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Absorption Spectra of the Samarium Ion in Solids. II.* Conglomerate Absorption of $SmCl_3 \cdot 6H_2O$ and a Partial Energy Level Diagram of the Sm^{+++} Ion as It Exists in Crystalline $SmCl_3 \cdot 6H_2O$

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Additional lines of the $SmCl_3 \cdot 6H_2O$ absorption spectrum obtained from conglomerates of crystal fragments are reported for four temperatures between 20° and 300°K. These new lines, along with ones previously reported for single-crystal absorption, are used to establish the existence of excited lower levels situated at 145, 160, 204, 217, and roughly 300 cm^{-1} above the basic level. It is probable that there are other levels more than 400 cm^{-1} above the basic one. Two components of the 300 level, at 295 and 315 cm^{-1}, are thought to be present, and there are indications that the other levels, particularly the basic one, may be complex.

IT HAS been shown previously[2] that for rare earth salts the absorption or "reflection" spectra of conglomerates of small crystals are almost identical with the spectra obtained from single crystals. The chief difference is an enhancement of the fainter lines, many of which are consequently observed for the first time in the conglomerate absorption. This is brought about by the fact that the effective path length of the ray of light of frequency corresponding to that of the absorption is very much greater in the conglomerate case. The increased refractive index of the crystal fragments for such a wave-length causes the beam, once it has entered the solid, to be totally reflected, on the average, a great number of times before it strikes the surface at such an angle that it can emerge. As might be expected, the lines seem to be shifted slightly to the red. This shift is small, however, and is about of the order of our error in measurement. Comparison of Fig. 1 and the corresponding reproduction of the single-crystal spectrum in the first paper of this series[3] shows that the conglomerate also causes quite an increase in intensity of *all* lines not already completely absorbed, which is in agreement with the above explanation.

Because of its enhancement of faint lines and disclosure of new ones, the conglomerate absorption is a very valuable addition to that of the single crystal and contributes much to the determination of the energy levels of the ion in the solid. Unfortunately the conglomerate spectra are not sufficient in themselves because of the excessive enhancement and consequent blurring of large regions of the spectrum.

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* Contribution from the Chemical Laboratory of the University of California.

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[2] Spedding and Bear, Phys. Rev. **39**, 948 (1932).

[3] Spedding and Bear, Phys. Rev. **41**, 58 (1932).

Experimental Part

The conglomerates employed were prepared from small single crystals and fragments by crushing these to a size of smallness sufficient to allow close packing in glass cells without reduction to a powder. The cells varied in thickness from 4 mm to 1 cm and were substituted for the single crystals in the apparatus described in the preceding paper. In general, the thicker layers composed of finer crystals brought out the greatest number of new lines, but this could not be continued indefinitely. Beyond certain limits the exposures required in photographing the spectra became of unreasonable and impossible length. A compromise between thickness of conglomerate and time of exposure had to be made. This varied with the region of the spectrum and the temperature, making it necessary to photograph conglomerates of several thicknesses and to use the parts of the plates which turned out to be most satisfactory.

