

The Absorption Spectrum of Eu^{+++} in Crystalline $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

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J. Chem. Phys. **2**, 421 (1934); 10.1063/1.1749501



The Absorption Spectrum of Eu^{+++} in Crystalline $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

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The absorption spectrum of $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ has been studied over the temperature range 14°K – 290°K . Measurements of the absorption lines are given for five temperatures. Intensity variations caused by a change in temperature have been used to establish definitely the existence

of levels 21 cm^{-1} and 41 cm^{-1} above the basic one, and to indicate the existence of 67 cm^{-1} , 86 cm^{-1} , and possible higher levels. An unusual feature of the spectrum is the constant energy difference occurring between many lines which are most intense at the lowest temperatures.

THE simple Hund theory predicted, with considerable accuracy, the magnetic susceptibilities of the ions of all the rare earths except Sm and Eu; Van Vleck and Miss Frank¹ have shown that no discrepancies exist if one uses the complete quantum-mechanical expression for calculating the susceptibilities, taking into account the "finite" width of the basic multiplet. These multiplet widths were unknown; Van Vleck and Frank have shown that agreement with experimental susceptibility measurements may be obtained by assuming the Goudsmit formula for calculating them; thus they calculated that the first excited state above the basic one occurs at about 930 cm^{-1} and 250 cm^{-1} for Sm^{+++} and Eu^{+++} , respectively.

Because of the action of the (generally asymmetric) crystalline fields, one expects, in general, a further splitting of the ground state of the ion.² It has been shown³ that in many salts of Sm^{+++} , excited levels do exist far below 930 cm^{-1} , and that their positions depend on the nature of the crystalline fields to which the Sm^{+++} is subjected (determined by the crystal structure of the salt in question).

The present work was undertaken to determine the existence of similar low-lying levels in Eu^{+++} .

EXPERIMENTAL PART

The salt chosen for investigation was $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. Because of the difficulty of obtaining large single crystals, the work was carried out with conglomerates of small crystals. The material was of such purity that none of the

strongest lines of Sm^{+++} (the most likely impurity) were observed. The crystal structure of the salt has not been determined; the crystallographic symmetry is presumably monoclinic.⁴

Photographs of 2–3 mm conglomerates were taken on a 3-meter concave grating (dispersion 5.5Å per mm), over the temperature range 14°K (obtained with liquid hydrogen under reduced pressure), to room temperature. The apparatus has been described previously.⁵ Measurements were made of the 14° , 20° , 77° (liquid N_2), 169° (liquid C_2H_4), and room temperature absorption. Additional photographs at the temperatures of liquid air and liquid methane (112°K) served confirmatory purposes.

RESULTS

In Fig. 1 are shown reproductions of the spectra corresponding to the temperatures indicated.

Table I gives the frequencies (cm^{-1}) of absorption lines at five temperatures, and, for 14°K , wave-lengths (Å). Very rough intensity estimates are given for 14°K and 77°K . Lines that increase in intensity with increasing temperature are marked *I*, those that decrease are marked *L*. The error in measurement is considered to be about 0.05Å in most cases, although for faint or diffuse lines the error is greater.

DISCUSSION OF RESULTS

As usual the lines increase markedly in sharpness as the temperature is lowered. The shift in position with temperature change is in most cases not much greater than the error in measure-

¹ See Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford, 1932) pp. 239–249.

² H. Bethe, *Ann. d. Physik* **3**, 133 (1929).

³ Spedding and Bear, *Phys. Rev.* **46**, 975 (1934); this paper contains references to earlier work.

⁴ Zachariasen, *J. Chem. Phys.* **3**, 197 (1935) has found this symmetry in $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$.

⁵ Spedding and Bear, *Phys. Rev.* **42**, 58 (1932).

