in Solids. IV. Absorption of $Sm(C_2H_5SO_4)_3 \cdot 9H_2O$ and Partial Energy Level Diagrams for the Sm^{+++} Ion as It Exists in Hydrated Crystalline Samarium Ethylsulfate, Samarium Iodide and Samarium Perchlorate

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The absorption spectrum of hexagonal $Sm(C_2H_5SO_4)_3 \cdot 9H_2O$ has been investigated in the temperature range 20° to 295°K. It is found to be simpler than that of the monoclinic $SmCl_3 \cdot 6H_2O$ previously reported. This is in agreement with theoretical conclusions that the greater symmetry of the hexagonal lattice should give rise to crystalline fields which would cause the energy levels of Sm^{+++} ion to be split apart less and to be in some cases more degenerate than would the more unsymmetrical monoclinic lattice. The ethylsulfate lines seem to be related chiefly to three lower levels, the basic one and two which are located higher on the energy scale by 55 and 65 cm^{-1}, respectively. Complete figures are given for the ethylsulfate absorption in the visible region. In addition results for the iodide and perchlorate of samarium are summarized. The lower levels found to be most important in these salts are situated at 0, 90, 107 cm^{-1} for the iodide; and 0, 104, 160 cm^{-1} for the perchlorate.

IN previous papers of this series[2] the absorption spectra of both single crystals and crystalline conglomerates of monoclinic $SmCl_3 \cdot 6H_2O$ and hexagonal $Sm(BrO_3)_3 \cdot 9H_2O$ were described. From the temperature behavior of the line intensities and from constant energy differences occurring throughout the spectrum it was possible to show the existence of certain low-lying levels of the Sm^{+++} ion in these solids, and energy level diagrams were constructed accordingly. This paper deals with a similar investigation of the absorption by hexagonal $Sm(C_2H_5SO_4)_3 \cdot 9H_2O$.

This second hexagonal salt is included in the series since the first one (the bromate) at low temperatures exhibited a phenomenon which somewhat complicated its spectrum. Though this complication could be partly eliminated in the interpretation of the spectrum, its underlying cause could not be determined definitely. It would seem desirable to have knowledge concerning a salt whose symmetry is great and whose spectrum does not have this complexity. The investigation of Spedding and Nutting[3] on the absorption of gadolinium compounds has indicated the choice of the ethylsulfate for such a purpose, and this is borne out by the facts now to be reported.

The spectra of two other salts were also found to indicate a greater symmetry of the fields about the samarium ion than in the chloride, but less than in the bromate and ethylsulfate cases. These are the iodide and perchlorate, whose absorption will be briefly described in the following.

Since in general the spectra of the three salts to be described at present resemble those of the chloride and bromate, we refer the reader to the former papers[2] for a general description of the appearance of the lines and bands, their behavior with temperature change, etc. In this report we shall treat only the points wherein the new spectra differ from the others. Just now we are content to confine ourselves to a descriptive discussion but intend at a later date, after reports on the interesting sulfate and bromide spectra appear, to make more thorough comparisons and deductions. In the meantime the data will be available to other investigators.

EXPERIMENTAL

$Sm(C_2H_5SO_4)_3 \cdot 9H_2O$ was prepared by mixing equivalent amounts of $Sm_2(SO_4)_3$ and $Ba(C_2H_5SO_4)_2$ in solution, centrifuging off the $BaSO_4$ precipitated, and recrystallizing the $Sm(C_2H_5SO_4)_3 \cdot 9H_2O$ crystals from the resulting solution by slow evaporation caused by a stream of dry air impinging on the surface. These operations were all carried out at room temperature and care was taken to avoid the presence

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[2] Spedding and Bear, Phys. Rev. **41**, 58, 76 (1932); **44**, 287 (1933).

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

of free acid, both precautions being necessary to avoid decomposition of the samarium ethylsulfate. The compound was obtained as fairly large crystals which were hexagonal prisms similar to those observed with the corresponding gadolinium salt, described elsewhere by Spedding and Nutting[3] and also by Benedicks.[4] The samarium crystals have been described by Jaeger.[5]

In other respects the experimental procedure was similar to that described previously. Both single-crystal and conglomerate spectra were photographed at 20°, 78° and 169°K and the conglomerate at room temperature. As with the bromate, the two types of spectrum were quite similar, being less different than in the chloride. The conglomerate spectrum, as usual, contained a few more lines and emphasized faint ones. The value of the single-crystal spectrum is simply the verification that the conglomerate spectrum is the correct one and not that of different crystal forms or decomposition products.

Results

As with other salts, the general presence and location of the multiplets are those typical of the samarium ion. More specifically the ethylsulfate groups of lines are situated toward longer wavelengths than the corresponding chloride ones, though remaining on the violet side of the bromate positions.

The temperature shift in positions of multiplets is slight in the ethylsulfate, less than in any of the other salts. In this case the high-temperature multiplets seem to shift slightly to the violet as the temperature is decreased, a behavior opposite to most, though there is not a marked difference. The red-most low temperature lines still shift to long wave-lengths. On the other hand the high temperature lines show a particularly noticeable shift to longer wavelengths as the temperature is lowered. The result of the two factors is a very apparent widening of the groups of lines at low temperatures, as well as a shift to longer wave-lengths. This widening seems to be caused chiefly by an increase in the difference in energy between the basic level and the slightly excited lower levels from which the high temperature transitions originate.