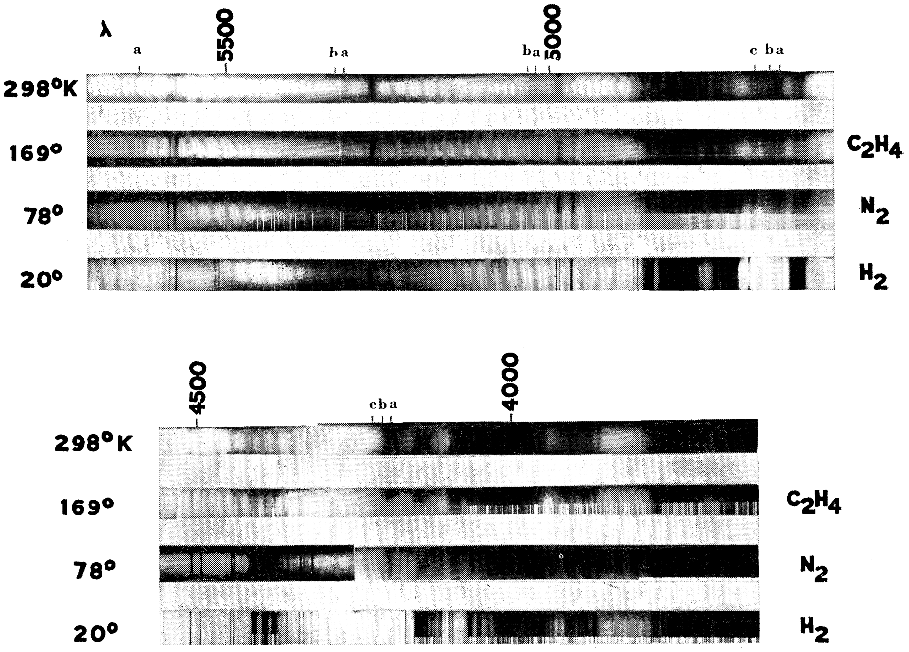

Fig. 1. Conglomerate absorption of $SmCl_3 \cdot 6H_2O$. The substances at whose boiling points the spectra were photographed are indicated on the right, the corresponding temperatures on the left. The small letters indicate various high-temperature lines of importance as explained in the text.

In Table I we have given the positions of the new lines as they were observed to appear in the conglomerate absorption spectra at four temperatures. The large number of lines given in the preceding paper is not repeated here, as the wave-lengths in both types of spectrum are practically the same. Only for some of the sharp lines could differences be detected, in which cases

TABLE I. *New absorption lines of* $SmCl_3 \cdot 6H_2O$ *disclosed by conglomerates.*

H (Type) = high-temperature line; L (Type) = low-temperature line; HL (Type) = probably both types are present; R.T., E.T., N.T., H.T. = Columns of measurements for room, ethylene, nitrogen and hydrogen temperatures, respectively; f, vf, vvf = degrees of decreasing intensity; s, vs = degrees of increasing sharpness; d, vd = degrees of increasing diffuseness; b = broad, frequently used for bands; # = line or band appearing more distinctly in conglomerate than in single-crystal spectrum, hence repeated; incl. = the conglomerate band includes lines and bands formerly given and still approximately correct. Primed values indicate band edges; c, centers.

This table is chiefly a supplement to the single-crystal one. Lines or bands appearing only at one temperature may have been given in the former table for other temperatures. Lines with no intensity designation are quite distinct and have approximately the intensity 1 or 2 on the scale of the former table.

Type	R.T. ν(cm^{-1})	E.T. ν(cm^{-1})	N.T. ν(cm^{-1})	Character	H.T. λ(A)	H.T. ν(cm^{-1})	Character
H	16783′ 16803′						
L			17128.8	s	5837.0	17127	s
L		17154′ 17162′					
L			17251.8	s	5795′ 5734′	17250′ 17432′	Many doubtful lines
L		17469′ 17480′	17475	d	5720.9	17475	d
H			17659	vvf			
H			17672	vvf			
H			17692	vvf			
H			17703	vvf			
H	17709′	17712′ 17723′	17716.3	s			
H	17727′	17732′	17730.6	s			
H		17744′	17748.6	s			
H		17768′	17763.1	s			
H			17848	d			
L	17872′ 17887′						
L	17902′						
L	# 17920′				5579.5	17918	f
L			17938	f	5572.4	17941	f
L			17954	f	5567.4	17957	f
L			17975	f	5561.4	17976	f
L			17991	f	5557.2	17990	f
L					5551.5	18008	vf
L					5546.2	18025	vf
L					5539.5	18047	vf
L					5536.7	18056	vf
L					5533.6	18066	vf
L					5530.2	18078	vf
L					5527.3	18087	vf
L					5520.1	18111	vf
L					5511.4	18139	vf
L			18197	fd	5495.5	18192	fd
L					5487.7	18218	vf
H	18720′ 18737′	18705′ 18733′					
H	18766′	18765′	18768.0	f			
H			18780.4	f			
H	18784′	18791′	18792.2	f			
L			18971	fd	5269.5	18972	fd
L		18998	18994.9	fs	5263.35	18994.1	fvs
L					5262.05	18998.8	fvs
L	19005		19016.3	fvs	5257.45	19015.4	fv
L	19026	19023	19021.0	fvs	5255.90	19021.0	fvs
L		19031′ 19041′					

TABLE I. (*Continued*)

