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Absorption Spectra of the Samarium Ion in Solids. I. Absorption by Large Single Crystals of $SmCl_3 \cdot 6H_2O$

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The visible and ultraviolet absorption of large single monoclinic crystals of $SmCl_3 \cdot 6H_2O$ has been studied at seven temperatures between 15° and 298°K. Measurements of the absorption lines and bands are given as they appear at four of these temperatures. The influence of temperature on the positions of lines and multiplets and on the width and intensity of lines is discussed. All phenomena are explained on the basis of three direct effects of temperature change on the crystal: Lattice contraction and expansion, temperature vibration of the lattice with consequent fluctuations in crystal fields, and Boltzmann distribution of the ions between excited lower levels about 160, 210 and 300 cm^{-1} above the basic level.

IN THE past few years the spectra of gaseous atoms and the simpler gaseous compounds have been fairly well interpreted, and many relations between the energy levels of the substances under investigation and their physical and chemical properties have been established. Since a large part of chemistry is concerned with solids and solutions, it would be very desirable if these relations could be extended to apply to them. Unfortunately, very little is known of the energy levels of solids. This paper is the first of a series covering observations on the absorption of the samarium ion in various solid compounds and aiming at the determination of the characteristics of energy levels in solids. These papers will thus deal with one phase of a systematic study of the energy levels of ions in solids and solutions that is being carried out in this laboratory. The rare earths, as has been demonstrated elsewhere,[2] offer the simplest field for such investigation.

Freed[3] in his investigations of the magnetic susceptibility of $Sm_2(SO_4)_3 \cdot 8H_2O$ at various temperatures has predicted that the basic level of the samarium ion must have one or more levels lying near it. At higher temperatures a certain percentage of the ions, determined by the Boltzmann factor, would be distributed among these higher levels. Freed and Spedding[4] have verified this prediction by means of photographs of the absorption of $SmCl_3 \cdot 6H_2O$ at various temperatures. They have reported that the multiplets observed can be divided into two classes: one group with intensities greatest at 20°K and another that is completely absent at 20°, making its appearance at 78° and increasing in intensity with the temperature. They attributed the former group to electronic transitions arising from the basic level and considered that the latter group arises from the excited levels.

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[1] National Research Fellow in Chemistry.

[2] Freed and Spedding, Nature **123**, 525 (1929); Phys. Rev. **34**, 945 (1929); Spedding and Nutting, J. Am. Chem. Soc., in press (1932).

[3] Freed, J. Am. Chem. Soc. **52**, 2702 (1930).

[4] Freed and Spedding, Nature, reference 2.

Because of the multiplicity of the lower levels of the Sm^{+++} ion it has been chosen for these investigations. The effects of temperature variation and of different crystal environments upon the lower levels are of course reflected in the spectra observed, and under such varying conditions the samarium ion should prove a powerful tool in the attempt to determine the nature of the energy levels of solids. To date we have photographed at several temperatures and under various conditions the absorption spectra of $SmCl_3 \cdot 6H_2O$, $SmBr_3 \cdot 6H_2O$, $Sm(BrO_3)_3 \cdot 9H_2O$, $Sm_2(SO_4)_3 \cdot 8H_2O$, $Sm(C_2H_5SO_4)_3 \cdot 9H_2O$, and $Sm(ClO_4)_3 \cdot xH_2O$. In this first paper we are considering only the absorption of single crystals of $SmCl_3 \cdot 6H_2O$, but in a second, which we are submitting at the same time, the conglomerate or so-called "reflection" spectrum of the chloride is described in detail. In the latter paper we give a partial energy level diagram for the samarium ion as it exists in the $SmCl_3 \cdot 6H_2O$.

The original plates made by Freed and Spedding were not suitable for this study in that they were taken with low dispersion which left most of the multiplets unresolved. We have for this reason taken new photographs at higher dispersion. This new work has been done also with conditions under better control and at several new temperatures.

EXPERIMENTAL PART

The photographs upon which this report is based were obtained from two large crystals and several smaller ones of $SmCl_3 \cdot 6H_2O$ which had been prepared from samarium material of exceptional purity purified by the late Professor C. James of New Hampshire College. Several such crystals have been examined by Dr. A. Pabst[5] of this university, who has reported that their external symmetry is monoclinic. The large ones were obtained as transparent yellow tablets about 1.5 cm square and 4 mm thick. These were used to secure the visible spectra, for which a 3 m Wood grating with dispersion of about 5.5A per mm in the first order was employed. A single photograph at liquid nitrogen temperature was taken with a 7 m grating but was too faint to be used for any but confirmation purposes. The larger grating proved unsatisfactory because of the long exposures required and the limited supply of liquid hydrogen available at any one time. At all other temperatures the smaller grating was found to be just as satisfactory, since the temperature blurring was larger than the resolving power of the instrument. The quartz extension of the Dewar used for the several ultraviolet photographs required smaller crystals about 5 mm wide and 1 mm thick. The ultraviolet spectra were obtained with a Hilger E 185 instrument with prisms so mounted as to give at one time about 3A per mm, at another 2, in the λ3100 region.

Most attention has been paid to the visible part of the spectrum, since most of the absorption occurs in that region and the effects of greatest interest are observed there. To facilitate work in the visible region over the temperature range employed, a special (Pyrex) Dewar was constructed and

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[5] A. Pabst, Journal of Science **22,** 426 (1931).

fitted out as shown in Fig. 1. The chief features are the triangular windows left in two sides; the crystal house with filter (for elimination of frozen solids from obstruction of the light path); the crystal holder of piston shape introduced through a metal tube, which enables exchange of crystals during a run without introduction of air (especially important with liquid hydrogen); and the liquefier used to produce the liquids ethylene, methane and nitrogen, at whose boiling points pictures were taken. The liquefier, which can be removed for runs at liquid hydrogen temperature, is essentially an air-tight can fitting within the top of the Dewar with independent openings to the outside. The liquefying agent, liquid air, was introduced into the can and the desired gas condensed on the outside, from which it was allowed to drop to the bottom of the Dewar. To liquefy nitrogen the liquid air of the liquefier was evaporated under reduced pressure. Liquid hydrogen was transferred from the laboratory liquefier directly into the Dewar. In addition to room temperature and

