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IS-461

JUN 4 1962

Thermal Study of Crystal Field Splittings in Erbium Ethylsulfate*

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ABSTRACT

The heat capacities of erbium ethylsulfate and yttrium ethylsulfate have been measured in the range 12 - 300°K. The magnetic contribution of the erbium ion has been evaluated with the help of an assumption concerning the difference in lattice contributions between the erbium and yttrium salts. This contribution agrees, to within experimental error, with the experimental energy level scheme for the $^4I_{15/2}$ state published by Erath.¹

INTRODUCTION

The usual approach taken in checking predicted crystal field splittings in rare-earth ions is to measure the visible or microwave absorption spectra of the ion in question. The visible spectra can lead to ambiguous results because of the difficulty of properly identifying all lines.

* Contribution No. 1156. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

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This paper was submitted for publication in the open literature at least 6 months prior to the issuance date of this Microcard. Since the U.S.A.E.C. has no evidence that it has been published, the paper is being distributed in Microcard form as a preprint.

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Paramagnetic resonance absorption is limited to levels within a few cm^{-1} of the ground level in the lowest state of the ground multiplet. This is the second in a series of investigations of ground state splittings in rare-earth ions through the use of heat capacity data in the range 12 - 300°K. The results thus obtained are sensitive to the total splitting of the ground state of the lowest multiplet and may be used to check identification of spectral lines and postulated crystal field constants.

The first investigation, hereafter referred to as I, was concerned with the splitting of the $^3\text{H}_6$ state in thulium ethylsulfate.² Heat capacity and magnetic susceptibility data were used to determine which of two proposed sets of crystal field constants was more nearly correct for this salt. Heat capacity measurements above 20°K were demonstrated to be useful for this type of investigation, and it was found that heat capacity data tend to be more sensitive to energy level structure than are susceptibility data.

The present work is concerned with the splitting of the $^4\text{I}_{15/2}$ state of tripositive erbium in the nine - hydrated ethylsulfate (ErE.S.). Heat capacity measurements on ErE.S. and YE.S. are used to determine the magnetic contribution of the erbium ion. This contribution is correlated with the experimental splitting of the $^4\text{I}_{15/2}$ state published by Erath.¹

EXPERIMENTAL

The calorimeter, sample preparation and analysis, and method of measurement were the same as described in I. Temperatures were measured on a capsule type platinum resistance thermometer. The triple point of water was taken as 273.16°K. The temperature scale was that of the National Bureau of Standards. The accuracy of the measurements was 2% at 15°K and 0.1% from 30 to 300°K.

RESULTS

The experimental heat capacity points of ErE.S. and YE.S. are given in Tables I and II, respectively. The points are ordered chronologically. The points used for water analysis are absent (see I for method of water analysis). The smoothed curve results and thermodynamic functions are given in Tables III and IV. The entropy of ErE.S. includes the value of $R \ln 2$ associated with the ground doublet of the erbium ion. This quantity, of course, is not picked up in measurements above 12°K.

The magnetic heat capacity of ErE.S. was obtained from the raw data using the same type of reasoning as in I. The raw data gave $\Delta Q/\Delta T$ of $1/n$ moles of ErE.S. plus the calorimeter and $1/m$ moles

of YE.S. plus the calorimeter. The formula

$$C_m = n [(\Delta Q/\Delta T \text{ ErE. S.} + \text{calorimeter}) - m/n (\Delta Q/\Delta T \text{ YE. S.} + \text{calorimeter}) - (1 - m/n) \text{calorimeter} - \Delta C(T)/n]$$

was then used to obtain C_m in order to minimize errors involved in subtracting out the contribution of the calorimeter. For this work, $(1 - m/n)$ was .0016.

$\Delta C(T)$, the difference in lattice heat capacity of the two salts, was taken as the difference between two Debye functions and was evaluated as follows:

1. The assumption was made that only the metal ions with their nine surrounding water molecules contributed to $\Delta C(T)$.

2. $\Delta C(T)$ was first taken to be zero and a "zeroth order" magnetic heat capacity, C_m° , was obtained. C_m° had the following characteristics:

- a. A peak at 10°K with peak height 10.25 joules (g at. wt deg)⁻¹,
- b. An experimental entropy (extrapolated to 400°K) of 22.4 eu.