Table I gives the positions of the lines and bands measured with estimated intensities. As in previous studies relative positions of two types of lines designated by H and L, according to whether they increase in intensity at high or low temperatures, respectively, can be used to determine low-lying energy levels. From the data obtained it is possible to state with certainty only that two levels exist apart from the basic one. These are separated from the normal state by about 55 and 65 cm^{-1}. Other low-lying levels may exist, possibly somewhere between 90 and 130 cm^{-1}, but these cannot be proved conclusively.

Fig. 1 shows a diagram indicating in a limited spectral region the possible explanation of the lines found therein. This illustration explains most of the important high temperature lines in the regions included, which are the simplest portions of the spectrum, offering possibilities for the most certain interpretation. The two lines that are most noticeably absent from the diagram are the intense high temperature lines at 20,365 and 23,898. The former is close to a correct distance from the nearest low temperature line and is possibly related to an "invisible" low temperature line. The second might be evidence for a level at about 95 cm^{-1} above the basic one if it were not for its rather too large intensity at 20°K and the slow increase in intensity at higher temperatures. Other similarly placed lines offer the same difficulty and probably also are satellites of non-appearing low temperature lines.[6] Perhaps the best evidence for higher levels is located at about 26,500, but here, as in other similar cases, the structure

[4] Benedicks, Zeits. f. anorg. Chemie **22**, 413 (1900).
[5] Jaeger, Proc. Amsterdam Acad. Sci. **16**, 1095 (1914).

[6] This difficulty is not limited to the ethylsulfate lines. An attempt was made to explain anomalous lines in such cases by the use of several levels very close to the basic one, which is the level ordinarily supposed to develop the strong low temperature lines. If selection rules favor a transition from another very close level other than the normal one, then certain constant discrepancies in the separations between the strong low temperature lines and their high temperature satellites should be noticed. Obviously other explanations are possible. Though lower temperatures (for sharpness) and instruments of higher resolving power will be necessary to decide the matter, it is quite possible that such levels, caused by crystal splitting of the $^6H_{5/2}$ level of the samarium ion, are actually present in all of the salts studied.

TABLE I. *Conglomerate absorption lines and bands of* $Sm(C_2H_5SO_4)_3 \cdot 9H_2O$ *in the visible regions of the spectrum.*

Frequencies are given at four temperatures, *R.T.* 298°, *E.T.* 169°, *N.T.* 78°, and *H.T.* 20° K. Columns of intensity and character are completely filled for *H.T.*, and only occasionally occupied for *N.T.* In all other regions at 78° relatively the same intensities as at 20° may be assumed. The "Type" column indicates by *H* and *L* the lines or bands that show their strongest intensities at high or low temperatures, respectively. *HL* signifies that probably both types overlap, and a question mark is placed beside doubtful assignments. Character of line is indicated by the following letters: *vd, d, nd, s, vs* are degrees of increasing sharpness, and *b* denotes a broad line or band. Sharp edges are noted by *se*, and a number in quotation marks signifies a probable but not clearly resolved multiplicity. Primed frequencies and wave-lengths are band edges, but all other values, including those marked *c*, are centers of intensity. Intensities are estimated on a scale of ten, with very faint or doubtful lines given as 0.