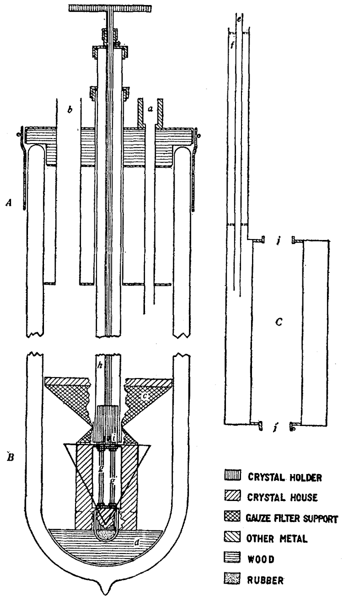

Fig. 1. Longitudinal cross section of Dewar for photography of visible absorption of solids at low temperatures, with *A*, top having inlet for liquid hydrogen, *a*, and outlet for gaseous hydrogen, *b*; *B*, crystal house with filter, *c*, and balsa "shock absorber," *d*; and *C*, liquefier for use with nitrogen, methane and ethylene having inlet for liquid air, *e*, and outlet for gaseous air, *f*. The triangular windows left in both sides of the silvered Dewar disclose the parts shown. The crystal is mounted between the two posts, *g* and *g'*, of the crystal holder, which can be introduced or withdrawn through the tube *h*. This tube is itself disconnectable from the crystal house at *i*, which permits insertion of the liquefier as follows. The liquefier when in position has the air outlet and inlet extending through and out of the hydrogen outlet of the top with the liquefier supports, *j* and *j'*, encircling the tube *h*. The inlet *a* is then used for entrance and exit of the gas to be liquefied. All of the above sets of concentric tubes and cylinders are made to fit snugly but not too tightly together, and the various metal parts, wherever possible, are constructed of German silver or Monel metal to avoid excessive conduction or corrosion. The dimensions of the Dewar are about 3 ft. by $4\frac{1}{2}$ in. It was found possible to secure a charge of hydrogen lasting 15 hours.

those of liquid ethylene, methane, nitrogen and hydrogen, the temperatures of nitrogen and hydrogen boiling under reduced pressure, about 60° and 15°K, respectively, have been utilized.

The photographs were taken with "Speedway" and hypersensitive panchromatic plates with exposures of from two to four hours, depending on the temperature (see below). It was found that slightly overexposed plates gave the most reproducible results with respect to band edges and structure within wide intense bands. The plates were measured with a comparator using a low-power eye piece. The whole gave a magnification of five times, which somewhat limited the accuracy, but was necessary since many of the lines are faint and diffuse.

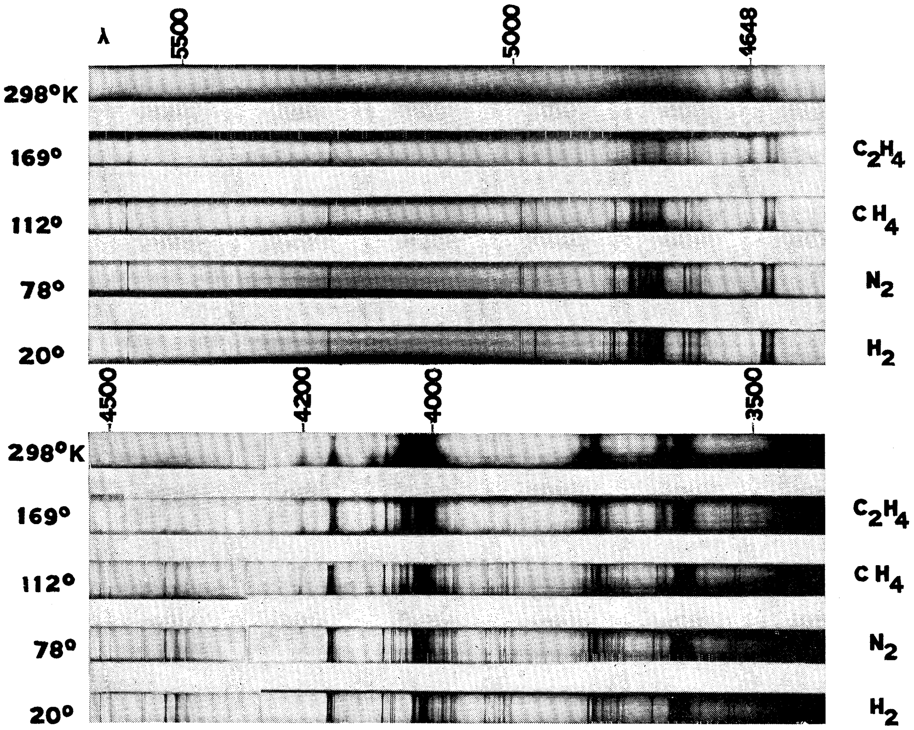

Fig. 2. Single-crystal absorption of $SmCl_3 \cdot 6H_2O$. The substances at whose boiling point the spectra were photographed are indicated on the right, the corresponding temperatures on the left. At λ4648 and λ4200 are the prominate high-temperature lines for which photometer curves are given in Fig. 3.

Results

In Fig. 2 are shown reproductions of the $SmCl_3 \cdot 6H_2O$ visible absorption spectrum at five of the seven temperatures investigated. (The photographs taken at "reduced-pressure" temperatures were practically identical with those for which the nitrogen and hydrogen boiled at atmospheric pressure.) An effort was made to keep the exposures as nearly comparable in intensity as possible. The pictures at room, liquid ethylene and liquid methane temperatures were taken under absolutely identical conditions as to crystal, position, exposure, etc., except for substitution of the proper liquid baths, but an increased transparency at lower temperatures made it necessary to shorten the exposure times when liquids nitrogen and hydrogen were used.