3. It was assumed, as is generally accepted, that the basic state of ErE.S. is $^4I_{15/2}$. In this case the experimental magnetic entropy would be $R \ln \frac{(2J+1)}{2} = 17.28 \text{ eu}$ (i. e. $R \ln(2J+1) - R \ln 2$ because the entropy of the ground doublet would not be seen in measurements starting at 12°K). It was assumed that the difference between 22.4

and 17.3 eu could be ascribed to $\Delta C(T)$ and that furthermore the temperature dependence of $\Delta C(T)$ could be obtained from the same type of reasoning as in I. Therefore $\Delta C(T)$ was adjusted to fit the following two criterion:

- a. The entropy under $\Delta C(T)$ was to be $22.4 - 17.3 = 4.1$ eu.
- b. The height of the peak at 40°K was to be lowered so to roughly equal the height of the peak obtained at 40°K using Erath's levels.

If the spacing of the true levels were appreciably different from those assigned by Erath, the second criterion could not have been used since the position of the maximum would be incorrect. Even if the experimental and calculated maxima could be made to coincide, but the other assigned levels were incorrect (as was the case with TmE.S. in I), the experimental and calculated curves would be markedly different over the remaining temperature range.

As described in I, $\Delta C(T)$ was taken to be $C_2 - C_1$. The Debye temperatures associated with the waters and the yttrium ion in C_1 were 80 and 188°K, respectively. These values were chosen to fit Meyer and Smith's data for YE.S. in the range 1.5 - 5°K.^{3,4} The Debye temperatures associated with the waters and the erbium ion in C_2 were taken to be 72.5 and 185.8°K. The C_m obtained using the above approximation for $\Delta C(T)$ is shown as the solid points in Fig. 1. Because of the magnitude

Fig. 1. Magnetic heat capacity of ErE.S. $\text{joules (g at. wt deg)}^{-1}$.

of the lattice contribution above 40°K and the decreasing accuracy of the measurements below 30°K, the accuracy of the experimental C_m points is estimated to be 15% over the temperature range below 200°K.

DISCUSSION

The heat capacity associated with the crystal field splitting of the $^4I_{15/2}$ state of erbium in the ethylsulfate, as taken from Erath,¹ was calculated according to the standard formula⁵

$$C_m = \frac{\partial}{\partial T} RT^2 \frac{\partial}{\partial T} \ln Z$$

where Z is $\sum_{i=1}^{2J+1} \exp(-E_i/kt)$. The curve obtained from Erath's levels is shown in Fig. 1. Attempts to calculate Erath's splittings from his listed field constants and corrected operator equivalents, and the angular part of the crystal field matrix elements calculated by Stevens and Elliot, proved impossible until it was recognized that the values of $\langle r^4 \rangle A_4^0$ and $\langle r^6 \rangle A_6^0$ had become transposed. Erath's crystal field constants for ErE. S. should have been listed as follows: $\langle r^2 \rangle A_2^0 = 125.80 \text{ cm}^{-1}$, $\langle r^4 \rangle A_4^0 = -81.19 \text{ cm}^{-1}$, $\langle r^6 \rangle A_6^0 = -31.06 \text{ cm}^{-1}$, $\langle r^6 \rangle A_6^6 = 387.19 \text{ cm}^{-1}$. This set of field constants yields an energy level scheme which agrees with the experimental C_m points to within 15% below 190°K.

ACKNOWLEDGEMENTS

The authors wish to thank Messrs. R. M. Stanton, E. Phillip, and Wm. Schickell for helping in the measurements, and Messrs. Wm. Haas and C. Eckroth for pointing out the transposition of the field constants in Erath's article.

TABLE I. Experimental values of C_p of ErE.S., joules (g at. wt deg)⁻¹.

Points corrected for curvature. 0°C = 273.15°K.

ΔT	T_{av} °K	C_p
Run 1		
2.939	196.90	575.47
5.355	201.04	584.08
8.161	207.80	599.03
9.540	216.65	618.38
9.284	226.05	639.54
9.056	235.22	659.68
8.843	244.16	679.53
8.644	252.89	699.09
8.367	261.38	729.78
9.656	270.37	737.88
9.450	279.90	757.68
Run 2		
0.278	12.59	23.77
0.837	13.19	20.76
0.918	13.99	22.55
1.522	15.17	27.67
2.004	16.91	33.62
1.602	18.68	41.80
1.824	20.42	48.48
1.897	22.26	57.52
1.641	24.03	65.62
1.606	25.67	72.78
1.443	27.19	79.95
1.376	28.59	85.88
1.297	29.92	92.52
3.575	32.36	103.64
5.873	37.08	124.94
4.796	42.41	148.09
4.699	47.15	166.02
5.807	52.40	186.42

TABLE I. (cont.)