R.T. (cm⁻¹)	E.T. (cm⁻¹)	Type	N.T. (cm⁻¹)	Int.	H.T. (cm⁻¹)	Int.
—	17254	L	17248	—	17248	3s
—	—	H?	17364	—	17354	1d
—	17404	H?	17390	—	17383	2d
—	—	L?	17453	—		
—	17787′	H	17786.8	6nd	17785.0	3vs
—	17799′	H	17796.0	5nd	17795.6	3s
17850′	17845′	L	17849.5	9nd	17850.2	10vs
—	17859′	H	17854	3d	—	—
17873′	17879′	H	17880	3d	17880′	0
17893′	17893′	H	17888	3d	17890′	
—	—	L	—	—	17898.6	1s
—	17901′	L	—	—	17905.3	10s
—	—	L	17907	9d	17908.3	10s
—	17911′	L	—	—	17910.8	8s
17916′	—	L	—	—	17915.8	1s
—	—	L	—	—	17921	2d "2"
—	—	L	—	—	17930	1d
—	—	L	—	—	17937	2d
—	17941′	L	17943	4d	17943.9	5s
—	—	L	—	—	17948	1nd
—	17953′	L	17950	4d	17952.6	5s
—	—	H?	17968′	1d	17970	1d
—	—	—	17977′	—	17979	1d
—	—	L	—	—	17986	0
—	—	L	—	—	17994	0
—	—	L	—	—	18004	0
—	—	L	—	—	18010	1d
—	—	L	—	—	18025	0
—	—	L	—	—	18032	1d
18820′	18818′	H	18816.0	7nd	18814.2	1s
18841′	18832′	H	18825.0	8nd	18824.7	2nd
—	18872	L	18876.9	9s	18878.1	10s
—	—	?	19015	0vs	Faintly evident	
—	—	?	19020	0vs	Faintly evident	
—	—	L	19126.5	2s	19125.3	2vs
—	—	L	Faintly evident		19150	0
—	19186	L	19185.2	4s	19185.0	4vs
—	19958′	H	19957.0	8nd	19954.1	3vs
19967′	19968′	H	19965	1d	19964	0
—	—	H	19971	4d	19971.6	3vs
—	19978′	H	19977.1	8nd	19974.5	3vs
—	19985′	H	19986.0	2nd	19985.3	1vs
19994′	—	—	—	—	19994′	0
—	—	—	—	—	20011′	—
20017′	20017′	L	20019.4	8nd	20019.4	9s
—	20024′	L	20024.5	7nd	20026.0	9s
20034′	20039′	L	—	—	20039.9c	1vs
—	—	H	20041′	—	—	—
—	—	—	20050′	1d	—	0
—	20058′	H	20059′		—	—
—	—	—	20066′	1d	20075′	—
20083′	20084′	L	—		20082.3	1s
—	—	L	—		20087.6	1s
—	—	L	20093c	3d	20093.8	5nd
20098′	20102′	L	20101c	6d	20097.4	8nd
—	—	L	20117	1d	20117	2d
—	—	L	—	—	20127	1d
—	—	L	20144	1d	20145	2d
—	—	L	—	—	20156′	0
—	—	L	—	—	20185c	1d
20367′	20365′	H	20365.4	9nd	20363.2	3s
20379′	20376′	H	20370	3d	—	—
20409′	20409′	H	20411.9	8nd	20410.6	3s
—	20420′	—	—	—	—	—
—	20428′	L	20432.4	8nd	20432.8	8s
20436′	20438′	—	—	—	—	—
—	20458′	H	20463	3d	20462	2d
—	20476′	L	20474	2d	20475.7	3s
—	20498′	L	20515	7d	20517	8d
—	20525′	L	20526	3d	20526	3d
—	—	L	20550′	—	20560	2d
—	—	L	20569′	—	20571.3	2nd
—	—	L	20586	—	20584.2	2nd

R.T. (cm⁻¹)	E.T. (cm⁻¹)	Type	N.T. (cm⁻¹)	Int.	H.T. (cm⁻¹)	Int.
20593′	—	—	20599′	—	—	—
—	20607′	L	20608′	—	20603.3c	6nd
—	—	—	20613′	—	—	—
—	20623′	L	20623′	—	20620c	8d
20631′	—	L	20640′	—	20634.9	3nd
—	—	L	—	—	20650c	2nd
—	20658′	L	20661′	—	20656c	2nd
—	20674′	H	20672′	8d	20669.0	4nd
—	—	L	—	—	20679	2nd
—	20688	L	20690′	—	20688	1nd
20698′	—	L	20701′	—	20698	1d
—	20709′	L	20716′		20720.3	5nd
—	20724′	L	20727′		20724.6c	9nd
20740′	—	L	—		20735.0c	4nd
—	—	L	—		20747.4	3nd
20771′	20764′	L	20759′		20761′	9db
—	20792′	—	20796′		20796′	—
20807′	—	L	20809′		20810′	6db
—	—	—	20822′		20824′	—
—	20834′	L	20836′		20835′	8db
20850′	20848′	—	20848′		20849′	—
—	—	L	20858′		20855′	7db
—	—	—	20866′		20867′	—
—	20886′	L	20876′		20880	4d
—	—	—	20885′		—	—
—	—	—	20893′		—	—
—	—	L	20905′		20902	4d
—	—	H	20930′		20926	1nd
—	20940′	H	—	8db	20938	1nd
20948′	20956′	H	20951′		20949	5d
20970′	—	L	20972		20968	3d
—	—	—	—		20975′	—
—	20991′	L	—		20990′	8db
20995′	—	—	20996′		20997′	—
21020′	21013′	L	21013′		21011′	8db
—	21039′	L	21031′		21045′	8db
—	—	—	—		21060′	—
21054′	21058′	L	21063′		21066′	8db
21078′	21073′	—	21078′		21081′	—
—	21097′	L	21095′		21100c	5d
—	21121′	L	21116′		—	—
—	—	—	21138′		21137′	2
—	21160′	—	21162′		21163′	—
—	21179′	L	21177′		21175′	5d
—	—	—	21265′		—	—
—	—	L	21283′		21274	1d
—	—	L	21327′		21329′	0
—	—	—	21342′		21349′	—
—	—	L	21363′		21361′	0
—	—	—	21378′		21383′	—
—	—	H	21415′	1d	—	—
—	—	—	21429′	—	—	—
—	21456′	—	21452′		—	—
21468′	21477′	H	21466′	8db	21460	5d
21493′	21492′	—	21487′		—	—
21511′	21506′	H	21501′	8db	21497	5d
—	21522	H	21511′		21515′	
—	21534	H	21533′	8db	21526′	5d
—	21539′	—	—		—	—
21550′	—	L	21552		21551	7d
—	21561′	H	21562	7d	—	—
21569′	—	L	21570′		21569′	9db "2"
21591′	21589′	—	21588′		21585′	—
21626′	21626′	—	21621′		21623′	—
—	—	L	21629′		—	8db
21646′	21640′	—	21641′		21643′	—
		?	21673		Faintly evident	
		L	21697		21697	1d
		L	21718′		21723′	0
			21728′		21735′	
	21748′	L	21746′		21747′	
	21767′		21758′		21759′	1d
		?	21789		Faintly evident	