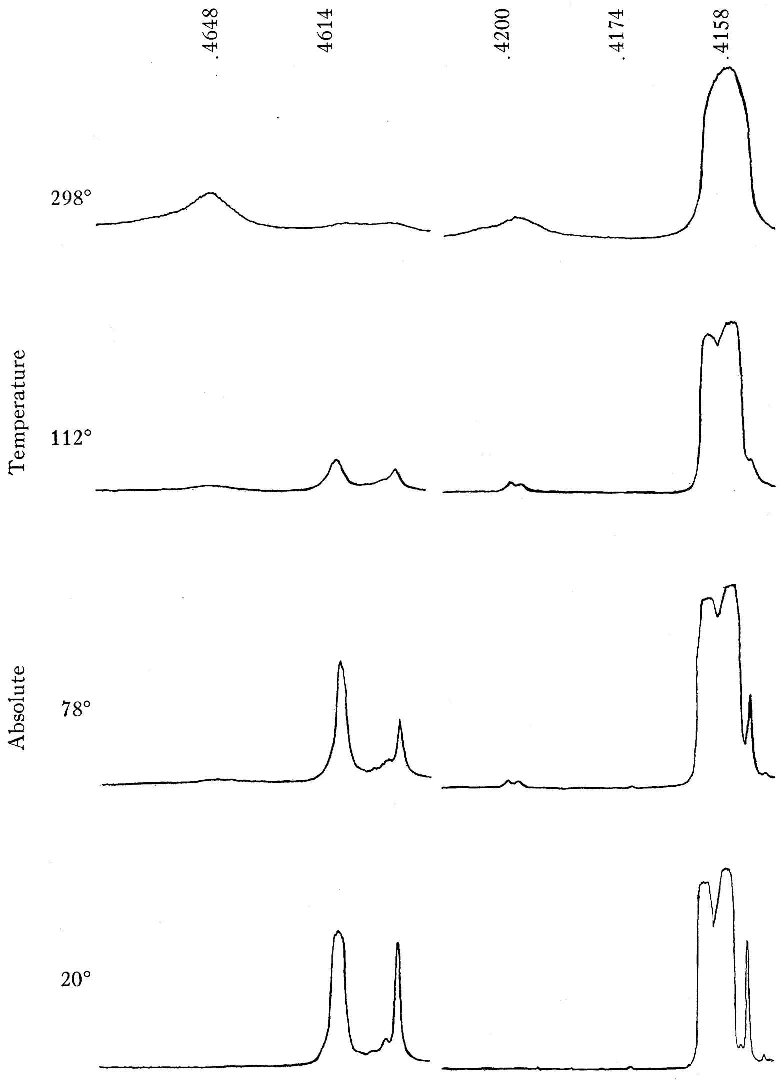

Fig. 3. Photometer curves.

Photometer curves of the two most outstanding multiplets of the visible region showing the decrease and increase of intensities are given in Fig. 3 for four temperatures. The ethylene curve is omitted because ethylene plates were found not to be comparable entirely in intensity under the high magnification and sensitivity employed in photometering the plates. This is caused possibly by a slight absorption of the ethylene itself in these regions.

Table I gives measurements of the absorption lines and bands at four temperatures. Room and hydrogen temperatures are of interest as the extremes, nitrogen temperature because it is the lowest at which the "high-temperature" lines appear appreciably (offering their greatest sharpness), while ethylene measurements represent a temperature at which the high-temperature lines have greater intensity and still the increased definition of a low temperature. In fact the Boltzmann factor begins to cause rapid fading just below liquid ethylene temperature. Exact study of the methane-temperature absorption is of little interest because of the similarity to that occuring at nitrogen temperature.

TABLE I. *Single-crystal absorption lines and bands of* $SmCl_3 \cdot 6H_2O$.

H (Type) = high-temperature line; L (Type) = low-temperature line; HL (Type) = probably both types overlap; R.T., E.T., N.T., H.T. = columns of measurements for room, ethylene, nitrogen and hydrogen temperatures, respectively; Int. = columns of intensity, complete for hydrogen temperature but only occasionally filled for nitrogen temperature. Intensity is estimated roughly on a scale of 10, with very faint or doubtful lines given as 0; s, vs = degrees of increasing sharpness; d, vd = degrees of increasing diffuseness; b = broad line or band, most frequently found with bands; "2," "3" = possibly double or triple, respectively. Primed values represent band edges; c, centers.

Type	R.T. ν (cm^{-1})	E.T. ν (cm^{-1})	N.T. ν (cm^{-1})	Int.	H.T. $\lambda(A)$	H.T. ν (cm^{-1})	Int.
L			17095		5848.1	17095	1d
L			17156.3		5827.20	17156.2	3s
L			17230		5802.2	17230	1d
L					5720.9	17475	1b
L		17877	17875.8		5592.65	17875.7	5s
L	17905′	17908	17908.0		5582.55	17908.0	7s
L	17912′		18103		5522.4	18103	1d
L			18124		5516.00	18124.1	1s
L	18930′	18929	18927.0		5282.05	18926.7	7s
L	18939′	18938	18937.4		5279.15	18937.2	7s
L			19032		5253.10	19031.2	2s
L					5221.4	19147	0
L	20016′	20026	20024.5		4992.55	20024.2	6s
L	20050′	20044	20042.5		4988.20	20041.8	4s
L		20112′	20115.5		4969.90	20115.5	7s
L		20124′	20123.6		4967.7	20124	2d "3"
L		20170′			4964.1	20139	1d "3"
L			20192		4951.1	20192	0
L		20200′	20204		4949.1c	20200c	1d
L					4947.5c	20207c	1d
H	20239′	20248′					
	20274′	20265′					
L		20408	20404.5		4899.65	20404.0	2s
L			20520.2		4871.90	20520.1	3s
L		20547	20544.8		4866.05	20544.8	4s
L					4862.3	20560.7	0 "2"
L		20577′			4858.8	20574	0
L			20585.7		4856.40	20585.7	8s
L		20592′	20595		4854.3	20595	1d
	20605′	20601′			4852.3′	20603′	
L					4851.5′	20607′	8d
		20618′	20611		4849.5′	20615′	
L			20631′		4845.4	20633	2d
L					4843.5	20641	2d
L	20642′	20645′	20648′		4842.2	20646	2d
L					4839	20660	1d

Table I. (*Continued*)