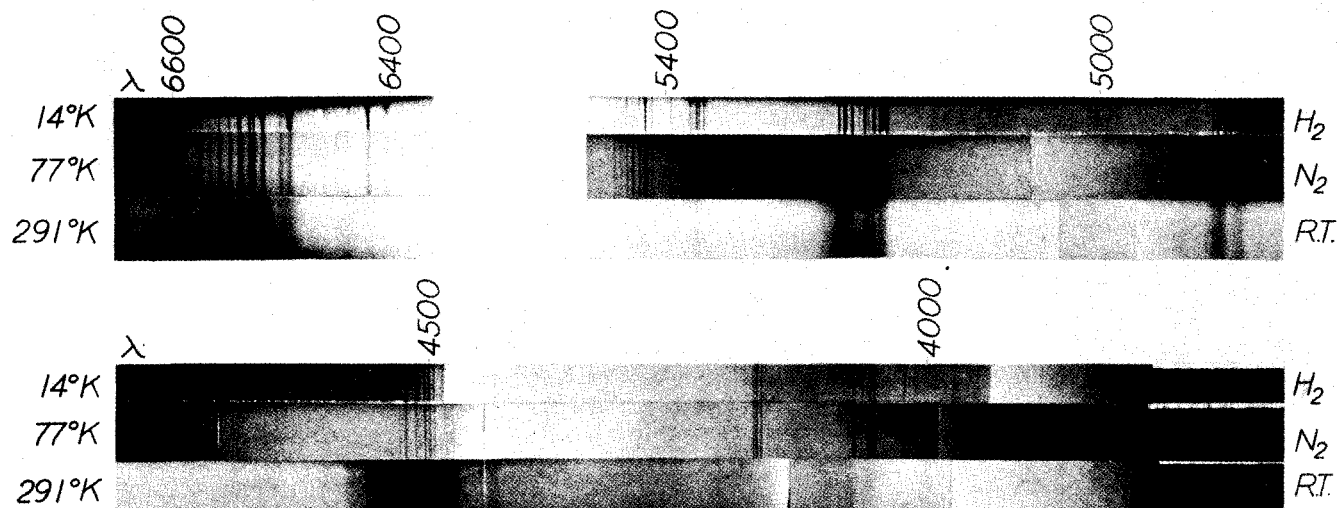


FIG. 1. Conglomerate absorption spectra of $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. On the right are given the substances used to obtain the temperatures given on the left.

TABLE I. Conglomerate absorption lines of $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ in the visible region of the spectrum.

Frequencies (cm^{-1}) are given for the temperature indicated; roughly estimated intensities, and characters, are given in the columns marked Int. Intensities are on the scale 0–10; the letters vd, d, nd, s, vs indicate increasing degrees of sharpness. ? indicates that the line is probably double.

