

Absorption Spectra of the Samarium Ion in Solids. V. The Absorption Spectrum and Energy Levels of the Sm^{+++} Ion as It Exists in Monoclinic Crystals of $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

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

IN previous papers of this series¹ we have described the absorption spectra of the samarium ion for monoclinic crystals of $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ and for hexagonal ones of $\text{Sm}(\text{BrO}_2)_3 \cdot 9\text{H}_2\text{O}$, $\text{Sm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and $\text{SmI}_3 \cdot 9\text{H}_2\text{O}$. The chloride spectrum was found to be distinctly different from those of the hexagonal group in that its individual multiplets were spread out somewhat more and frequently contained more lines. These results were in agreement with those of Spedding and Nutting² for the corresponding gadolinium compounds, i.e., the extension within multiplets and the number of components of each of the multiplets of the rare earth ions seem to depend more on the positions of surrounding atoms or ions in the crystal and less on the chemical composition of the compound, except insofar as the composition affects the crystal structure.

This paper describes the spectrum of a second monoclinic salt, $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. The magnetic susceptibility³ and heat capacity⁴ of this solid have already been measured over a wide temperature range, and a spectroscopic determination of the energy levels will be useful in attempting to understand the results of these other investigations. Here we present only the experimental facts. In a later paper we shall introduce a discussion of the relation between the physical and chemical properties of samarium salts and their energy levels.

EXPERIMENTAL PART

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

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

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

¹ Spedding and Bear, *Phys. Rev.* **42**, 58, 76 (1932); **44**, 287 (1933); **46**, 308 (1934).

² Spedding and Nutting, *Phys. Rev.* **38**, 2294 (1931); *J. Am. Chem. Soc.* **55**, 496 (1933).

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

⁴ Ahlberg and Freed, *Phys. Rev.* **39**, 540 (1932).