Type	R.T.	E.T.	N.T.	Int.	H.T.		Int.
L					4837.	20670	1d
L					4832.	20690	1d
	20698′	20703′	20706′		4828.1′	20706′	
L					4827.2	20710	5d
L		20724′	20722′		4824.7	20721	9d
L					4822.3	20731	8d
	20739′	20738′	20736′		4820.7′	20738′	
L					4817.8	20751	1d
L					4816.0	20758	1d
			20770′		4813.4′	20769′	
L		20773′			4812.8	20772	9d
L					4811.3	20779	9d
	20784′	20788′	20782′		4810.5′	20782′	
			20811′		4804.3′	20810′	
L					4803.1	20814	8d
	20819′	20819	20822′		4799.7′	20829′	
			20836′				
L		20842′	20840		4796.9	20841	7d
L			20861		4793.8	20855	5d
L		20866′	20864′		4791.9	20863	5d
L	20895′	20892′	20893′		4787.4	20882	3d
					4784.9′	20893′	
L			20902		4782.7	20903	10d
					4781.3′	20909′	
L	20919′	20922′	20927		4778.4′	20922′	
			20935′		4775.3′	20935′	6d
L					4772.1	20949	1d
L					4766.0	20976	1d
	20992′	20985′	20980′		4763.4	20988	1d
H	21024′	21024′	21025′		4757.	21015	0
		21069′	21069′		4745.2′	21068′	
L			21074		4744.1	21073	8d
		21085′	21078′		4743.0′	21078′	
L	21104′	21109′	21108′		4735.9c	21110c	3d
L		21129′	21118′		4734.3c	21117c	3d
	21154′	21145′	21147′		4726.9′	21150′	
L					4726.1	21153	2d
			21161′		4725.1′	21158′	
		21168′	21175′		4721.5′	21174′	
L			21178		4720.3	21179	4d
	21189′	21183′	21182′		4718.8′	21186′	
		21205′	21209′		4713.9′	21208′	
L					4712.7	21213	2d
		21225′	21224′		4711.6′	21218′	
		21302′	21301′		4693.0′	21302′	2d
L	21329′	21340′	21314′		4691.5′	21309′	
H	21351′						
		21397′					
H	21423′	21426′					
H	21489′	21480′	21486′				
	21526′	21510′	21504′				
L		21517	21515.1		4646.65	21515.0	1s
			21536′		4642.1′	21536′	0
L			21548′		4640.2′	21545′	
			21607′		4626.2′	21610′	
L	21629′	21620′	21620′				8b
	21646′	21639′	21639′		4620.1′	21639′	
L			21649′		4617.8	21649	3d
L			21661.8		4615.15	21661.8	4d
L		21674′	21675.4		4612.25	21675.4	5d
	21684′	21685′					
L		21691	21690		4609.1	21690	8b
	21701′	21696′					
H	22066′	22073					
	22084′						

TABLE I. (*Continued*)

Type	R.T.	E.T.	N.T.	Int.	H.T.		Int.
L	22157′	22153	22151.8		4513.25	22150.8	6s
	22169′						
L	22225′	22227	22221.6		4498.90	22221.5	2s
	22237′		22228.8		4497.45	22228.6	5s
L			22423.6		4458.50	22422.8	2s
L	22445′	22468	22466.9		4449.70	22467.1	6s
L	22494′	22488	22487.9		4445.55	22488.2	6s
L	22511′	22519′	22527.8		4437.75	22527.6	3s
L	22556′	22536′	22543.1		4434.8	22543	2d
					4416.4′	22637′	
L	22643′	22641′	22645′		4414.5′	22646′	8b
		22658′	22656′		4412.1′	22659′	
L	22675′				4409.4	22672	0
L					4405.1	22695	0
	22733′	22729′	22726′		4399.2′	22725′	
L			22739.6		4396.35	22739.8	6d
L		22748′	22742′		4391.70	22763.8	4d
	22762′	22758′	22763.6				
		22772′			4391.1′	22767′	
L					4385.6	22796	1d
		22809′					
L	22813′	22824′	22816.4		4381.60	22816.4	4d
L		22842′	22838.1		4377.50	22837.6	3d
		22866′					
L	22874′	22885′	22876		4370.4	22875	1d
L	22922′	22918′	22921.9		4361.45	22921.7	2d
	22942′	22926					
		22933′					
L	22966′		22965		4353.7	22963	1d
	22984′						
L			22995		4347.6	22995	3d
L		23017′	23023.8		4342.20	23023.4	2d
L		23033′	23058		4335.8	23057	2d
	Very	23057					
L	faintly	23086	23083		4331.1	23082	0
	present	23118′					
L		23131′	23123		4323.5	23123	2d
	23597′						
H	23653′						
H		23719					
H	23737′	23738	23731.8	2s			
	23753′						
H			23778	1d			
H	23783′	23786′	23789.2	4s			
		23792					
H	23802′	23806	23804.9	4s			
H	23824′	23811′	23840	0			
H		23857	23854	0			
	23879′	23879′					
H		23883	23881.5	1s			
	23902′	23901′					
H			23895.0	1s			
L			23912.3		4181.05	23910.8	1s
H			23928	1d			
L					4174.70	23947.0	2s
L		23951′	23949.8		4174.30	23949.5	3s
H		23973′	23973	1d			
H			23996	1d			
L					4165.30	24001.0	1d "2"
L					4162.85	24015.2	1d
	24030′	24034′			4159.4′	24035′	
L		24039	24036				10b
L			24051		4156.1′	24054′	
	24060′	24067	24066		4154.8′	24062′	
L		24081			4152.7′	24074′	10b
L			24081		4152.7′	24074′	10b
	24087′	24086′			4151.0′	24084′	

TABLE I. (*Continued*)

Type	R.T.	E.T.	N.T.	Int.	H.T.		Int.
L					4149.65	24091.6	2s
L		24105	24102		4148.0	24101	6dw
L			24122.0		4144.45	24122.0	4s
L					4142.85	24131.1	2s
L		24136′	24140.6		4141.25	24140.4	4sw“2”
L		24152′	24152.1		4139.25	24152.2	2d“2”
L					4137.20	24164.2	1d
L		24174′	24173		4135.5	24174	2d
L		24190′	24189.8		4132.75	24190.3	2d
L		24209′			4129.4′	24210′	2d
			24213		4128.6′	24215′	
	24223′	24228′			4126.9	24225′	
L			24229		4125.9	24230	2d
					4123.8′	24243′	
					4122.4′	24251′	
			24255		4121.6	24256	2dw
L					4120.9′	24260′	
		24266′	24266		4120.2′	24264′	
L		24273	24273		4119.1′	24270′	2d
					4118.2′	24276′	
L		24282′			4118.1′	24277	2d
	24298′				4117.4′	24280′	
H			24310.1	2d			
L					4111.9	24316	2d
H	24325′	24331	24324.2	1s			
LH	24350′		24352.1	3d	4105.4	24351	2d
L					4104.3′	24358′	2d
					4103.1′	24365′	
H			24367.1	3d			
	24377′	24372′					
		24375					
HL		24384	24381.7	3d	4100.2	24383	2d
H		24388′	24395.5	1d			
HL	24408′	24411	24408.6	3d	4096.3′	24405′	1d
					4094.1′	24418′	
HL	24434′	24428	24424.7	3d	4091.5′	24434′	1d
H		24444	24440.7	3d	4090.1′	24442′	
H			24457.8	1d	4087.8′	24456′	1d
HL			24472.0	1d	4086.1′	24467′	
			24489′				
H		24503	24499	1dw			
			24508′				
			24514.0	1d			
L	24541′	24536′	24537.3		4074.30	24537.3	8sw
L	24558′	24552′	24544.5		4073.20	24543.8	8sw
L		24570	24568.6		4069.15	24568.1	4s
L		24589	24586.2		4066.20	24586.0	4s
L	24613′	24619	24617.1		4061.10	24616.9	10sw
L		24637	24634.6		4058.15	24634.8	10sw
L	24644′	24654	24652.8		4055.15	24653.0	10sw
L					4054.85	24654.9	1s
	24675′	24681′	24674′				
H		24690′	24687	3d			
H			24699	4d	4048.1′	24696′	
H	24709′		24717	1d“2”			
H			24732	1d“2”	4043.1	24727	0
					4042.1′	24733′	
H	24740′	24745′	24747	4d	4040.4	24742	0
H			24759	5d	4037.9	24758	0
?					4036.1	24769	0
?	24768′	24775′	24772′		4034.6	24778	0
L					4031.50	24798	1d