ν , 291°K	ν , 169°K	ν , 77°K	Int.	ν , 20°K	ν , 14°K	λ , 14°K	Int.	ν , 291°K	ν , 169°K	ν , 77°K	Int.	ν , 20°K	ν , 14°K	λ , 14°K	Int.		
14886.0								18527.8	18528.3	18525.2	1	18525.2	18525.3	5396.53	3vs		
14970.0								18531.2	18532.3		2	18532.2	18532.4	5394.47	4vs		
15010.0								18534.4									
15105.0									18566.1		2		18565.6	5384.97	1		
L	15131.8	4s	15121.0	15132.0	6006.69	4s		H	18577.9	18577.0	18575.6(2?)	3	18572.5	18572.6	5382.79	1	
			15131.8										18577.0	5381.51	2vs		
			15140.2										18580.4	5380.51	1		
L	15166.0	15162.4	15162.7	7s	15161.1	6594.03	5s	L		18585.2	2s	18583.1	18583.8	5379.54	4vs		
			15220.9					L	18590.1			18592.1	18592.7	5378.96	4vs		
H	15205.0	15205.9	15204.2	5s	15203.9	6575.45	1	H	18597.2	18596.3	4	18596.5	18596.9	5375.75	3vs		
			15222.7										18600.4	5374.66	3vs		
			15228.5					L	18606.8	18607.8	3s	18606.6	18606.9	5372.87	3vs		
L	15225.1	15226.2	3vs	15225.8	15225.5	6566.11	5vs	L	18612.2	18613.0(2?)	3	18615.3	18615.7	5370.32	8s		
			15229.0					L	18629.6	18618.2							
L	15246.0	15245.2	15244.7	6s	15245.3	15245.0	6557.70	7vs		18634.4			18624.7	5367.72	8s		
			15260.2					L	18638.5	18639.7	6	18639.1	18639.4	5363.48	8s		
L	15267.6	15267.7	15268.1	8s	15266.2	15266.1	6548.67	6vs	L	18644.9			18647.5	18648.1	5361.00	7s	
H			15268.8	5s	15269.1	15269.1	6547.37	0		18649.1	18648.4	6					
L	15285.4	15285.4	8vs	15285.7	15285.5	6540.34	8vs			18656.4							
L	15289.8	15290.5	15290.7	8nd	15290.6	6538.15	8vs			18661.0	18660.9	2					
L			15297.5	1	15297.7	15297.4	6535.24	0		18665.9							
H	15305.5									18672.2	18670.1	1					
L		15309.2	15309.8	9nd	15310.0	15310.2	6529.81	9s		18675.0							
L	15318.5	15318.8	15319.0	9nd	15318.6	15318.8	6526.07	8s		18677.5							
										18683.3							
L	15335.0	15336.9	15338.0	9nd	15338.2	15338.0	6522.21	0		18688.1							
H			15345.4	2d		15338.5	6517.76	9s		18693.2							
L	15380.0	15373.9	15376.2	8d	15377.2	15377.2	6501.35	5s		18720.6							
L		15397.3	15395.7	8d	15396.5(2?)	15395.6	6493.58	8s	18784.0								
L						15399.3	6492.01	5	18957.0								
	15409.2									18964.5							
		15424.9	0							18967.5							
L		15440.5	0	15449.0	15450.7	6470.43	3vs		18979.0								
L	15451.5	15452.1	1		15452.5	6469.67	3vs	H		19013.3							
L					15468.1	6463.14	3vs	H	19035.4	19033.3	19029.4	4nd					
	15471.5	15472.4	3	15472.1				H		19046.1							
L	15474.7			15474.6	15474.3	6460.56	3vs	H	19057.6	19055.7	3nd	19057.7	19056.7	5246.03	1vs		
L	15478.8	15476.5	1	15478.8	15478.7	6458.69	3vs	H	19075.8	19075.4	19074.4	5vs	19074.2	19074.1	5241.17	2vs	
L					15480.8	6457.82	3vs	H	19098.1	19098.3	19096.4	8s	19096.1	19095.8	5235.31	9vs	
	15484.4									19101.5	19101.5	8s	19101.6	19101.6	5233.72	2vs	
	15501.4	15498.9	3	15498.9	15497.9	6450.69	2vs			19108.0							
L		15510.6	2	15510.6	15510.8	6445.33	2vs	L	19118.5	19116.2	19115.4	9s	19115.5	19116.0	5229.76	10s	