Type	R.T.	E.T.	N.T.	Character	H.T.		Character
L			19070	fd	5242.9	19068	f
L			19084	f	5238.5	19084	f
L			19097	fd	5235.0	19097	f
L					5232.0	19108	f
L			19146	vfd	5229.1	19118	f
L					5226.3	19129	f
H			19811	vfd			
H		19825′	19825	f			
	19837′	19834′					
H	19868′		19865.5	f			
H		19881′	19882.7	s			
		19887′					
H	19898′	19897′	19897.0	s			
	19915′	19805′	19925′				
H			19945′	vf			
H		19953′	19956′	vfb			
		19978′	19981′				
HL			20070′	vvfb	4982.6c	20064c	
			20078′				vvf
HL			20088′		4975.9c	20091c	
			20097′	vvfb	4972.1	20107	vvf
L			20136	d			
L					4960.0c	20156c	vvf
L					4954.8c	20177c	
		# 20194′					
		20207′					
			20218	f	4949.5′	20213′	vfb
			20230	f	4940.5′	20235′	
		20242′	20246	d			
H		# 20253′					
		20267′	20259	d			
H			20280	vf			
H			20299	vf			
H			20328	vf			
H	20359′		20361	f			
H			20386	f			
H	20432′		20421	fd			
H		20517′					
L		20527′					
L			21356′	fb	4676.2′	21379′	fb
			21393′		4673.2′	21393′	
			21474′		4654.1	21480	vfs
			#	db	4651.4	21493	vfs
			21514′		4648.30	21507.2	s
			21553′				
					4613.2′	21671′	
L					# 4610.0′	21686′	db
					4606.1′	21704′	
					4598.7′	21739′	
L			21773′	vfb	4592.1′	21771′	vfb
			21789′		4588.5′	21787′	
L			21826′	vfb	4580.5′	21825′	vfb
	to next band		21839′		4577.8′	21839′	
	21843′						
L			21887	vf	4567.3′	21889′	vfb
L			21898	vf	4565.3′	21898′	
L			21950′	vf	4552.9′	21958′	vfb
			21968′		4550.4′	21970′	
H	21991′		21994	d			
H	22016′		22006	d			
H			22069	d			
H			22082	d			
H			22172	vf			
H			22190′	vfb			
			22203′				

TABLE I. (*Continued*)

Type	R.T.	E.T.	N.T.	Character	H.T.		Character
L			22248′	vf	4493.5	22248	vf
L			22263′		4491.0	22260	vf
L					4488.4	22273	vf
L			22303	vfd	4482.4	22303	vf
H	22309′		22327	vf			
H	22337′		22341	vf			
H	22374′		22384	vf			
H	22402′		22399	vfd			
			22567′	fd			
L			22577′		4429.0	22572	d
L		22599′	22592′		4424.5	22595	d
L					4420.7	22615	d
		incl.	22626′		4418.6′	22625′	
L			#		# 4416.4′	22637′	b
			22669′		4411.5′	22662′	
		22681′	to next band				
L					4400.85	22716.5	s
L		22960′					
		22979′					
L	23126′				4327.6	23101	d
L	23144′				4318.9	23148	d
H			23272	vf			
H			23282.9	s			
H	23352′						
	23387′						
H	23507′						
	23535′						
H	# 23589′						
	23612′						
H	# 23629′	23621′					
	23651′	23647′					
H			23717	fd			
H			23750	fd			
H			23761	fd			
H			23823	fd			
H			#23840	f			
H			#23852	f			
L		23907′					
		23921′					
	23943′	23948′					
L		23953					
	23966′	23957′					
		24019′					
L		incl.					
	to next bd.	24108′					
	24160′						
L					4133.15	24187.8	s
L					4132.55	24191.3	s
L					4127.45	24221.2	s
L					4122.45	24250.7	s
L					4121.55	24256.0	s
L					4120.6	24262	d
L					4118.60	24273.2	s
L					4117.85	24277.6	s
L					4116.80	24283.8	s
L					4116.15	24287.7	s
L					4112.9	24307	d
L					4109.40	24327.7	s
L					4108.30	24334.0	s
		24349′					
H		incl.					
					4100.7′	24379′	
L					4099.5′	24386′	fb
					4098.4′	24393′	
		24482′					

TABLE I. (*Continued*)

Type	R.T.	E.T.	N.T.	Character	H.T.		Character
L					4071.40	24554.7	s
L					4070.90	24557.7	s
L					4070.30	24561.3	s
L					4067.60	24577.7	s
		24609′			4061.8′	24613′	
L					# 4061.35	24615.4	intense
L					4060.65	24619.7	intense
					4060.3′	24622′	
L					4054.00	24660.1	s
L					4052.35	24670.2	s
L		incl.			4050.55	24680.9	s
		25163′					
L		25419′					
		25448′					
L			25646.2	f			
L					3854.9	25934	fd
		25960′			3850.2′	25966′	fb
		25994′	25992	bd	3845.2′	25999′	
L			26041	fd	3839.5	26038	fd
L			26070	vfd	3835.2	26067	fd
L		26104′	26097′		3830.3	26100	d
L				fd	3828.50	26112.4	s
		26131′	26120′				
H		26205′					
		26226′					
H		26263′					
		26274′					
H		26309′					
		26324′					
H		26391′					
		26424′					

the average shift was about 0.3 wave number to the red. This is about the error of measurement for sharp lines, and of course is even less important for diffuse or broad lines and bands.