TABLE I.—*Continued.*

R.T. (cm^{-1})	E.T. (cm^{-1})	Type	N.T. (cm^{-1})	Int.	H.T. (cm^{-1})	Int.
		L	21812		21805′	0
					21820′	
	21829′					
	21841′	L	21845		21846	1d
		L			21865	0
		L	21892′		21895′	1d
			21906′		21910′	
		L	21947′		21957′	0
			21967′		21972′	
	22051′	H	22049.1	3s		
	22063′	H	22059.2	2s		
22105′		H	22100.6	3nd		
22128′	22111	L	22110.9		22111.5	9vs
		L			22162.7	2vs
22158′	22164	L	22165.7		22166.7	10vs
22174′						
		L			22345	0
		L			22382	0
	22438′	H	22441	5d	22441	0
	22450′	L	22466	1d	22464.4	2s
		H?	22479	0		
		H	22495c	3d	22495	1s
22510′	22506′	H	22505.1	8nd	22501.4	4s
	22516′	H	22517.7	7nd	22517.8	3nd
	22531′	L	22534.5		22536.2	10s
22552′	22550′	L	22547.5		22548.7	10se
	22567	L	22573.8		22573.2	10se
		L			22593c	0
		L	22614′		22603c	0
		L	22632		22633	1d
		L			22645	0
		L	22666		22662	1d
	22679′	H	22681	3d	22682	0
	22695′	H	22692	2d	22690	0
	22714′	L	22713′		22717.3c	7nd
	22729′	L	22727′		22725.5c	7nd
	22747′	L	22755		22755.9	7s
	22771′		22771		22774	1d
		L			22806	1d
	22826′	L	22827′		22819	1d
		L	22837′		22831	2d
	22845′	L	22845		22844	3d
		L	22869		22862	1d
	22908′	L			22893′	
	22923′	H?	22923	2d	22922′	1vd
		L	22943c	1d	22943.6	2s
		?	22954c	1d	Obscured by	
	22972′	H?	22964	2d	plate edges.	
	22983′					
	23026	L?	23027	6d		
		L?	23047	2d		
		H	23288′	00		
			23306′			
		H	23310	Ovs		
		L	23361.2		23361.3	3vs
23712′		H				
23735						
23761′		H				
23786						
	23808′		23807′			
	23823′	H	23820′	2d	23811	0
		H	23844	2d	23843	0nd
	23859′	H	23857	1d		
	23862′	H	23866	2d		
23871′		H	23873	2d		
23891′	23901	H	23896	5d	23897.5	4vs
	23926′		23923′		23926.9	9s
23937′	23935	H	23933′	10d "2"		
	23944	H	23939.3	9nd	23937.5	6s
23960′	23950′					
		H	23963.8	8s	23962.5	3s
	23969	H	23972.4	6s	23973.0	3s
		H	23984.7	2nd		
		L			23992.3	1nd
		H	24005	1d	24009	0
		H	24012	1d		
24021′	24017′		24020′		24021′	
		L			24022.8	10s
	24025	L	24029′		24027.6	10nd
	24039	L	24037′		24035.2	10nd
					24042′	
24048′	24047′	L	24050′		24051′	10d
		L	24066		24066.3	6s
	24073′	L			24073.6	1nd
		L			24085.0c	5nd
		L	24088		24089.8c	6nd
24100′		L	24101		24101.8	4nd
		L	24111		24113.2c	5nd
		L	24120		24120.0c	5nd