L	15515.2	15515.3	1	15515.5	15516.0	6443.20	3vs	L, H		19124.1	19122.8	5vs	19123.0	19122.8	5227.85	5vs	
		15521.2	2	15520.9	15520.3	6441.39	4vs	H		19132.2	19132.0	2	19131.0				
L					15523.1					19137.8							
L		15528.0	2	15528.4	15528.2	6438.14	4vs	L	19142.7	19144.0	19143.0(2?)	6d	19142.1	19142.5	5222.56	10vs	
L		15540.0	0	15540.3	15540.1	6433.18	3vs	H		19160.6	19155.8	2nd					
L		15548.6	1	15548.4	15548.8	6429.59	3	L, H	19168.2	19168.2	19167.3	5vs	19166.8	19167.3	5215.78	4vs	
					15560.3	6424.85	1	H		19177.7	19176.6	4s	19176.8	19176.6	5213.25	1	
L	15568.4	15568.6	15569.7	9d	15570.0	15569.8	6420.90	9s	L, H	19184.0	19186.7	19185.5	9s	19186.9	19186.9	5210.45	10s
					15578.2					19200.7	19200.7	9s	19199.0	19199.5	5207.03	4vs	
H		15588.0	4d	15588.0	15589.0	6413.2	0	L	19220.0	19219.9	19218.2	8s	19217.5	19217.9	5202.05	10vs	
L	15601.0	15603.4	15607.9	6d	15610.7	15610.2	6401.30	6nd	H		19222.1	7s	19222.3	19222.6	5200.77	3vs	
	18094.0							L	19240.0	19240.0	19241.9	9s	19241.6	19241.7	5195.61	10s	
	18181.0							L	19259.2	19260.2	19261.1	9s	19261.3	19261.2	5190.34	10s	
	18240.0												19269.8				
	18290.0								20252.4								
		18302.8	2s						20292.6								
H	18346.7	18347.6	4vs		18347.3	5448.87	0		20374.0	20362.3	1						
		18364.5	1s							20391.3	1						
H	18367.2	18368.9	18369.1	4vs	18367.3	18368.4	5442.62	2vs		20430.0	20424.4	1					
L	18388.3	18388.0	18388.5	5vs	18388.0	18388.2	5436.77	6vs					20434.5				
		18391.9								20448.5							
		18397.5						H	20471.9	20469.3	20468.1	5s	20467.4				
	18400.9				18402.5	5432.53	0			20475.8							
H		18406.3	18406.7	7s	18406.5	18407.0	5431.22	1		20480.0							
L	18422.8	18428.7	6s	18428.8	18428.8	5424.79	5vs			20484.7							
H	18443.4							L		20490.8	20490.3	7s	20489.5	20489.6	4879.13	5vs	
L		18447.5	18448.5	8s	18448.3	18448.4	5419.03	10s	H	20494.2	20499.1	20498.6	6s	20498.7	20498.5	4877.05	2
		18461.3			18455.3	5417.00	2vs	L		20509.6	20509.2	7vs	20509.3	20509.0	4874.55	6vs	
					18458.8	5415.97	1vs	L	20524.4	20521.0	20520.2	8s	20520.5	20520.7	4871.73	6vs	
					18463.2	5414.68	1vs	L	20542.0	20540.0	20540.1	8s	20540.1	20539.9	4867.22	6vs	
					18467.5	5413.42	1vs	L		20561.9	20560.4	3s	20560.8	20560.8	4862.27	4vs	
L	18471.4	18470.5	4vs	18469.5	18470.9	5412.43	4vs										
L	18476.9	18476.7	0		18477.7	5410.43	2vs			20571.0							
					18483.6	5408.69	0										
	18488.4									20576.8	3s	20576.6	20577.2	4858.40	3vs		
	18496.0									20582.3	3s	20582.3	20587.1	4856.06	3vs		
H	18499.7	18500.5	1							20592.4	20595.6	4s	20594.9	20594.7	4854.27	4vs	
										20598.3	20601.6	3s					
	18503.0												20603.7	4852.14	3vs		
	18510.9									20606.2	20607.2	3s	20606.2(2?)	20608.5	4851.02	3vs	
	18513.3									20614.5	3s	20614.1	20614.2	4849.68	4vs		
		18518.8	1		18517.6	5398.77	1vs			20624.3	20625.6	3s	20624.7	20625.5	4847.03	4s	