In the violet, where the multiplets of greatest intensity are located, the conglomerates cause even greater absorption. The result is a blurring of the multiplets into wide bands which make it impossible to examine very accurately the absorption occurring beyond about 3700A. (No ultraviolet investigation of the conglomerate absorption was undertaken, mainly because of the long exposures required.)

DISCUSSION OF RESULTS

Most of the new lines which are reported here belong unmistakably to one or the other of two classes. Some owe their low absorption coefficients to the small population in the lower levels producing them and are usually found on the red sides of the more intense multiplets. They thus resemble (and are) "high-temperature" lines (see the first paper of this series[3]), being similar to them in all ways. Lines of a second class have low absorption coefficients because of small transition probabilities for the electronic changes producing them. These occur on the violet sides of the multiplets and are identical with one type of "low-temperature" line discussed previously. The first class of the new conglomerate lines is valuable in determining the positions of the lower levels lying near the basic one, while the others are useful in showing how the final excited levels are split in the crystal field and in locating levels which do not easily form electronic transitions with the basic level because of selection rules, etc.

The absorption lines at temperatures near the absolute zero can be considered as an energy-level diagram of the excited levels, since at these temperatures all lines must arise from a single basic level. As the temperature is raised the population in slightly higher levels increases as the Boltzmann factor dictates. As a consequence new lines appear which are separated from the more intense lines by amounts equal to the separation of the excited lower levels from the basic one.

At 15°K, the lowest temperature photographed by us, lines arising from levels more than 50 cm^{-1} from the basic level would likely be distinguishable

TABLE II. *Doublets of 160 cm^{-1} separation (78°K).*

Low-temperature line	High-temperature line	$\Delta\nu$ (cm^{-1})
17875.8	17716.3	159.5
17908.0	17748.6	159.4
18927.0	18768.0	159.0
20024.5	19865.5	159.0
20042.5	19882.7	159.8
20404.5	20246	158.5
20544.8	20386	158.8
20520.2	20361	159.2
22151.8	21994	157.8
22228.8	22069	159.8
22487.9	22327	160.9
22543.1	22384	159.1
23949.8	23789.2	160.6
24001	23840	161
24015	23854	161
25646.2	25486	160.2
26611	26453	158
26627.1	26467.8	159.3
26700.9	26541.5	159.4
27570	27412.8	157.2
27591.4	27431.1	160.3

TABLE III. *Doublets of 145 cm^{-1} separation (78°K).*

Low-temperature line	High-temperature line	$\Delta\nu$ (cm^{-1})
17875.8	17730.6	145.2
17908.0	17763.1	144.9
18937.4	18792.2	145.2
20042.5	19897.0	145.5
20404.5	20259	145.5
22151.8	22006	145.8
22228.8	22082	146.8
22487.9	22341	146.9
22543.1	22399	144.1
23949.8	23804.9	144.9
25646.2	25501	145.2
26627.1	26482.9	144.2
26700.9	26556.3	144.6
26714.3	26570	144.3
27591.4	27445.9	145.5

in the photographs taken, and we should be able to detect lines resulting from levels 20 cm^{-1} or more distant from the lowest one. The first new lines to make their appearance, however, do so between 20° and 60°K and appear to originate from levels differing in energy from the basic level by about 145 and 160 cm^{-1}. In Tables II and III are given the frequencies of lines forming doublets of these separations; each doublet is composed of a high-temperature line and a low-temperature line. Only lines well separated from others are used for these tables, although in almost every multiplet evidence of these separations can be found. No other values for such differences are found to occur with nearly the same frequent repetition, and at liquid nitrogen temperature these two levels are sufficient to account for nearly all of the important, more intense high-temperature lines found in both the single-crystal and the conglomerate spectra. (See lines *a*, Fig. 1.)