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

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

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

RESULTS

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

Close examination of the photographs at low

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

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

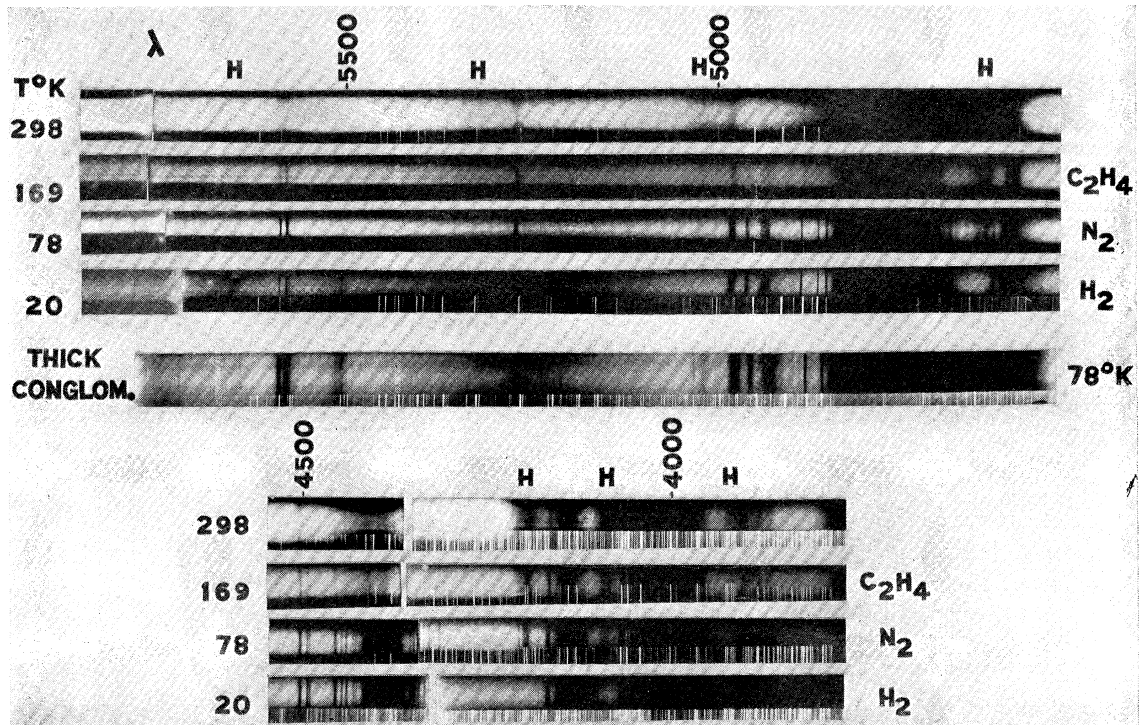


FIG. 1. Conglomerate absorption of $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. The substances at whose boiling points the spectra were photographed are indicated on the right, the corresponding temperatures on the left. *H* is placed above regions wherein the most prominent high-temperature lines are located.

TABLE I—(Continued.)

R.T. ν (cm ⁻¹)	E.T. ν (cm ⁻¹)	Type	N.T. ν (cm ⁻¹)	Int.	H.T. λ (A)	H.T. ν (cm ⁻¹)	Int.	R.T. ν (cm ⁻¹)	E.T. ν (cm ⁻¹)	Type	N.T. ν (cm ⁻¹)	Int.	λ (A)	H.T. ν (cm ⁻¹)	Int.
{19820'	{19822'	H	{19811	1d	4996.2	20009		20555	{20562'	L	† 20544		4866.4	20544	1d
{19842'	{19840'	H	{19831	3d	{4992.3'	20025		{20602'	{20573'	L	‡ 20569		4860.40	20568.7	10ms
	{19867'	H	{19858'	2d	{4987.80c	{20038.3c}				L			4856.10	20586.9	1s
{19883'		H	{19870'	3d	{4989.05c}	20054.8	10ms			L	20598'		4854.35	20594.4	1s
	{19904'	H	{19883'	2d	4977.4	20085	0			L			4851.80	20605.2	2s
{19915'		HP	{19895	0	4974.7	20096	0		20621	L			4850.1'	20613'	10d
	{19942'	H	{19897'	1d	{4969.6'	20107	00			L			4849.2	20616	10d
	{19974'	H	{19911	0	{4967.7'	{20124'}	9d			L			4847.5	20624	10d
		H	{19942'	1d	{4965.5'	20133	0			L			4846.5'	20628'	9d
		H	{19973'	1d	4962.7	20145'	0			L			4843.9	20639	2d
		L	{20005'		4960.4	20154	0			L			4841.0	20651	2d
{20029'		L	{20009		4984.95	20054.8	10ms			L			4839.7'	20657'	10db
		L	{20037'		4981.9	20067	3d			L			4835.0'	20677'	10db
		L	{20045'		4977.4	20085	0			L			4831.7'	20691'	10db
{20061'		L	{20050'		4974.7	20096	0			L			4826.2'	20714'	10db
		L	{20060'		4972.0	20107	00			L			4821.6'	20734'	10db
		L	{20072'		{4969.6'	20117				L			4816.8'	20755'	10db
{20095'		L	{20083'		{4967.7'	{20124'}	9d			L			4813.5'	20769'	10db
		L	{20085'		4965.5'	20133	0			L			4808.0'	20793'	10db
		L	{20092'		4962.7	20145'	0			L			4804.4'	20808'	10db
		L	{20097		4960.4	20154	0			L					
		L	{20115'		4956.15	20171.3	2nd			L					
{20133'		L	{20124'		4953.40	20182.5	2nd			L					
		L	{20136'		4951.00	20192.3	2nd			L					
		L	{20137'		4948.1	20204	6d			L					
		L	{20137'		4945.7	20214	8d			L					
		L	{20154		4943.0	20225	9d			L					
		L	{20169'		{4940.3'	{20236'}				L					
		L	{20171		{4938.5'	20243'				L					
		L	{20182		4936.8	20250				L					
{20198'		L	{20193		4934.80	20259				L					
		L	{20201		4931.7'	20271.1	0s			L					
		L	{20204		4929.2'	20282'	0			L					
		L	{20214		4926.1	20294				L					
{20224'		L	{20223'		4923.0	20307'				L					
		L	{20226'		4920.2'	20320'				L					
		L	{20228'		4918.0	20328				L					
		L	{20239'		4915.9'	20337'				L					
		L	{20248'		4910.9	20357'				L					
		L	{20248'		4909.1	20386				L					
		L	{20248'		4901.1	20398				L					
		L	{20248'		4897.6	20413				L					
{20283'		HL	{20293'		4894.00	20427.5	10s			L					
		L	{20299							L					
		L	{20302'							L					
{20308'		HL	{20302'							L					
		L	{20308'							L					
		L	{20343							L					
		L	{20355'							L					
		L	{20366							L					
		L	{20387							L					
		L	{20397							L					
		L	{20397							L					
{20407'		HL	{20423'							L					
		L	{20423'							L					
{20430'		L	{20429							L					
{20444'		L	{20431'							L					
		H	{20456							L					
		HP?	{20465'							L					
		L	{20512'							L					
{20524		L	{20522.2							L					
		L	{20527'							L					