TABLE I. (*Continued*)

Type	R.T.	E.T.	N.T.	Int.	H.T.		Int.
L	24805	24805′			4029.75	24808	1d
			24823′		4027.8′	24821′	
L	24830′		24827		4027.2	24825	7d
L			24846		4023.8	24845	7d
			24850′		4022.9′	24850′	
?			24864.9				
L			24876.7		4018.70	24876.7	5d
			24890′		4016.9′	24888′	
L			24896		4016.2	24892	10b
L			24950		4007.2	24948	
			24953′		4006.5′	24953′	
					4005.6′	24958′	
L			24965		4004.8	24963	5d
					4003.9′	22469′	
L	24975′	24978′	24984		4001.40	24984.1	3s
L			24996		3999.35	24996.9	2d
L			25006′		3997.65	25007.8	4s
			25007.6				
L			25018.3		3995.90	25018.5	4s
L	25020′	25026′	25024		3994.70	25026.1	3d
L			25033′		3993.7	25033	3d
L			25047.9		3991.30	25047.6	3d
		25068′	25067′		3988.5′	25065′	
L					3987.45	25071.7	3d
L		25074			3986.40	25078.1	3d
		25079′	25080′		3985.9′	25081′	
L	25090′				3984.90	25087.8	2s
L		25101′	25097		3983.35	25097.5	3d
L			25107		3981.70	25107.7	4d
			25114′		3980.8′	25114′	
L					3980.0	25119	5d
	25120′	25123′	25123′		3979.1′	25125′	
		25140′					
L		25145	25145.3		3975.70	25145.7	5d
		25153′					
L					3973.8	25158	2d
	25195′	25191′	25188′		3969.1′	25187′	
L		25199			3968.5	25191	7d
		25207′	25201′		3966.6′	25203′	
		25219′	25221′		3963.8′	25221′	
					3963.0′	25226′	4d
L	25235′	25229′	25233′		3962.1	25232	4d
L			25250		3959.1	25251	3d
L			25275′		3955.4′	25275′	
L					3954.4	25281	2d
			25284′		3953.2′	25289′	
L			25326.8		3947.30	25326.6	2s
L	25335	25331	25535		3945.5	25338	1d
L		25361′	25360.6		3942.20	25359.4	2s
L	25368′	25368	25370		3940.2	25372	1d
	25380′	25374′					
L			25422′		3932.50	25422.1	2s
			25430′				
L			25439′		3929.5	25441	1d
			25445′				
H	25475′	25479′	25486	3d	3921.5′	25493′	0
H	25500′	25505′	25501	3d	3918.9′	25510′	
L	25520′	25525′	25527.2		3916.35	25526.7	5sw
L	25548′	25543′	25537.5		3914.80	25537.0	4s
L					3912.3	25553	1d
	25575′	25567′	25570′		3909.6′	25571′	
L					3909.1	25574	3d
		25588′	25580′				
	25600′		25593′		3906.2′	25593′	

TABLE I. (*Continued*)

Type	R.T.	E.T.	N.T.	Int.	H.T.		Int.
		25622′			3901.7′	25623′	
L	25630′		25626.2		3901.20	25625.9	4d
	25647′	25643′	25637		3899.1′	25640′	
L					3897.90	25647.4	1s
L			25658		3896.25	25658.5	2s
L	25670′	25669′	25671.2		3894.35	25671.0	5s
		25673					
L		25686	25684.6		3892.30	25684.5	4s
	25692′	25691′					
		25715′					
L	25720′	25723	25719.5		3887.00	25719.4	5d
L		25733	25730.3		3885.45	25729.9	5d
	25750′	25738′					
	25790′	25788′					
L		25791	25786.8		3877.00	25786.0	4s
L		25805	25799.8		3874.90	25799.8	4s
L		25810′	25807		3874.00	25805.8	3d
L	25825′		25822.1		3871.65	25821.4	2d
L					3868.0	25846	0
L					3865.0	25866	0
H	26310′						
	26342′						
H	26395′	26406′	26394	0			
H	26430′	26425′	26409	1d			
L			26423.3	2d	3783.60	26422.5	2s
H			26437	0			
H			26453	1d			
HL	26457′	26468	26467.8	2d	3779.2′	26453′	1wd“2”
					3776.3′	26474′	
H	26490′	26488	26482.9	2d			
H		26513	26510.5	3d			
H		26526	26524.8	3d			
HL		26544	26541.5	3d	3767.7′	26534′	1dw
H	26553′	26558	26556.3	3d	3765.0′	26553′	
H			26570	1d			
	26600′	26609′	26608′		3756.85′	26610.3′	
L			26611		3756.35′	26614.2′	8s
L					3756.35′	26614.2′	8s
L		26624′	26618		3755.75′	26618.3′	
	26630′	26629	26620′				
L			26627.1		3754.60	26626.5	9s
	26657′	26657′	26659′		3749.5′	26663′	
L		26664			3749.1	26666	10d
		26670′	26670′				
L		26682c	26680		3747.4	26678	10d
			26682′		3747.0′	26681′	
L	26688′		26690.7		3745.65	26690.2	5s
L		26704	26700.9		3744.20	26700.4	6s
L			26714.3		3742.25	26714.4	5s
L	26725′	26722“2”	26727.6		3740.55	26726.4	2d
L		26747	26744.0		3738.20	26743.2	3s
L		26768	26764.4		3735.25	26764.3	5s
L	26775′		26775.2c		3733.75	26775.2	5s
L		26782	26780.9c		3733.00	26780.5	5s
L	26795′				3730.50	26798.3	1s
L	26820′	26815	26816.3		3728.05	26816.2	2d
L			26838		3725.10	26837.5	1d
L	26856′		26856.4		3722.40	26856.7	2d
L		26874	26869.4		3720.80	26868.5	4s
L	26877′		26884		3718.6	26884	0
L					3717.4	26893	0
L		26907	26906		3715.65	26905.6	4s