ΔT	Tav °K	Cp
5.116	57.87	206.47
5.243	61.46	219.54
4.789	66.49	236.66
5.018	75.57	265.45
5.092	80.63	281.89
5.045	85.70	297.47
5.083	90.77	312.54
5.162	95.89	326.59
10.134	103.54	346.61
9.423	113.32	373.23
10.516	123.30	399.51
9.928	133.52	425.37
10.987	143.98	451.35
10.466	154.71	477.26
10.006	165.41	502.80
9.816	175.32	525.87
8.115	184.29	546.53
9.072	192.88	566.05
9.919	202.38	587.30
10.459	212.56	609.65
8.663	222.12	630.97
10.221	231.56	651.58
11.010	242.17	675.03
10.206	252.77	698.89
9.859	262.78	731.00
10.635	272.35	741.49
11.892	283.59	766.06
11.576	295.29	792.17
Run 3		
9.577	289.74	779.06
10.922	299.95	802.22

TABLE I. (cont.)

ΔT	Tav °K	Cp
Run 4		
0.944	64.87	231.26
2.393	66.54	236.77
3.449	69.46	246.24
3.280	72.82	256.41
3.136	76.03	267.08
3.010	79.11	277.02
4.034	82.63	288.18
4.280	86.79	301.04
5.784	91.82	315.37
5.583	95.47	325.35
5.332	100.93	340.32
5.121	106.16	354.17
4.937	111.19	367.93
7.088	117.21	383.70
9.838	125.68	405.51
10.260	135.73	430.83
7.403	137.48	435.36
9.432	145.90	456.18
10.137	155.69	479.80
4.960	163.24	497.84
11.274	171.36	516.68
9.354	181.67	540.57
9.070	190.88	561.35
Run 5		
0.726	13.47	20.55
1.909	14.78	25.47
1.919	16.69	33.02
2.015	18.66	41.38
2.103	20.72	50.74
1.777	22.66	59.14
1.663	24.37	66.91
1.646	26.01	74.52
1.657	27.65	81.96
1.716	29.33	89.53
2.131	31.24	98.41
3.475	34.04	111.12
2.992	37.27	125.45
3.078	40.30	138.56

TABLE I. (cont.)

ΔT	$T_{av} \text{ } ^\circ K$	C_p
Run 6		
3.688	33.66	109.56
3.869	37.43	126.15
3.908	41.32	143.47
3.446	44.99	157.33
3.687	48.56	171.61
4.500	52.65	187.29
5.774	57.79	200.35
6.676	64.01	233.08

TABLE II. Experimental values of C_p of YE.S., joules (g at. wt deg)⁻¹.

Points corrected for curvature. 0°C = 273.15°K.

ΔT	T_{av} °K	C_p
Run 1		
9.670	141.01	438.03
9.236	150.47	462.68
8.884	159.53	484.79
9.424	168.68	506.61
9.109	177.95	528.29
8.837	186.92	548.48
8.587	195.63	568.48
7.614	203.73	586.48
10.255	212.66	606.63
10.083	222.83	629.24
9.807	232.77	651.99
11.227	242.88	678.52
10.009	253.48	716.31
7.493	262.22	742.04
9.789	270.87	733.78
10.253	280.89	760.60
10.010	291.01	784.14
Run 2		
10.011	170.12	509.65
9.664	179.96	532.38
10.279	189.92	555.10
11.584	200.85	579.85
10.467	211.86	605.65
Run 3		
1.939	22.77	52.48
2.831	25.19	62.52
5.520	29.38	80.84
6.026	35.19	106.09
7.155	41.80	135.84

TABLE II. (cont.)