TABLE I—(Continued.)

R.T. ν (cm ⁻¹)	E.T. ν (cm ⁻¹)	Type	N.T. ν (cm ⁻¹)	Int.	H.T. λ (A)	H.T. ν (cm ⁻¹)	Int.	H.T. λ (A)	H.T. ν (cm ⁻¹)	Int.
{24387}	24362	H	24357	3d	4102.5	24369	7d	{3876.7' 3874.4'	{25792' 25800' 25819'	{25788' 25803'
{24386' 24401' 24415' 24429'	{24386' 24397c 24412c 24422c	L H HL L	{24368 24389c 24397c 24412c 24422c	7d 7d 7d 7d	4097.5 4095.2	24398 24412	2d 9d	3871.7 3868.8	25822 25837 25839'	25821 25840
{24443' 24460' 24477	{24443c 24452c 24477	H H L	{24445c 24452c	7d 7d	4090.9	24438	7d	3866.1	25858 25902 25928'	25859
{24486' 24550' 24580'	24477 24522' 24546' 24554 24566 24572' 24584	L L L L L L L	24494 24513 24545' 24570' 24583 24599 24611 24636 24651 24658c 24668c 24681' 24697'	6d 3d 0	4087.2 4082.8 4079.0' 4072.5 4069.6 4066.9c 4064.3 4062.1 4058.1 4055.4 4053.0 4050.5 4048.2 4034.4'	24060 24486 24509' 24548 24565 24582c 24598 24611 24635 24651 24666 24681 24695 24780'	4d "2" 10d 9d 10d 4nd 10d 10d 10d 10d 10d 1d	{3857' Absorption too strong.	{25924' 25950' 25971 25987 26014 26027' 26043 26052' 26074' 26214 26254' 26285' 26335' 26370' 26397' 26419 26451' 26500' 26530' 26580' 26603' 26630' 26653' 26695' 26815' 26860 26890 26926 26940 27010 27130' 27132' 27150' 27190' 27200' 27218' 27235' 27330' 27380' 27420' 27470' 27545' 27660' 27695' 27720' 27920' 27953' 27980' 28004' 28061 28081 28100' 28126' 28193 28280 28280' 28310' 28330 28330 28342'	{26057' 26414c 26420c 26434 26449 26480' Abs. too strong.
{25135' 25215' 25255'	25160' 25181	L L L	{24702' 24845' 24880' 24930' 24960' 25155' 25177' 25189' 25204' 25222' 25234' 25255' 25272 25293 25311 25342 25360' 25370'	10b	3945.1 3941.2 3940.1' 3937.1 3933.6 3929.6 3927.2 3923.2 3920.7 3916.4 3912.7'	25341 25366 25373' 25392 25415 25440 25456 25482 25498 25527 25551'	Too Intense for Intensity Estimation	{26940' 27040' 27132' 27165' 27200' 27235' 27330' 26940' 27040' 27132' 27165' 27200' 27235' 27330' 27380' 27420' 27470' 27545' 27660' 27695' 27720' 27920' 27953' 27980' 28004' 28061 28081 28100' 28126' 28193 28280 28280' 28310' 28330 28330 28342'	{26057' 26414c 26420c 26434 26449 26480' Abs. too strong.	
25377	25369	L	25413 25440							
H {25431' 25462' 25475' 25520'	{25431' 25432' 25478' 25500'	L L L L L L	25413 25440 25485 25499 25528 25561 25571' 25590' 25598' 25617' 25640' 25650' 25659 25676 25686 25702 25720' 25729' 25742' 25749'							
{25574' 25619'	25584 25605	L L	{25571' 25590' 25598' 25617' 25640' 25650' 25659 25676 25686 25702 25720' 25729' 25742' 25749'							
{25708' 25764'	25700 25724 25745	L L L	{25571' 25590' 25598' 25617' 25640' 25650' 25659 25676 25686 25702 25720' 25729' 25742' 25749'		3880.3'	25764'				