TABLE I. (*Continued*)

Type	R.T.	E.T.	N.T.	Int.	H.T.		Int.
L			26931′				
L			26933.4		3711.80	26933.6	4dw
L		26935′	26937.7		3711.25	26937.4	2d
		26939	26940′				
		26944′					
	26950′						
L		26957	26954.3		3708.90	26954.5	4s
L			26967.9		3707.10	26967.8	2s
L	26980′				3705.55	26979.1	1s
		26993′					
L		27001	26999.1		3702.80	26998.9	3d
	27012′	27010′					
L			27013.7		3700.6	27014.8	2d
L					3698	27035	0
L					3695	27055	0
			27076′				
L			27092′		3691	27085	0
	27120′	27124′	27129′		3684	27135	0
H	27160′	27141′			3679	27175	0
	27210′		27203′		3673	27220	0
H	27262′	27256′	27261′				
	27295′	27280′	27276′	1b	3665	27275	0
?			27303	0	3662	27300	0
L	27340′	27334′	27333.2		3657.55	27332.9	3s
L	27362′	27348′	27344.8		3656.00	27344.4	7s
L		27378	27374.1		3652.00	27374.4	3s
H			27392	1s			
HL	27410′	27411	27412.8	4s	3646.80	27413.4	2s
HL		27432c	27431.1	4s	3644.1	27434	1d
H	27443′	27450′	27445.9	4s			
H		27466′	27466.0	1d			
H		27487′	27480	1d			
		27511′	27519′		3632.6′	27521′	
		27548			3629.1′	27542′	
L	27557′	27556	27553				
					3627.5′	27559′	9d
L		27571	27569c		3626.8′	27565′	9d
	27585′	27576′			3625.4′	27575′	
L		27594	27591.4		3623.30	27591	9d
	27610′	27608′	27606′		3622.0′	27601′	
L					3621.4	27606	
L		27614	27615		3620.3	27614	6d
L		27634	27629		3618.2	27630	9d
	27638′	27647′	27640′		3617.6′	27635′	9d
L		27663′	27668′		3616.3	27645	3d
					3613.5′	27666′	
L	27685′	27681′			3612.8	27671	6d
L		27688			3610.7	27688	8d
L		27708			3608.2	27707	8d
	27715′	27714′					
L					3605.9	27724	6d
			27726′		3605.6′	27727′	
L		27748′	27743		3603.50	27742.9	6d
L	27765′		27761′		3600.80	27763.8	3d
L			27764		3599.60	27773.1	2d
L		27771′	27783		3598.25	27783.2	3d
		27787′	27785′				
L	27795′		27795		3596.65	27795.8	2s
L			27806		3594.8	27810	1d
		27822′	27821′				
L			27826		3592.90	27824.7	2d
L		27840′	27832′		3592.0	27832	2d
L			27861		3588.2	27861	2d
L			27881		3585.6	27881	2d
L	27895′	27890′	27896′		3583.0c	27902c	3d
L	27910′	27912′	27910′		3582.1c	27909c	2d

Table I. (*Continued*)

Type	R.T.	E.T.	N.T.	Int.	H.T.		Int.
L			27933		3578.95	27933.3	2d
L			27961		3575.2	27963	1d “2”
L					3571.6	27967	1d
H		28003					
L					3466.0	28034	0
H	28045′	28043			3563.7	28053	0
	28068′				3561.3	28072	0
H	28100′	28097′	28094′				
	28123′	28118′	28121′				
L	28162′	28164	28161.3		3550.00	28160.8	3s
	28183′						
L			28198		3545.3	28199	1d
L			28236′		3541.0	28233	1d
L			28246′		3539.8	28242	1d
L	28250′	28258′	28256.9		3538.05	28256.2	4s
L		28264	28264.5		3537.05	28264.2	4s
L	28278′	28270′			3533.9	28290	0
L					3532.2	28303	0
	28320′	28319′					
L		28324	28322.2		3529.75	28322.5	5s
L	28340′	28328′	28334.5		3528.45	28333.2	1s
L			28662.4		3487.93	28662.1	2vs
L		28669	28667.8		3487.34	28667.0	3vs
L					3485.9	28679	0s
L		28694	28691.3		3484.49	28690.4	3vs
L					3482.8	28704	0
L			28719.8		3481.05	28718.8	3vs
L		28732	28733.2		3479.34	28732.9	2vs
L			28745		3478.25	28742.0	1s
L			28760		3475.50	28764.7	1vs
L		28768′	28772.2		3474.58	38772.3	2vs
	28780′	28797′					
H		28827′	28833.9	0			
H	28852′		28845	0			
L			28856.4		3464.55	28855.5	4s
L			28877		3462.3	28874	0
	28882′	28885′					
L			28894.3		3460.00	28893.7	5s
		28906′					
L		28928′	28926.9		3456.10	28926.2	4d
L	28933′		28939c		3454.6	28939	5d
L			28949c		3453.6	28947	5d
	28962′	28957′					
L		28990	28990		3448.50	28989.8	6d
L					3446.7	29005	1d
	29027′	29020′	29023′		3444.6′	29023′	
L			29027.7		3444.05	29027.3	6d
L			29040.8		3442.50	29040.4	6d
	29053′	29052′	29048′		3441.7′	29047′	
L		29081	29078		3438.2	29076.7	6d
L			29102.1		3435	29104	0
L			29125.4		3432.45	29125.4	1d
L			29138		3430.9	29139	2d
L		29152	29151		3429.3	29152	3d
L	29166′				3428.1	29162	2d
L	29189′	29184	29186		3425.4	29186	2d
L			29206		3422.9	29207	1d
L	29221′		29220.7		3421.30	29220.3	1d
L		29239′	29237		3419.3	29237	1d
	29248′		29256′		3417.2′	29255′	
L					3416.9	29258	3d
L	29264′				3415.9	29266	3d
	29285′	29272′	29270′		3915.6′	29269′	
L					3412.0	29300	1d