R.T. (cm^{-1})	E.T. (cm^{-1})	Type	N.T. (cm^{-1})	Int.	H.T. (cm^{-1})	Int.
		L			24137.0c	1nd
	24157′	L	24145		24147.7c	4nd
	24172c	L	24170		24165.8′	6se "2"
					24175.0′	
		L			24182	0s
		L			24186.3	2nd
	24196′	H	24197	4d	24202	1d
	24214′	L	24213		24215.2c	5nd
		L			24223.0c	3nd
	24241′	L	24232′		24238	1d
		L			24250.2	2nd
	24261′	L	24261c		24263	6d "?"
		L			24276	1nd
	24290′	L			24287	1nd
		L			24300	2nd
	24304′	L	24305		24309.7	6nd
		L	24331		24332.1	2nd
					24350′	
		L	24360		24358′	3db
					24370′	
		L			24378	1d
		L			24389	1d
	24462	H	24463c	3d		
	24492′	H	24492.8	10nd	24492.8	4s
					24497.8	2s
	24501	H	24501	10d	24502.5	6s
24505′					24507.5	9s
	24515	H	24512	10d	24514.0	2s
24526′	24523′		24519′			
		H	24528.1	9s	24526.6	2s
	24533	H	24537.3	9nd	24537.6	2nd
24542′	24541′	L	24545.0c		24544.8c	10nd
	24552′	L	24550.1c		24549.8c	10nd
24559′	24560	L	24562.1		24562.0	10s
	24570	L	24571.9		24572.7	10s
	24583′	H	24589	3d		
	24596′					
	24603′	L	24602′			
			24614′		24610	1d
	24625′	L	24624′		24623	1d
	24634′		24636′			
	24654′	L			24655′	2d "2"
	24667′		24664′		24668′	
	24684′	L			24682	3d
		L	24692′		24689	3d
	24704′	L			24697	0
	24730′	L	24722		24723.1	4nd
	24744′	H	24738	5d	24739	4d
		L			24751	1d
	24760′	H	24763	2d	24771	2d
	24781′	H	24785	4d	24784	1d
	24803′	H	24798	4d	24797	2d
	24809′		24811′			
24815′		H	24816	10d	24814.8	2nd
		H	24831	10d	24828	8d
24841′		L	24842′		24842.4	10nd
24856		L			24852.4	10nd
		L			24862.7	10nd
		L			24872′	
					24874	10d
24894′	24898′		24905′		24905′	9
24920′	24916′		24923′		24921′	
24946′	24950′	L	24944′		24941′	10db
		L			24952.7	2nd
	24965′	L			24963.6	2nd
	24980′	L	24973c		24975.6	6nd
		L			24987c	3d
24994′		L			24995c	3d
	25002′	L			25006.2	3nd
25020′	25018′	L	25011		25015.0	8nd
	25030′	L	25024		25026.1	3nd
	25040′	L			25037.5c	3nd
		L	25042		25045.6	6nd
	25061′	L	25057		25059.7	4nd
25083′			25071		25078′	2
	25091′	L	25094		25093c	9d
25103′	25103′	L			25098.8c	9nd
25112′	25118′		25124		25118′	
	25128′	L				9b
25 138′	25137′				25133′	
		L			25141.9	1nd
		L			25153.7	1nd
		L			25166.0	4s
25172′	25177′	L	25175c		25176.9	4s
		L	25186		25183.7′	9se
25192′	25194′				25195.0′	
		L	25199c		25202	6d
	25223′	L	25229′		25221	1vd

TABLE I.—*Continued.*

R.T. (cm^{-1})	E.T. (cm^{-1})	Type	N.T. (cm^{-1})	Int.	H.T. (cm^{-1})	Int.
	25235′	L	25238′		25241.1c	4nd
		L	25244′		25249.6	5nd
	25253′	L	25258′		25257.6c	5nd
		L	25266		25268	1d
		L	25281		25282.4	7vs
		L			25292.8	0s
		L	25303′		25305	1d
		L	25321′		25315	1d
		L	25335′		25343	1d
		L	25356′		25359	1d
		L			25377	1d
		L			25388	0d
		L	25406		25407.9	3nd
		L	25418		25419.2	3nd
		L			25438	1d
		L	25451′		25456′	1d
			25466′		25470′	
	25501	H	25496	4d	25493	2d
25526′	25524	H	25516.5	8nd	25515.5	3nd
		L			25529	1d
					25540′	
25542′	25545′		25545c		25547′	
25554′		L	25556		25561′	9b
25569′	25563′		25567c		25566′	
		L	25584		25579	2d
25592′	25587′	L	25596	"2"	25589.9′	9se
25612′	25603′				25602.9′	
	25620	L	25620.2		25621.3	9s
25651′	25654	H	25646.0	5nd	25644	1d
	25666	H	25659.7c	3nd	25656	0
25671′		H	25669.4c	2nd	25669′	2b
		L			25681′	
	25698	H	25693.1	6nd	25691	2d
25704′		H	25701.3	2nd		
	25724	L	25723		25723.7	9s
25757′	25751	L	25752		25752.7	9s
		L			25775	1d
	25795	L	25795		25795	1vd
	25825	L	25825		25825	1vd
		L			25854	1d
		L	25861′		25868	1d
		L	25885′		25884	1d
		L	25920′		25924′	1db "2"
			25946′		25952′	
		L	25987		25980′	1db
					25997′	
		L	26023		26027	1d
	26323	H	26318.1	3nd		
		H	26474	1d		
26505′	26493′	H	26495c	1d		
26550′	26536′	H	26530c	2db	26525′	0
					26538′	
		H	26554	3d		
		L			26565.8	1nd
	26575′	H	26576.3	9nd	26575.4	3nd
		HL	26585.9c	10nd	26583.8	2s
	26598	H	26597.3c	10nd	26596.6	9nd
26604′		H	26610	10d	26609.0	7s
"2"	26615	H	26617	10d	26619.0	8s
26640′	26633c	L	26631		26629.7	10s
26662	26653	L	26650		26648.5c	10nd
		L			26654.4c	10nd
		L			26664.1	2s
26670′	26675	L	26673		26673.8	10se "2"
		L			26684	1d
26698′	26694	H	26692	9d	26691.9	3nd
	26718	L	26716.9c		26718.3	10s
		L	26723.8c		26725.5	7s
26735′		L	26735.8c		26737.4	8s
	26746	L	26746.3c		26747	9d
26770′	26759′	L	26770c		26772	6d
	26777′	L	26782′		26782	2d
	26795′	L			26794	1d
		L	26802c		26803c	5d
	26815′		26815′		26812′	"2"
		L	26826′		26827c	5d
		L			26832c	5d
26844′	26839′	L	26842c		26842.0	5nd
	26855′	L	26854		26854	6d
26873′	26875	L	26873		26875	3d
26900	26900	L	26897		26897c	7d
					26911′	"2"
	26915′	L	26921		26922	5d
		L			26934	0
26943′	26951′	L	26944		26946	6d
		L			26963	0
		L	26983		26983	2d
	26997′	L	27008		27009	3d
	27017′					
		L	27073		27075	1vd
		L	27158′		27166	1d
			27178′			