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

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

In spite of the trouble in locating the exact position of the individual components of the doublets, it has been found possible to determine pretty definitely the situation of the lower levels that are most important spectroscopically. This has been done by working with centers of doublets and diffuse lines or bands. The results for the most clear multiplets (the same ones previously diagrammed for the chloride) are given in Fig. 2, though many of the less important faint *low-temperature lines* of these regions are not included. All of the most intense *high-temperature lines* in these multiplets can be explained by the use of the levels 0, 160, 188

and 225 cm^{-1} . Evidence from other more complex portions of the spectrum supports these values in general. Again *both constant energy separations and proper temperature behavior of intensity* have been made the requirements for the location of the lines in the diagram.

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

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

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

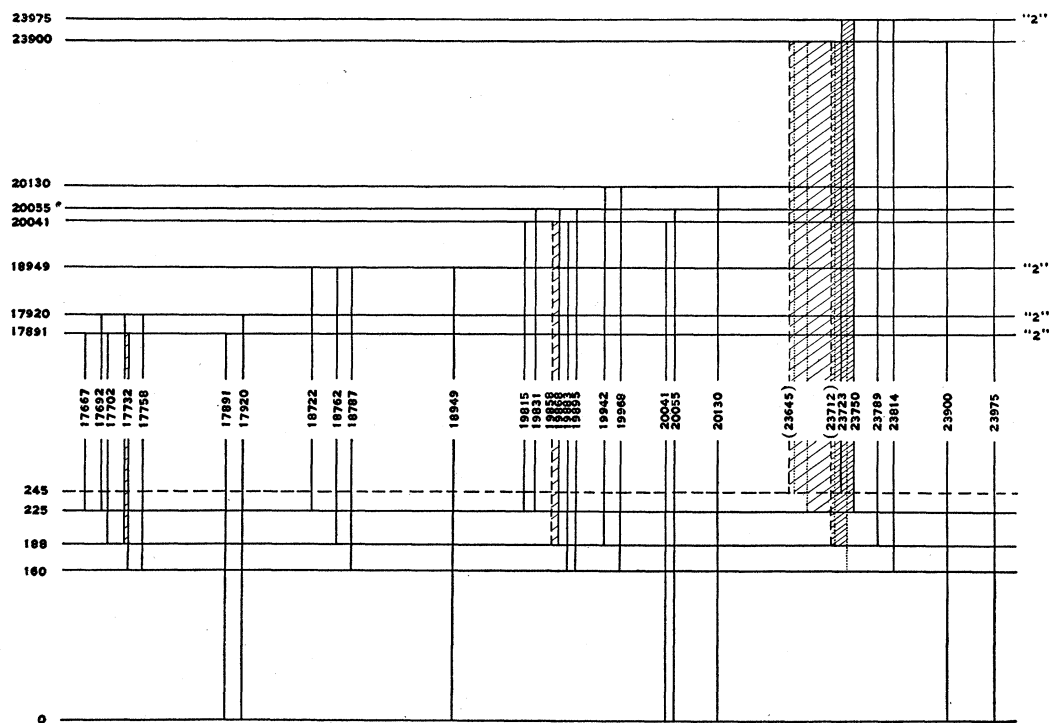


FIG. 2. Energy levels of $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. Shaded areas represent bands. Figures in parentheses denote band edges measured at ethylene temperature. All other figures are from plates taken at 78°K . Levels which are actually probably double are indicated by "2."