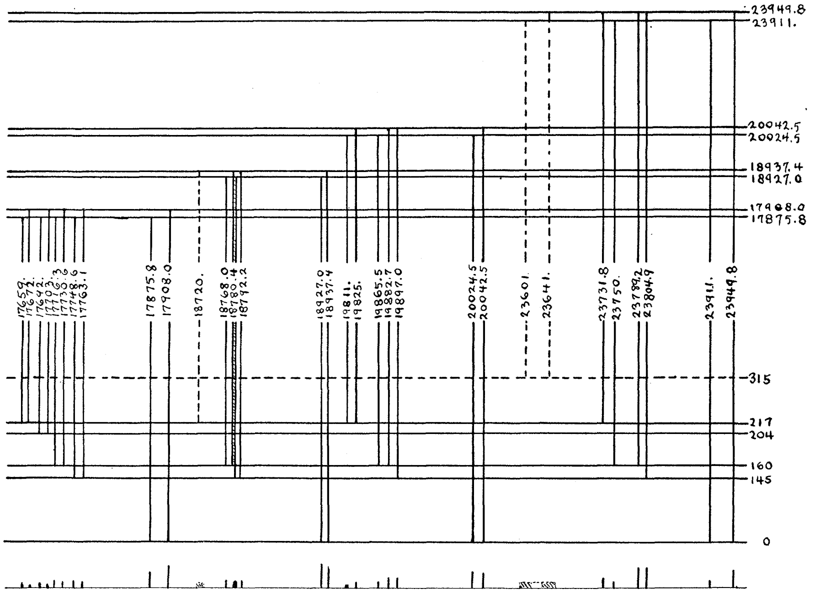

Fig. 2. Diagram of some of the multiplets of the $SmCl_3 \cdot 6H_2O$ absorption spectrum. Below the energy levels appears a representation of the lines as they appear on photographs, plotted however, within the multiplets, according to wave numbers. Relative intensities are indicated roughly by the heights of the lines used, though faint absorption is somewhat exaggerated. The solid lines in the levels or transitions indicate low-temperature values. The dotted lines show dependence on high-temperature measurements.

At higher temperatures another group of lines which indicate two more levels at 204 and 217 cm^{-1} make their appearance (lines *b*). At liquid ethylene and room temperatures a third group resulting from one or more levels about 300 cm^{-1} (295 to 315 cm^{-1}) can be discerned (lines *c*). Finally, one or two bands found only at room temperature seem to require separations of more than 400 cm^{-1}, since they occur quite far from the nearest low-temperature lines.

In Fig. 2 is given a diagram of several multiplets that occur well apart from other lines and offer most clear and convincing proof of the existence of most of the levels described above. Except for the levels and transitions indicated by dotted lines, the values given are those at liquid nitrogen temperature. As a general rule the intensities of the lines arising from the 160 and 217 levels are a little greater than those of lines from the 145 and 204 levels, respectively. The lines from the 145 and 160 levels are, of course, much stronger than those from higher levels.

Each of the levels listed above not only has been established by from four to thirty measurements of lines whose temperature behavior supports the explanation given for them, but they also are consistent with many other lines that occur in complex regions of the spectra and cannot be determined with the same accuracy. The levels may very well be complex with a spread of from 2 to 30 cm^{-1}, but the accurate determination of this complexity is difficult for two reasons. In the first place the lines broaden as the temperature is increased with the result that at room temperature they are more than 10 cm^{-1} in width. Since the levels in many of the excited multiplets are separated by about this amount, it is impossible to tell whether the broad bands which make their first appearance at high temperatures are caused by transitions from one or more lower levels. The same is true for smaller separations in the lines appearing at lower temperatures. As a result we could not distinguish lines which might indicate 2 cm^{-1} separations in the 160 and 145 cm^{-1} levels or a 30 cm^{-1} separation in those at 300 cm^{-1}.

A second confusing factor is the fluctuating fields caused by the vibrations of the crystal, most important at higher temperatures. These probably cause partial uncoupling of the orbits or spins of the electrons with the field and produce instability in some of the upper levels. The multiplets then tend either to contract to a new center or else fade out entirely. While this latter effect is very pronounced in the case of $PrCl_3 \cdot 6H_2O$, which has been studied by one of us,[4] for the samarium salt the fading is not very great until room temperature is reached.