R.T. (cm^{-1})	E.T. (cm^{-1})	Type	N.T. (cm^{-1})	Int.	H.T. (cm^{-1})	Int.
		L			27197	0
		L			27225	
		H	27237	2d		0
		L			27253	0
		H	27267c	7d		
	27274′				27275.2c	4nd
27280′		H	27278c	10d	27279.7c	5nd
27300′	27290′	L			27295	1vd
	27310	H	27305.7	3nd		
	27331	L	27328.8		27329.5	9nd
		L			27334.4	3nd
		L			27348.3	2nd
27350′	27354′	L	27358.7c		27360.1	8s
27370′	27376′	L	27380′		27374	2d
		L	27406′		27407	1d
	27423′	L	27429′		27432	2d
			27440′			
	27472′	H?	27467′		27480c	8d
27480′	27485′	H?		10db "2"	27487c	10d
	27494′	H?				
	27511′		27508′			
27523′		?			27514	3d
	27530′	HL	27526′		27534c	10d
27543′	27542′	HL		10db	27544c	10d
	27547′					
27575′	27568′	H	27561′		27555	3d
	27584′	L?	27584′		27595c	10d "2"
27605	27610′	L?	27614′		27608c	10d
	27627′	L?	27629′		27636c	10d
27643	27657′	L?			27647c	10d
27685′		L	27685′		27672	5d
		L	27702		27702	4d
	27714′	L	27721		27721	6d
	27741′	L			27749	0
	27767′	L	27762		27766	1d
		L	27785		27785.7	5nd
27795′	27802′					
27825′	27822′	L	27812		27813	6d
27858′	27853′	L	27860′		27868c	5d
27883′	27886′	L	27877c		27879c	6d
	27901	L	27908		27911.5	5nd
		L	27939		27930′	2db
					27949′	
		L			28006	0
		L			28033	0
		H	28097c	2d		
28119	28109	H	28104c	3d	28103	1d
		L			28127	0
28158′	28160	L	28157		28156.4c	10vs
					28160.8c	7vs
28180′		H	28176	0		
			28188′			
28200′	28197′	H	28199	4d	28196	0
	28214′	H	28210c	4d	28209	0
28226′		?	28223.4		28224.9	1vs
		?	28230.1		28231.5	1vs
					28256c	2d
28261	28263	L	28263		28264c	9d
		L	28296		28298	3vd
		L	28330		28330	3d
		H	28590.7	1nd		
		H	28601.7	1nd		
		H	28622c	1d		
		H	28630c	1d		
		H	28643.3	4s		
28650′	28651	?	28654.4		28654.7	8vs
28672′	28677	?	28674.4		28675.0	10vs
		?	28685.6		28685.4	4vs
28800′	28803	H	28794	9d	28792.0	2nd
		?	visible		28803.1	1nd
		L	28818.2		28818.7	9nd
28830′		?			28832.2	1nd
	28848′	?	28842′		28843.5	1nd
	Too	L?	Too		28857.0	8s
	faint		faint		28882	2vd
					28901.7	7s
28933′					28928′	b
					28947′	
28973′					28963	d
Too					29003	d
faint					29019	d
					29058.3	nd
					29080	d "2"
					29100.0	nd
					29172	d
					29192	d
					29250	d
					29274	d
					29334	d
					29352	d
					29525	d
					29554.6	nd
					29582.6	nd