TABLE 1. (Continued.) Conglomerate absorption lines of $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ in the visible region of the spectrum.

	ν , 291°K	ν , 169°K	ν , 77°K	Int.	ν , 20°K	ν , 14°K	λ , 14°K	Int.		ν , 291°K	ν , 169°K	ν , 77°K	Int.	ν , 20°K	ν , 14°K	λ , 14°K	Int.		
L	25361.0	25306.1	0		25309.1	25309.8	3949.93	3s			26400.3	26400.3	2s	26399.9	26399.5	3786.88	2vs		
		25520.1	0	25523.2					L		26420.4	26421.5	2d	26407.4	26418.8	3784.11	4s		
				25531.5										26419.2					
		25541.5	1s	25541.3	25541.7	3914.06	0				26448.7	26446.5	1s	26447.3	26446.7	3780.12	1s		
L		25563.1	2s	25563.5	25563.5	3910.72	4vs							26456.2					
				25573.4					L		26461.7	26462.0	2d	26467.6	26467.8	3777.11	4s		
		25580.7	1s	25581.1	25581.6	3907.96	1				26482.3	26481.3	1	26483.1	26484.5	3774.73	0		
L		25602.8	2s	25602.0	25602.9	3904.70	3vs		L		26502.2	26500.8	2nd	26501.9	26502.7	3772.13	4s		
L		25627.1	2s	25627.7	25628.8	3901.07	3vs		L		26522.1	26522.7	2nd	26522.3	26522.3	3769.35	3s		
				25634.4					L	26534.0	26543.0	26541.5	2d	26543.1	26542.8	3766.43	4s		
				25641.3								26672.4	0						
				25666.4	25663.7	3895.45	1s					26705.0	0		26706.3	3743.39	0		
		25706.6	1nd	25706.9	25707.0	3888.89	2s							26774.5					
		25743.8	1s	25747.1										27272.3					
L		25767.2	1s	25766.8	25766.5	3879.92	2s							27258.0					
		25788.1	0	25780.5										27301.3					
	25795.0			25793.7	0	25792.6								27318.5	27312.3	1s	27314.1	3660.07	1
		25814.8	1	25812.0	25813.0	3872.9	2							27323.8					
		25832.1	0						L		27340.8	27334.2	1s	27335.7	27335.3	3657.24	2vs		
		25839.8	0	25838.0	25840.0	3868.9	2		L		27357.7	27353.1	1s	27356.0	27356.1	3654.45	2vs		
		25844.6	0						L		27377.1	27377.7	1s	27377.7	27377.0	3651.66	3vs		
		25851.4	0	25850.9					L			27388.7	1s	27384.0	27386.0	3650.5	0		
				25857.8										27392.4	27392.5	3649.60	0		
		25865.4	0	25868.0	25869.0	3864.6	1				27401.0	27400.0	1	27401.0	27402.0	3648.3	1		
		25879.4	0	25885.0	25883.0	3862.4	1							27410.0	27411.0	3647.0	1		
				25887.0										27420.0	27421.0	3647.0	1		
				25900.0	25896.0	3860.6	1							27419.0	27420.0	3645.9	1		
		25903.8	0	25908.0	25905.0	3859.2	1							27432.0	27433.0		2		
		25913.1	0	25913.9	25914.4	3857.77	0							27440.5	27440.7	3643.16	2		
		25922.1	0	25924.0	25921.0	3856.8	0							27444.1	27444.1				
				25940.3							27454.6	27451.5	1s	27452.4	27451.4	3641.77	2s		
														27457.4	27456.9	3641.04	2s		
H	26198.0	26247.2										27464.0	0	27463.0					
H		26278.2	26271.0	2s							27470.0	27470.0	0	27474.0	27472.0	3639.1	2		
			26286.7	1s								27477.0	0		27476.5	3638.44	2s		
H		26297.9	26286.7	0								27485.0	0	27488.8					
		26306.5	26303.2	0							27493.0	27504.0	0						
H		26309.3			26308.6									27510.0	27510.3	3633.97	2s		
		26316.8	26316.7	2s	26317.0	26317.9	3798.62	1						27600.1					
		26324.5			26324.4									27609.0	27610.0	3620.8	1		
H		26330.3	26328.9	2s	26330.0	26330.8	3796.76	0						27618.0					
L		26339.0	26338.6	2s	26339.1	26339.1	3795.57	3vs						27629.0	27629.0	3618.3	0		
					26346.1	26345.9	3794.58	0						27638.0					
H		26356.8	26355.4	2d	26352.2	26351.8	3793.73	1vs				27661.0	0	27653.0	27649.0	3615.8	0		
L					26359.0	26358.2	3792.81	4vs				27673.0	0						
L	26365.0			26372.2	26371.6	3790.89	4vs					27694.0	0						
		26376.4	26377.8	2d	26378.7									27926.0					
														27971.0					
														28090.0					

ment ($0.2\text{--}0.3\text{ cm}^{-1}$). Although in many salts of Sm^{+++} and Gd^{+++} , there seems to be a real shift to longer wave-lengths at lower temperatures, there appears to be no such marked shift in this salt of Eu^{+++} .

Variations in intensity with change of temperature may be noted in every group of lines, the most striking result being the pronounced increase in intensity of the red-most side of the group as the temperature is raised. In explaining this behavior one assumes that lines intense at the lowest temperature ("L.T.") originate in transitions between the basic level and excited upper levels, since at 14°K any excited state (except one very close to the basic one) must have a very small population. Those lines which are very faint or entirely absent at 14°K , and which increase in intensity with the temperature ("H.T.") may be interpreted as originating in transitions from levels close to the basic one, to

the same excited upper levels. Evidently one must expect to find constant energy differences (corresponding to the separations of the low-lying levels from the basic one) between "L.T." and "H.T." lines.

Evidence for levels at 21 cm^{-1} and 41 cm^{-1} above the basic one is given in Table II (for hydrogen temperatures) and in Table III (for nitrogen temperature); it is reasonably certain that levels also exist at 67 cm^{-1} and at 86 cm^{-1} , although the evidence is less satisfactory. In addition, higher levels at $100\text{--}200\text{ cm}^{-1}$ seem to be indicated; and two very diffuse lines appearing at room temperature are over 350 cm^{-1} from the nearest low temperature line. It is, however, not possible to determine definitely these higher levels.

The occurrence (described later in more detail) of a separation, in a number of pairs of L.T. lines, approximately equal to the difference of

TABLE II. Averages of values at 14°K and 20°K.