TABLE I. (*Continued*)

Type	R.T.	E.T.	N.T.	Int.	H.T.		Int.
	29324′	29316′	29316′		3410.4′	29314′	
L					3407.5′	29339′	1b
	29349′	29342′	29356′		3406.4′	29348′	
L					3402.4	29383	1d
L			29641.1		3372.85	29640.0	4s
L	29654′	29655	29656.3		3371.10	29655.5	3s
	29674′						
H	29817′						
	29858′						
H	29883′						
	29906′						
LH	29961′		29969.8		3335.90	29968.1	4s
	30000′						
L	30037′	30038′	30043′		3327.50	30044.2	7d
		30047	30048′				
L		30058′	30055		3326.50	30052.9	5d
			30056′				
			30076′		3324.00	30075.8	7d
L	30101′	30082	30081′				
L			30137′		3317.15	30137.9	3s
L			30153′		3316.25	30145.8	3s
L			30198′		3310.30	30200.1	4s
L		30203	30205′				
L	31138′		31141.7		3210.40	31139.8	6s
	31157′						
H	31197′						
	31201′						
H	31233′						
	31252′						
H	31283′	Not photographed					
	31301′						
L	31346′		31345′		3189.5′	31344′	10d
	31365′		31352′		3189.0′	31349′	
L			31377.3		3186.20	31376.1	8s
	31389′		31385′		3185.4′	31384′	
L			31386′		3185.2′	31386′	10d
	31405′		31392′		3185.0′	31388′	
			31416′		3182.3′	31415′	
L	31418′		31417.3		3182.10	31416.5	9s
L			31420.5		3181.90	31418.5	9s
	31438′		31423′		3181.8′	31420′	
L			31444′		3179.30	31444.5	9d
L	31449′		31445.5		3178.70	31450.3	9d “2”
L			31453.0				
	31462′		31455′				
L			31479′		3175.7′	31480′	9d “2”
	31492′		31487′		3175.3′	31484′	
L			31549.6		3168.90	31547.5	5d
L			31564.4		3167.55	31561.0	4d
L			31576.7c		3165.85	31578.2	3d
			31581.2c				
	31592′		31588′		3164.8′	31588′	
L			31599′		3133.7′	31599′	10b
	31646′		31635′		3160.9′	31627′	
H	32532′						
	32553′						
H	32573′		32581.1				
H	32592′		32592.3				
L	32696′		32698.0		3057.60	32696.1	10s
L	32713′		32739.6		3053.70	32737.5	5s
L	32755′		32752′		3052.4′	32752′	10b
	32774′		32767′		3051.2′	32764′	
H	33503′						
	33512′				Not photographed		

TABLE I. (*Continued*)

Type	R.T.	E.T.	N.T.	Int.	H.T.	Int.
	33524′					
H	33541′		33538.8			
L	33695′		33700.8			
L	34392′		34386.7			
	34407′					
L	34421′		34425.7			
	34436′					
L	34472′					
L	34486′		34486			
L	34510′		34513			
H	35689′					
	35719′					
L	35782′		35790.3			
	35805′					
L	35846′		35853.1			
	35868′					

From measurements of seven nitrogen and three hydrogen plates in a region where the lines are fairly sharp it has been found that because of the nature of the lines and the low magnification used in measuring them it is difficult to expect results to be accurate within less than 0.05A. Band edges and more diffuse or faint lines cannot be given even to this accuracy. As a result of measurements of the best parts of two plates at each temperature, with confirmation by sharp lines of others, we have the figures as quoted in the table. Wave numbers are given, with wave-lengths for hydrogen temperature only. Figures are quoted to units or tenths of units (cm^{-1}) according to the accuracy thought possible. Intensities are estimated for hydrogen temperature only, except for an occasional nitrogen-temperature line which does not appear at hydrogen temperature, i.e., a high-temperature line. These intensities are very roughly determined on a scale of ten and represent the appearance of the lines on our plates. They are meant only for rough comparison and consequently are not to be used from one region of the spectrum to another. It will be noticed that only the most intense lines have appeared in the ultraviolet region. This is probably due to the fact that much thinner crystals were used in that part of the investigation.

DISCUSSION OF RESULTS

Effect of temperature on the positions of lines and multiplets

In general the centers of the multiplets shift to the red with decreasing temperature. At the same time the separations of the lines within the multiplet become greater, so that, although most of the lines are shifted to the red, occasionally one on the high-frequency side is shifted to shorter wavelengths. The shift in either direction is small, rarely over 5 cm^{-1}, certainly not over 10 cm^{-1}, and takes place mostly above liquid nitrogen temperature. These results are in good accord with those already reported for gadolinium compounds.[6] Such shifts are probably caused by effects discussed in the

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[6] Freed and Spedding, Phys. Rev., reference 2.

previous report, briefly, the contraction of the crystal which brings the neighboring ions closer to the samarium ions and thus increases the field acting on them. This would result in a greater spreading of the levels, just as an increased external electric field would. The closer approach also would be expected to affect the higher excited levels more than the deeper basic level, so that the multiplets would be shifted to the red. This effect is again demonstrated by the fact that the red shift of the multiplets is greater for the high-energy levels which cause the ultraviolet lines, than it is for the levels that are responsible for the lower-energy multipets to the red.

Width of lines

At liquid hydrogen temperature the lines can be divided into three classes: (1) broad sharp lines which are undoubtedly narrow multiplets with intense outer components; (2) fine sharp lines, relatively few in number, which are probably truly single; and (3) narrow diffuse bands which are also unresolved multiplets but whose edges are either faint or whose levels are not constant over the time of photographic exposure. (A similar effect of temperature is discussed for wider multiplets.) In the table these are designated respectively, by s, vs and d. In addition wide bands are indicated otherwise.

As the temperature is increased all these lines become broader and more diffuse at the edges. The higher the temperature the more pronounced the effect, with the result that at room temperature most of the multiplets have merged into broad diffuse bands. These facts are also in good accord with the theory that the multiplets are caused by the electric fields of the neighboring ions. At low temperatures the oscillating movement of the neighboring ions would be absent and the magnitudes of the fields fairly constant during the length of the photographic exposure. As the ions begin to move at higher temperatures the fields vary correspondingly, and at one instant the levels might be split but slightly, while at the next, a momentarily increased field would cause wider separations. The photograph registers the integrated effect over a large time interval, which appears as a blurring of lines.