ΔT	Tav °K	Cp
Run 4		
2.104	21.44	46.70
3.362	24.23	58.77
4.042	27.97	74.79
4.342	32.19	93.30
5.566	37.16	114.69
7.940	43.91	142.81
Run 5		
11.579	61.33	209.52
5.707	69.99	239.28
6.447	76.07	259.09
14.841	86.72	292.54
5.540	96.91	322.43
10.653	105.01	344.66
9.894	115.29	372.63
9.312	124.89	397.97
10.513	134.81	423.82
9.986	145.07	449.52
9.544	154.70	472.97
9.647	164.30	496.06
9.304	173.78	518.41
9.810	183.33	540.69
10.157	193.32	563.52
9.846	203.31	585.72
10.571	213.52	608.90
10.730	224.17	627.71
10.375	234.73	655.70
9.952	244.88	693.18
9.758	254.73	709.72
9.801	263.60	735.04
10.794	273.91	744.39
10.522	284.55	768.40
10.271	294.93	792.13

TABLE II. (cont.)

ΔT	Tav °K	Cp
Run 6		
9.387	83.25	282.26
8.538	92.22	308.75
7.926	100.46	332.71
1.907	105.38	345.60
1.878	107.29	351.12
1.853	109.16	356.12
Run 7		
1.855	14.34	20.22
2.287	16.46	27.97
2.999	19.13	37.81
2.719	22.02	49.47
2.937	24.87	61.28
Run 8		
1.984	15.15	22.12
1.940	17.17	30.01
4.062	20.19	41.79
Run 9		
5.219	37.46	109.50
8.574	44.36	144.27
6.773	52.06	175.48
6.251	58.59	200.10
6.634	65.05	223.07
7.731	72.24	246.71
6.242	34.91	104.96
5.966	41.02	131.45
6.672	47.34	156.20

TABLE II. (cont.)

ΔT	Tav °K	Cp
Run 10		
6.945	46.08	151.08
5.761	52.43	176.38
5.964	58.29	198.58
6.335	65.28	223.87
6.234	71.57	244.51
Run 11		
1.876	13.68	18.39
2.522	15.99	26.23
1.892	18.24	34.52
3.230	20.83	44.64
3.637	24.29	59.59

TABLE III. Thermodynamic functions of ErE.S., joules (g at. wt deg)⁻¹.

1 g at. wt = 705.68 g. 0°C = 273.15°K. Entropy at 1°K

includes R ln 2 from ground doublet.

T°K	C _p	S°	$\frac{H^\circ - H_0^\circ}{T}$	$-\frac{(F^\circ - H_0^\circ)}{T}$
1		5.76		5.76
2		5.76		5.76
3	0.12	5.78	0.02	5.76
4	0.31	5.84	0.07	5.77
5	0.84	5.96	0.17	5.79
6	1.71	6.19	0.36	5.83
7	3.03	6.55	0.64	5.91
8	4.93	7.07	1.06	6.01
9	7.32	7.79	1.62	6.17
10	9.89	8.68	2.32	6.36
11	12.89	9.76	3.15	6.61
12	15.95	11.02	4.08	6.94
13	19.25	12.42	5.12	7.30
14	22.75	13.98	6.26	7.72
15	26.42	15.67	7.48	8.19
16	30.33	17.50	8.79	8.71
17	34.47	19.46	10.17	9.29
18	38.75	21.55	11.64	9.91
19	43.04	23.76	13.18	10.58
20	47.33	26.08	14.78	11.30
22	56.30	31.00	18.15	12.85
24	65.33	35.81	21.70	14.09
26	74.57	41.87	25.42	16.45
28	83.70	47.73	29.25	18.48
30	92.92	53.82	33.19	20.63
35	115.44	69.80	43.33	26.47
40	137.03	86.61	53.69	32.92
45	157.14	103.91	64.07	39.84
50	176.95	121.49	74.37	47.12
55	196.16	139.25	84.57	54.68
60	214.61	157.21	94.63	62.58
65	231.99	174.97	104.53	70.44

Table III. (cont.)