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

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

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

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

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

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

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

CONCLUSIONS

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

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

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

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

Elastic Electron Scattering in Potassium

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

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

INTRODUCTION

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

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

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

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

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

³ Hughes, McMillen and Webb, Phys. Rev. **41**, 154 (1932).

⁴ F. L. Arnot, Proc. Roy. Soc. **A144**, 360 (1934).

⁵ E. C. Childs and H. S. W. Massey, Proc. Roy. Soc. **A141**, 473 (1933).

⁶ E. C. Childs and H. S. W. Massey, Proc. Roy. Soc. **A142**, 509 (1933).

⁷ F. L. Arnot, Proc. Roy. Soc. **A140**, 334 (1933).

⁸ E. B. Jordan and R. B. Brode, Phys. Rev. **43**, 112 (1933).

* National Research Fellow.

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

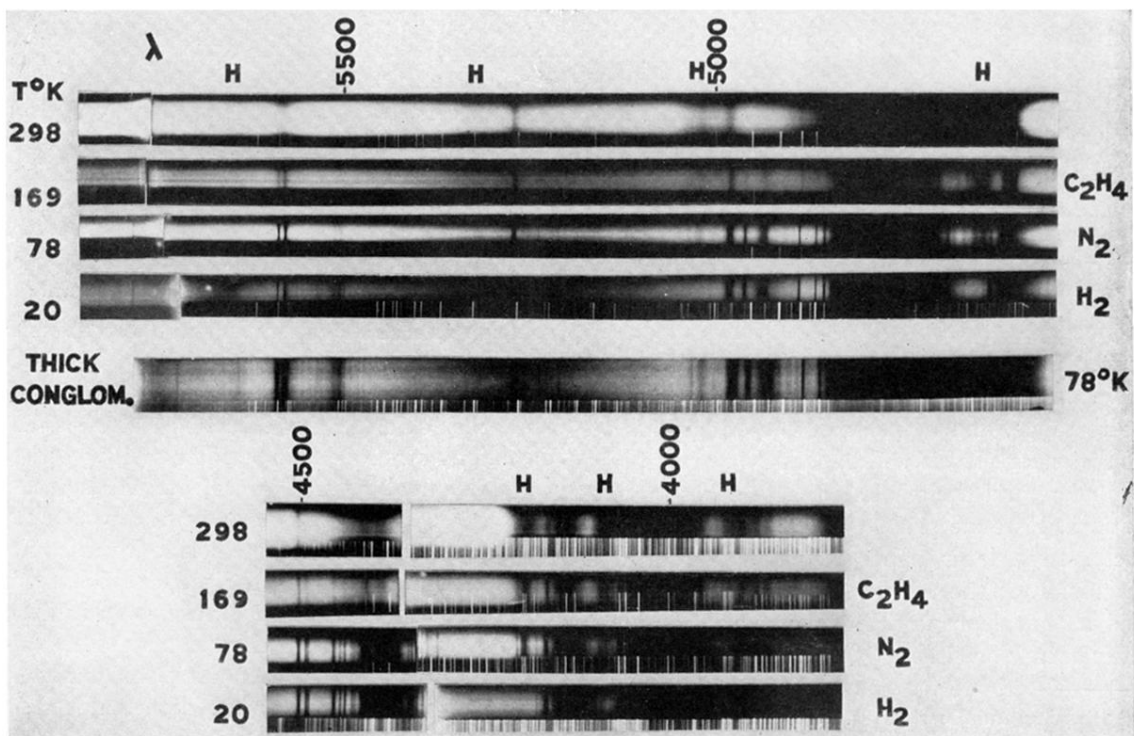


FIG. 1. Conglomerate absorption of $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. The substances at whose boiling points the spectra were photographed are indicated on the right, the corresponding temperatures on the left. *H* is placed above regions wherein the most prominent high-temperature lines are located.