L.T.	H.T.	$\Delta\nu_1$	L.T.	H.T.	$\Delta\nu_2$
15225.7	15203.7	22.0	15161.3	15121.0	40.3
			15245.2	15206.3	38.9
15290.6	15269.1	21.5			
15318.7	15297.6	21.1			
15520.6	15498.4	22.2			
15610.5	15588.5	22.0			
18388.1	18367.9	20.2	18388.1	18347.3	40.8
18428.8	18406.8	22.0			
18592.4	18572.6	19.8			
18615.5	18596.7	18.8	18615.5	18577.0	38.5
19096.0	19074.3	21.7	19096.0	19057.2	38.8
			19142.3	19101.3	41.0
19186.8	19167.1	19.7			
19199.3	19176.7	22.6			
19241.7	19222.5	19.2			
			20489.6	20450.4	39.2
			20509.2	20467.4	41.8
20520.6	20498.6	22.0			
			20625.1	20586.3	38.8
22599.1	22577.8	21.3			
			23964.9	23921.1	43.8
24556.1	24536.2	19.9			
24598.5	24577.2	21.3			
25563.5	25541.5	22.0	25563.5	25523.2	40.3
25602.5	25581.4	21.1			
26339.1	26317.5	21.6			
26371.9	26352.0	19.9	26371.9	26330.4	41.5
26399.7	26378.7	21.0			
26467.7	26446.7	21.0			
27335.5	27314.5	21.0			
Average = 21.0 cm ⁻¹			Average = 40.3 cm ⁻¹		

TABLE III. Values at 77°K.

L.T.	H.T.	$\Delta\nu_1$	L.T.	H.T.	$\Delta\nu_2$
15226.2	15204.2	22.0			
15290.7	15268.8	21.9			
15319.0	15297.5	21.5			
			15395.7	15355.4	40.3
15521.2	15498.9	22.3			
15607.9	15588.0	19.9			
18388.5	18369.1	19.4	18388.5	18346.9	41.6
18428.7	18406.7	22.0			
18615.0	18596.3	18.7			
19096.4	19074.4	22.0	19096.4	19055.7	40.7
			19143.0	19101.5	41.5
19186.5	19167.3	19.2			
19200.1	19176.6	23.5			
19241.9	19222.1	19.8			
			20509.2	20468.1	41.1
20520.2	20498.6	21.6			
			20625.6	20585.7	39.9
			22167.4	22128.0	39.4
			23964.1	23922.5	41.6
24556.0	24537.3	18.7	24556.0	24514.8	41.2
24597.2	24578.2	19.0			
			24670.8	24629.9	40.9
25563.1	25541.5	21.6	25563.1	25520.1	43.0
25602.8	25580.7	22.1			
26338.6	26316.7	21.9			
27334.2	27312.3	21.9			
Average = 21.0 cm ⁻¹			Average = 41.0 cm ⁻¹		

the 21 and 41 cm⁻¹ levels, in some cases has made difficult the decision as to with which member of the pair a given H.T. line should be associated. It is believed, however, that a reasonably certain choice may be made by the comparison of calculated populations and observed intensities by using especially the data for 14°K and 20°K.⁶

⁶ It is perhaps noteworthy that, when one plots the frequencies of occurrence of residuals from the average of

An unusual feature of the spectrum appears in the separation of certain L.T. lines. One expects these lines to give essentially the energy level diagram of the excited states, assuming that they originate at a common basic level. In this case, in the 15,000 cm⁻¹ group, one finds 4 pairs of L.T. lines separated by very nearly the same interval, and in every other group but one, one or more similar pairs. Table IV gives the evidence.

TABLE IV. Constant separation of low temperature lines.

(Frequencies are the averages of 14°K and 20°K measurements; intensities are those for 14°K.)

L.T. ₁	Int.	L.T. ₂	Int.	$\Delta\nu$
15245.2	7	15225.7	5	19.5
15285.6	8	15266.2	6	19.4
15310.1	9	15290.6	8	19.5
15338.4	9	15318.7	8	19.7
18448.4	10	18428.8	5	19.6
19115.8	10	19096.0	9	19.8
19261.3	10	19241.7	10	19.6
20509.2	6	20489.6	5	19.6
20540.0	6	20520.6	6	19.4
22215.8	5	22196.4	6	19.4
22241.2	6	22221.4	5	19.8
23983.7	5	23964.9	4	18.8
24671.3	6	24651.9	4	19.4
26358.6	4	26339.1	3	19.5
26522.3	3	26502.3	4	20.0
27356.1	2	27335.5	2	20.6

Average = 19.6 cm⁻¹

This effect was not found in the Sm⁺⁺⁺ salts.