T°K	Cp	S°	$\frac{H^\circ - H_0^\circ}{T}$	$\frac{-(F^\circ - H_0^\circ)}{T}$
			T	T
70	248.20	192.75	114.21	78.54
75	263.99	210.42	123.67	86.75
80	279.85	227.97	132.94	95.03
85	295.06	245.39	142.03	103.36
90	309.78	262.67	150.94	111.73
95	323.91	279.80	159.67	120.13
100	337.59	296.77	168.22	128.55
110	364.36	330.21	184.84	145.37
120	385.74	362.84	200.69	162.15
130	416.53	394.93	216.11	168.82
140	441.39	426.72	231.31	195.41
150	466.06	458.02	246.14	211.98
160	490.07	488.87	260.63	228.24
170	515.51	519.29	274.82	244.47
180	536.41	549.29	288.72	260.57
190	558.92	578.89	302.35	276.54
200	581.61	608.14	315.74	292.40
220	626.29	665.70	341.94	323.76
240	670.77	722.01	367.49	354.52
260	715.16	776.57	392.53	384.04
273.15	744.43	813.57	408.76	404.81
280	760.36	832.21	417.17	415.04
298.15	801.21	881.24	439.31	441.93
300	805.29	886.20	441.55	444.65

TABLE IV. Thermodynamic functions of YE.S., joules (g at. wt deg)⁻¹.

1 g at. wt = 626.44g. 0°C = 273.15°K. Data below 12°K

obtained from Meyer and Smith.^{3,4}

T°K	C _p	S°	(H° - H° ₀)/T	-(F° - H° ₀)/T
2	0.03	0.01	0.01	0.00
3	0.11	0.03	0.03	0.00
4	0.31	0.09	0.07	0.02
5	0.79	0.21	0.17	0.04
6	1.56	0.42	0.34	0.08
7	2.67	0.74	0.59	0.15
8	4.24	1.20	0.95	0.25
9	6.27	1.81	1.43	0.38
10	8.41	2.58	2.02	0.56
11	10.95	3.50	2.71	0.78
12	13.50	4.56	3.51	1.05
13	16.25	5.75	4.38	1.36
14	19.19	7.06	5.33	1.72
15	22.31	8.49	6.36	2.12
16	25.70	10.03	7.46	2.57
17	29.33	11.70	8.64	3.05
18	33.14	13.48	9.90	3.58
19	37.00	15.38	11.22	4.15
20	40.90	17.37	12.61	4.76
22	49.16	21.65	15.55	6.09
24	57.54	26.28	18.70	7.58
26	66.23	31.23	22.02	9.20
28	74.89	36.45	25.49	10.96
30	83.68	41.92	29.08	12.83
35	105.38	56.42	38.43	17.98
40	126.68	71.86	48.13	23.73
45	146.84	87.94	57.97	29.96
50	166.82	104.43	67.86	36.57
55	186.39	121.25	77.74	43.50
60	205.14	138.27	87.58	50.68
65	222.88	155.39	97.30	58.08
70	239.46	172.51	106.87	65.64
75	255.62	189.58	116.24	73.34
80	271.84	206.60	125.46	81.13
85	287.40	223.55	134.53	89.01

Table IV. (cont.)

T°K	C _p	S°	(H° - H° ₀)/T	-(F° - H° ₀)/T
90	302.45	240.40	143.44	96.96
95	316.90	257.14	152.19	104.95
100	330.88	273.75	160.77	112.98
110	358.18	306.58	177.48	129.10
120	380.10	338.70	193.45	145.24
130	411.35	370.36	209.01	161.34
140	436.62	401.77	224.36	177.40
150	461.48	432.75	239.34	193.40
160	485.84	463.31	253.99	209.32
170	509.50	493.48	268.32	225.15
180	532.65	523.26	282.36	240.89
190	555.38	552.67	296.13	256.53
200	578.30	581.75	309.67	272.07
220	623.40	639.00	336.14	302.85
240	668.26	695.18	361.95	333.23
260	712.97	750.44	387.23	363.21
273.15	742.40	786.34	403.62	382.72
280	758.40	804.93	412.10	392.82
298.15	799.40	853.84	434.43	419.41
300	803.50	858.80	436.69	422.10

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- ³ H. Meyer and P. L. Smith, J. Phys. Chem. Solids 9, 285 (1959).
- ⁴ Meyer and Smith's data for YE.S. ran 1.5% higher than the present data in the range 13 - 20°K. We attributed this difference to excess water in Meyer and Smith's sample, since they made no attempt to remove occluded water. Because of this difference, the Debye temperatures for C_1 were actually obtained from Meyer and Smith by scaling their data for YE.S. by a factor of 0.985.
- ⁵ G. S. Rushbrooke, "Introduction to Statistical Mechanics" (Oxford University Press), p. 92.