Effect of temperature on the intensity of lines

The lines can be alternatively divided into three groups on the basis of their intensity changes with temperature.

(1) A large group, present on every plate, increase in intensity as the temperature is lowered. This group can be divided into two subgroups: in one the lines are located in the violet and ultraviolet and show very little intensity change, while in the other, which is situated between 6000 and 4320 A, a marked intensity change with temperature is observed.

(2) Many fainter lines appear on the violet sides of the multiplets. These are weak at hydrogen temperature and rapidly fade out as the temperature is raised.

(3) A group of lines located on the red side of each multiplet are absent at 20°K but appear at all higher temperatures, usually increasing in intensity with the temperature. A few, however, pass through a maximum and then decrease in intensity as the temperature is raised, for reasons which shall appear later.

The first group, which we call a low-temperature group, consists of lines which originate from transitions between the basic level and excited higher ones.[7] The lines of the second group are probably similar in origin to the first group but are fainter because of low transition probabilities.

The lines of the third group, which we term high-temperature lines, originate from transitions between several low-lying levels situated in groups separated from the basic level by about 160, 210 and 300 cm^{-1}, etc., and the same high excited levels that cause the low-temperature lines.

The intensities of both of these groups of lines will depend in part on the population in the lower levels, and this in turn will be governed by the Boltzmann factor. At hydrogen temperature the number of ions of energy corresponding to the excited lower levels will be extremely small, and consequently the lines originating from these should be absent. At liquid nitrogen temperature and higher these high-temperature lines are permitted by the Boltzmann factor and should increase in intensity. As the population in the excited lower levels increases, that of the basic level, and consequently the intensities of the lines arising therefrom, should decrease.

A factor which tends to mask the intensity changes of the low temperature lines is their great intensity. Certain strong lines and bands may be completely absorbed before the light has penetrated the whole path through the crystal. Consequently, a change in intensity would not be noticed.

The intensities of the lines depend also on the transition probabilities, which are not entirely independent of temperature in solids. In the case of the group of multiplets between 6000 and 4320A this may be responsible for the great decrease in intensity, which is enough to make some of these multiplets almost disappear at room temperature.

Probably another factor aiding this abnormal decrease in intensity is the fluctuation of the crystal field at high temperatures previously mentioned. Under such conditions the coupling between the lattice and the orbits of the electrons or between the orbital and spin momenta of the electrons may be broken, especially in the final higher levels, and many of these levels may thus become potentially unstable, just as many similar levels do in the case of diatomic molecules. An electron jumping to one of these unstable levels would not be sharply quantized and would give rise to a continuous absorption. This

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[7] This basic level may be nondegenerate up to about 20 cm^{-1}, since it would be necessary for us to go to liquid helium temperature to detect the change in population between levels of this separation. It is possible to look for levels of this sort in the position of the lines themselves. However, since the separations of the sub-levels composing the "basic level" appear to be fairly small multiples of our error in measurement and because such separations frequently cause the lines to be wide or diffuse and are often unresolved, such levels would be very uncertain. Nevertheless, as we shall show in the paper on the conglomerate spectra, a degeneracy covering about five inverse centimeters is highly probable.

is observed to cause a continuous "general" absorption, which has already been mentioned to occur at high temperatures and which makes necessary at room temperature almost twice the exposure required at hydrogen temperature to secure the same blackening of the plate.

On the basis of the explanations given above for the intensity changes of the absorption lines it would appear possible to construct an energy level diagram for Sm IV. However, in the conglomerate spectra many additional lines appear or faint ones are intensified, with the result that more complete and convincing evidence is presented therein for the existence of the various lower levels we have postulated. Consequently a more complete and exact account of the various separations observed between the corresponding high- and low-temperature lines follows in the second paper of this series.

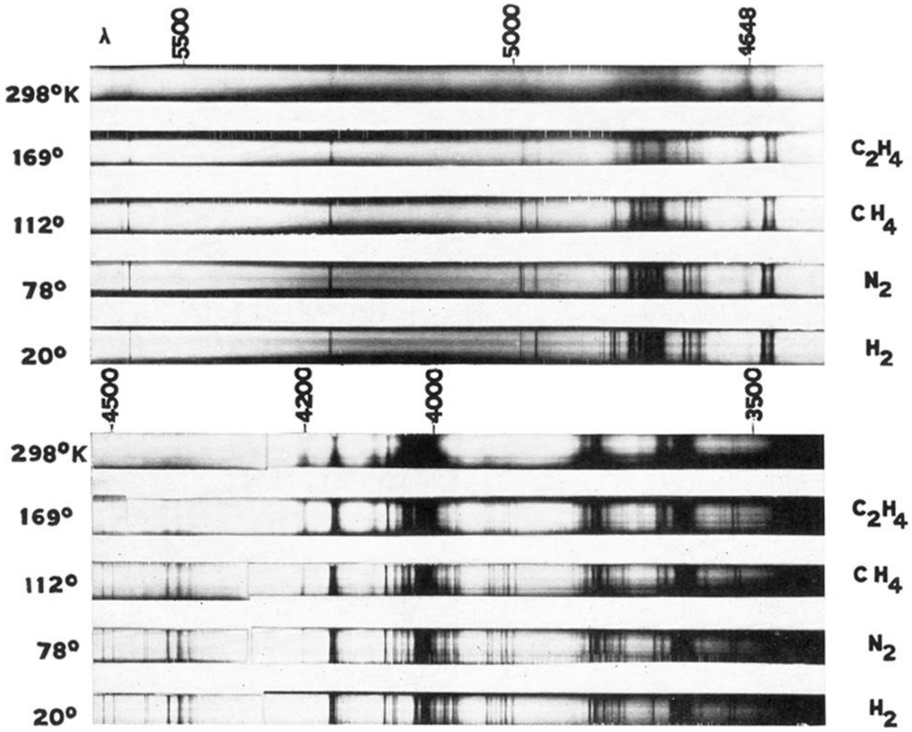

Fig. 2. Single-crystal absorption of $SmCl_3 \cdot 6H_2O$. The substances at whose boiling point the spectra were photographed are indicated on the right, the corresponding temperatures on the left. At λ4648 and λ4200 are the prominate high-temperature lines for which photometer curves are given in Fig. 3.