One may assume (in the 15,000 cm⁻¹ group for example) that the levels in the excited state are separated by exactly the same amount, and that the same interval occurs elsewhere; it seems much more reasonable to ascribe the existence of this constant difference to the basic level. The troublesome feature is that in every case the members of the pair are of about the same intensity, so that, if the upper level of the assumed doublet has at 14°K the population determined by the Boltzmann distribution, its statistical weight must be 5 or 10 times greater than that of the lower level; if the statistical weights are of the same order of magnitude, then the upper level cannot have an equilibrium population. Because of the relatively low intensities of some of the pairs (4 or 5 on the scale 0-10), one cannot escape the fact of approxi-

the 21.0 cm⁻¹ level, one does not find a true error curve; the lines seem to fall into two groups separated by about 2 cm⁻¹ at 20°K. This is a quite unexpected result; but the splitting cannot be regarded as definitely proven. It seems not to exist in the 41 cm⁻¹ level.

mately equal intensities (and say that one member is really much stronger) by assuming that the transition probabilities are so high, that each line is completely absorbed in the light path in the conglomerate.

Because of this uncertainty, it has not been considered advisable at present to draw an energy level diagram.

CONCLUSIONS

The existence of levels at 21 cm^{-1} and 41 cm^{-1} above the basic one has been proven; the probable existence of higher levels is indicated. These levels must yet be regarded as of uncertain origin. The existence of a constant energy difference between "low temperature" lines is described.

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The Vapor Pressure of Barium

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The vapor pressure of barium has been determined for temperatures from 525 to 750°C by a method based on molecular effusion. The metal was obtained by decomposition of barium azide in vacuum. The evaporated deposits were determined by microtitration to about 10^{-8} mole. The values obtained for the pressure range from 5×10^{-5} to 2×10^{-2} mm. They are well represented by the equation: $\log p$ (in mm) $= 6.99 - 8980/T$. This corresponds to a latent heat of evaporation of 4.09×10^4 cal. mole.

INTRODUCTION

DATA on the vapor pressure of metals are very useful in work on thin metal films, since one of the simplest methods of obtaining such films is that of evaporation in vacuum. If a knowledge of the thickness of the deposit is required, it is mostly necessary to know the rate of evaporation from the source as a function of the temperature. For relatively volatile metals of low ionization potential such as the alkali metals, the ionization method of Langmuir and Kingdon¹ has been used down to very low values of pressure. Accurate measurements have been made for Hg, Cd, Zn and some others, including alkali metals, by using the Knudsen method² of molecular effusion. In these cases the temperatures are so low, that the metal can be placed in direct contact with the glass wall of the tube and its temperature controlled from the outside by a suitable furnace. Vapor pressure values for a number of the less volatile metals, have been computed by Langmuir³ and his collaborators⁴

from measurements of the rate of evaporation from filaments. To obtain the vapor pressure from such data, one must know the reflection coefficient r of the emitting surface for atoms of the vapor in equilibrium with the metal. This quantity has not, in general, been determined by direct experiments. In the work referred to, r was assumed to be negligible compared with unity. In the effusion method the uncertainty about r is eliminated, since here the rate of evaporation is measured from a hole in the wall of an enclosure containing the metal. The relation between such a source and a filament source is clearly similar to that between a "hohlraum" black body emitter and a plane surface of the same temperature in thermal radiation: the emissivity of the surface corresponds to the quantity $1 - r$, the accommodation coefficient, in the case of evaporation. Recently one of us has reported some new vapor pressure determinations for calcium, using a method based on molecular effusion.⁵ In continuation of this work, we have now measured vapor pressures for barium by the same method but with a new, improved apparatus.

¹ Langmuir and Kingdon, Proc. Roy. Soc. A107, 61 (1925).

² Knudsen, Ann. d. Physik 29, 179 (1909).

³ Langmuir, Phys. Rev. 2, 329 (1913).

⁴ Jones, Langmuir and Mackay, Phys. Rev. 30, 201 (1927).

⁵ Rudberg, Phys. Rev. 46, 763 (1934).