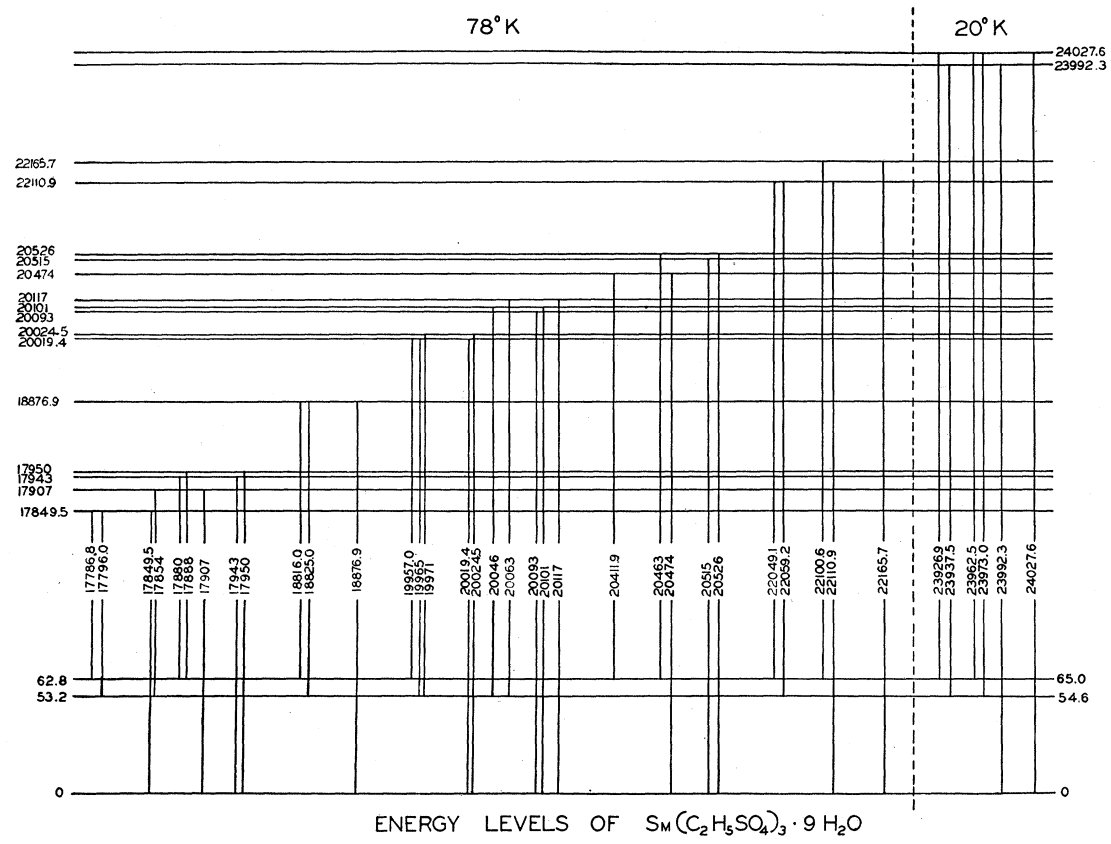

FIG. 1.

thereabout is so complex as to make it difficult to determine with which low temperature line a given satellite must be placed. Consequently, definite values for these higher levels cannot be assigned. Two very hazy bands between 23,700 and 23,800, making their first appearance at room temperature, may indicate levels over 250 cm^{-1} from the normal state, but one has to be careful in accepting too readily faint bands obtained only at high temperatures, since then there is a tendency for decomposition to occur upon absorption of the intense light beam. These particular bands, however, are not directly in positions occupied by intense sulfate bands, which would be the most probable results of decomposition. No other ethylsulfate bands offer supporting evidence for these relatively high lower levels.

Tables II and III give the evidence concerning the two levels at 55 and 65 cm^{-1}. Nearly all the lines agree within what we consider to be the accuracy in each case. The averages of the best values at the two temperatures indicate the separations 54.6 and 65.0 at 20°K and 53.2 and 62.8 at 78°. The mean position of the two excited levels is accordingly 59.8 at 20° and 58.8 at 78°. It can be estimated that the corresponding mean positions at the other temperatures are about 56 at 169° and 52 at room temperature.

Comparison with the measurements of Freed and Harwell[7] on the absorption of samarium ethylsulfate in the limited region of the violet where that is possible shows considerable discrepancies. Aside from a shift toward longer wave-lengths in their values which is several times our possible error, we are inclined to attribute most of the differences to a lack of sufficient dispersion and resolving power in the instruments available to the other authors. We were unable to locate a level at 12 cm^{-1}. The

[7] Freed and Harwell, Proc. Amsterdam Acad. Sci. **35**, 979 (1932).

TABLE II. *Prominent "low temperature" lines and their "high temperature" satellites (20°K).*

Low temp. line ν cm^{-1}	Satellite A ν cm^{-1}	$\Delta\nu_A$	Satellite B ν cm^{-1}	$\Delta\nu_B$
17850.2	17795.6	54.6	17785.0	65.2
(17949)			17885	64
18878.1	18824.7	53.4	18814.2	63.9
20019.4	19964	55	19954.1	65.3
20026.0	19971.6	54.4		
20039.9	19985.3	54.6	19974.5	65.4
20475.7			20410.6	65.1
20526			20462	64
20724.6	20669.0	55.6		
20983	20926	57		
21004	20949	55	20938	66
21551	21497	54		
21577	21520	57		
22548.7	22495	54		
22573.2	22517.8	55.4		
22755.9			22690	66
23992.3	23937.5	54.8	23926.9	65.4
24027.6	23973.0	54.6	23962.5	65.1
24572.7			24507.5	65.2
26629.7	26575.4	54.3		
(26651.4)	26596.6	54.8		
26673.8	26619.0	54.8	26609.0	64.8
26747	26691.9	55		
27329.5	27275.2	54.3		
27334.4	27279.7	54.7		
27534	27480	54		
28156.4	28103	53		
28857.0	28803.1	53.9	28792.0	65.0

( ) indicates center of two strong lines.