It is rather interesting that the separations given in Tables II and III are spread over a range of 159 ± 2 and 145 ± 2. This range is thought to be somewhat larger than the usual error would allow, though the combined errors of two lines might be that great. It is particularly noteworthy that the residuals, when plotted, instead of giving the ordinary Gaussian curve, seem to fall roughly into three groups. If this is true it would indicate that perhaps the

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[4] Spedding, unpublished work. Discussion of this will probably appear in Physical Review. Many lines which are strong at 80°K are faint at 195° and absent at 300°. $PrCl_3 \cdot 6H_2O$ also appears to have electronic isomers spread over some distance (105 cm^{-1}, etc.). In this case, however, these low levels are apparently affected at high temperatures in a manner similar to that indicated for the excited upper levels of the Sm^{+++} ion. As a consequence an increase in temperature results at first in an accompanying increase in the intensity of the lines arising from these levels, whose populations are governed by the Boltzmann factor. Finally, as the temperature becomes still higher, these lines fade because of the disappearance of the levels from which they originate. Similar phenomena have been observed by J. Becquerel (J. Becquerel, Gedenboek H. Kammerlingh Onnes, Leiden, 1922) in the case of Nd^{+++}.

basic level is split into three components, a very attractive result. The basic level of Sm IV as predicted by Hund[5] is a $^6H_{5/2}$, and it would be expected to split into three doubly degenerate levels in a moderate electric field.[6] However, without additional evidence it can only be mentioned as highly probable.

CONCLUSIONS

As a result of the above evidence it is safe to conclude that in $SmCl_3 \cdot 6H_2O$ the samarium ion has levels situated at 145, 160, 204, 217 and 300 cm^{-1} above the basic one. It is highly probable that these levels are complex, especially that the 300 level is double, with components at 295 and 315, and that other levels exist at 400 and greater wave-number separations from the lowest level. These levels are in good agreement with the predictions of one of us from magnetic data.[7]

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[5] Hund, Zeits. f. Physik **33,** 855 (1925).

[6] Kramers, Proc. Amst. Acad. **32,** 1176 (1929). Bethe, Ann. d. Physik **3,** 133 (1929).

[7] Spedding, J. Am. Chem. Soc. **54,** 2593 (1932). While these levels are for $SmCl_3 \cdot 6H_2O$ and the predictions are for $Sm_2(SO_4)_3 \cdot 8H_2O$, preliminary photographs and measurements show that the levels of the two salts are similar.

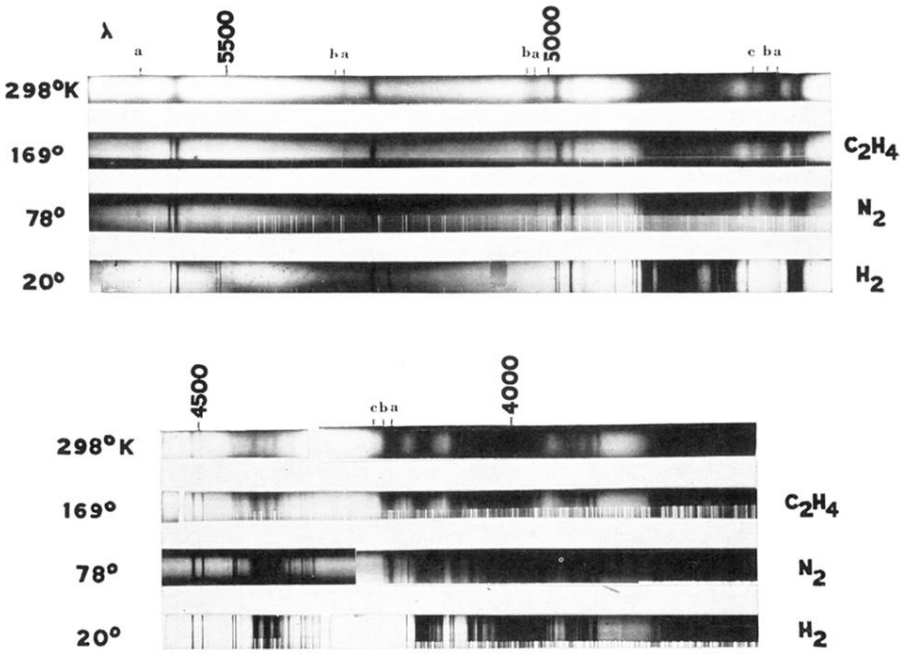

Fig. 1. Conglomerate absorption of $SmCl_3 \cdot 6H_2O$. The substances at whose boiling points the spectra were photographed are indicated on the right, the corresponding temperatures on the left. The small letters indicate various high-temperature lines of importance as explained in the text.