TABLE III. *Prominent "low temperature" lines and their "high temperature" satellites (78°K).*

Low temp. line ν cm^{-1}	Satellite A ν cm^{-1}	$\Delta\nu_A$	Satellite B ν cm^{-1}	$\Delta\nu_B$
17453			17390	63
17849.5	17796.0	53.5	17786.8	62.7
17907	17854	53		
17943			17880	63
17950			17888	62
18876.9	18825.0	51.9	18816.0	60.9
20019.4	19965	54	19957.0	62.4
20024.5	19971	54		
20101	20046	55		
20117	20063	54		
20474			20411.9	62
20526			20463	63
20722	20667	55		
21552	21594	58		
21579	21522	57		
22110.9	22059.2	51.7	22049.1	61.8
22165.7			22100.6	65.1
22534.5	22479	56		
22547.5	22495	53		
22573.8	22517.7	56.1		
22755			22692	63
24261			24197	64
25723	25669.4	54	25659.7	63
26631	26576.3	55		
26650	26597.3	53	26685.9	64
26673	26617	56		
26746.3	26692	54		
27328.8	27278	51	27267	62
27358.7	27305.7	53.0		
28157	28104	53		
28263	28210	53	28199	64
28654.4	28601.7	52.7	28590.7	63.7
28674.4	28622	52		

10 cm^{-1} interval between the 55 and 65 levels causes the only frequent separation of that order, but it obviously cannot be related to any really basic levels. We agree upon the existence of the 60 cm^{-1} level but find it double. We cannot confirm the higher levels suggested by Freed and Harwell, though it is not possible to deny them positively. The fact that they have found a level at about 160 cm^{-1} and that we have discovered the most important low excited level of samarium sulfate to be at such a separation might indicate that their crystal had partly decomposed. In several of our plates decomposition to the sulfate is indicated very clearly by the appearance of some of the stronger sulfate lines. However, we were careful in obtaining the photographs upon which this report is based to use only fresh and undecomposed material each time. None of the strongest sulfate lines were observed after such precautions.

As noted before, the ethylsulfate produces the best example studied so far of the "hexagonal" type of spectrum, first introduced by the bromate. The bromate, however, had a particularly peculiar behavior at low temperatures, and because of that and other factors tending to increase the complexity, the expected greater simplicity of spectrum was not quite so marked as might have been desired. The ethylsulfate is more satisfactory in this respect. In many places components of doublets can be observed to have approached each other and small groups of lines to have coalesced.

THE PERCHLORATE AND IODIDE SPECTRA

At this point mention may be made of two other salts which at first glance seem to have the spectrum of the hexagonal type. Their most important low-lying levels are closer together than are those of the "monoclinic" spectra as exemplified by that of the chloride.

These two new salts are the perchlorate and iodide, each prepared by dissolving the oxide in the proper acid and crystallizing the salt from the resulting solution. The perchlorate forms what appears to be a glass-like solid but under closer examination seems to be an interlocking network of fine crystals. The water of crystallization is unknown, and indeed its great tendency to take up water from the air would make it difficult to determine any definite composition. The iodide crystals are known to contain nine molecules of water per molecule of salt and under microscopic examination appear to be hexagonal, though again the hygroscopic nature

of the compound makes prolonged and thorough examination difficult.

We have not attempted to make a complete study of these salts, but examination of photographs of the spectra absorbed at 78°K has disclosed the most important levels. In such a study relative position and intensity, as well as appropriate separation, of pairs of neighboring lines are used to determine the levels. In the perchlorate many satellites occur at about 104 cm^{-1} from stronger lines, while with the iodide a separation of 90 cm^{-1} is most frequently observed. Other levels at 160 for the perchlorate and 107 for the iodide are indicated. Tables IV and V give the best evidence.

The positions of the multiplets are interesting. The iodide lines are displaced to longer wavelengths than the corresponding chloride multiplets, as are also lines of other hexagonal spectra to a greater extent. The perchlorate positions are about those of the chloride. This last fact along with absence of noticeably greater simplicity of spectrum and the existence of the 160 cm^{-1} level would indicate that the perchlorate has not a hexagonal spectrum but an intermediate type with definite leanings in the monoclinic direction. The iodide, too, shows an intermediate character, but its spectrum is more nearly the hexagonal type. The terms "hexagonal" and "monoclinic" in this connection signify simply greater and less symmetry, respectively, about the samarium ion in the crystal environment.

TABLE IV. *Samarium perchlorate satellites (78°K).*

Low temp. line ν cm^{-1}	Satellite A ν cm^{-1}	$\Delta\nu_A$	Satellite B ν cm^{-1}	$\Delta\nu_B$
18037	17933	104		
18925	18821	104	18784	161
18945	18842	103		
20011	19908	103	19851	160
20088	19983	105		
20138	20036	102		
20168	20063	105		
20449	20345	104		
20488	20384	104		
20519	20415	104		
20705	20600	105		
22166	22061	105	22002	164
22207	22103	104		
22241	22136	105		

TABLE V. *Samarium iodide satellites (78°K).*

Low temp. line ν cm^{-1}	Satellite A ν cm^{-1}	$\Delta\nu_A$	Satellite B ν cm^{-1}	$\Delta\nu_B$
17799	17709	90		
17859	17769	90	17752	107
18893			18787	106
19964	19874	90	19857	107
20001	19910	91	19892	109
20562	20471	91		
21572	21482	90		
21606	21516	90		
22197	22107	90		
22414	22323	91		
23950	23859	91		