Thermophysical properties of the lanthanide sesquisulfides. IV. Schottky contributions, magnetic, and electronic properties of ϵ-phase Yb_2S_3 and Lu_2S_3

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The heat capacities of ϵ-phase Yb_2S_3 and Lu_2S_3 have been determined from 6 to 350 K and their thermodynamic properties evaluated. The resolution of the Schottky and magnetic properties by evaluation of the lattice heat capacity is shown to be in accord with spectroscopically determined energy levels. The lattice heat capacity of Yb_2S_3 was determined by means of the Komada–Westrum phonon distribution model. Excess heat-capacity contributions were thus evaluated and analyzed as Schottky and magnetic heat capacities. A phase transition associated with magnetic ordering was detected in the heat capacity of Yb_2S_3 near 7 K with an entropy content of $0.68R$. The entropies at 298.15 K are $22.77R$ and $19.74R$ for Yb_2S_3 and for Lu_2S_3.

I. INTRODUCTION

The electronic and magnetic behavior of the γ-phase lanthanide sesquisulfides have been elucidated in the first three papers in this series[1–3] by separating the excess heat capacity from the lattice heat capacity by using both the volumetric priority[4] approach and the Komada–Westrum[5] approach. The analysis of the crystalline electric field splitting, the Raman and infrared spectra, and magnetic susceptibility are consistent with the resolved thermophysical values for the γ-phase sesquisulfides.

Lanthanide sesquisulfides including Ho, Er, Tm, Yb, and Lu adopt δ- (or D- or Ho_2S_3)-type or the ϵ- (or E- or rhombohedral Al_2O_3)-type structures. Other structure types which have been reported for these compounds[6] are not pertinent to this study. Lanthanide sesquichalcogenides (Ln_2Ch_3; Ln=lanthanide, Ch=S, Se, and Te)[7] and systems involving mixed chalcogenides (e.g., S with Se or Te)[8] are of interest particularly from the materials science point of view. Heat capacities of some Ln_2Ch_3, Ln_3Ch_4 systems and mixed lanthanides with Ln_2Ch_3 have also been explored.[8–11]

Yb_2S_3 and Lu_2S_3 crystallize into the ϵ-phase structure. The structure was first observed by Flahaut *et al.*[12] and later confirmed by Range and Leeb.[13] In this structure, the cation is displaced along the ternary axes toward a trigonal face of the S octahedron in such a way that three M–S bonds are shorter than the other three.

Since Lu^{3+} has 14 electrons in its $4f$ orbital and a $^1S_0$ ground state, Lu_2S_3 exhibits only lattice heat-capacity contributions. Yb_2S_3 with 13 $4f$ electrons, however, does not have a closed shell and shows both magnetic and Schottky contributions. Moreover, the $^2F_{7/2}$ ground-state manifold of the cation Yb^{3+} in the ϵ phase is subjected to a crystalline electric field that has C_2 point group symmetry. The manifold is split into four doubly degenerate electronic energy levels. The lattice heat capacity of Yb_2S_3 cannot be determined experimentally in the subambient region and has to be evaluated by a parametric approximation based on the lattice heat capacity of Lu_2S_3. The method is essentially the same as that employed for the lattice heat capacities of γ-phase lanthanide sesquisulfides based on La_2S_3 and Gd_2S_3.[1–3] The heat capacities of ϵ-phase Yb_2S_3 and Lu_2S_3 have been reported between 1.2 and 20 K.[9,10]

This paper concerns the experimental thermodynamic properties of the two lanthanide sesquisulfides between 6 and 350 K and the resolution of the Schottky and magnetic contributions of the ϵ-phase Yb_2S_3 compound.

II. EXPERIMENT

A. Sample provenance and characterization

The Yb_2S_3 and Lu_2S_3 samples were prepared at the Ames Laboratory by direct combination of the pure elements in a manner similar to that described by Gschneidner *et al.*[10] The lutetium and ytterbium metals used were prepared in the Ames Laboratory,[14] sublimed

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TABLE I. Lattice parameters and analyzed compositions of ϵ-phase Yb_2S_3 and Lu_2S_3 ($R=8.3144$ J K^{-1} mol^{-1}).

Sesquisulfide	Lattice parameters (Å) Present study	Lattice parameters (Å) Ref. 16	S/Ln mole ratio (by analysis)	V^b (cm^3/mol)	ρ^d (g/cm^3)	m (g)[c]	M (g mol^{-1})	Color
Yb_2S_3	$a_0=6.7478\pm0.0003$[a]	6.748	1.502 ± 0.003	71.993	6.1421	42.60	442.26	Yellow gold
	$c_0=18.1900\pm0.0008$	18.191						
Lu_2S_3	$a_0=6.7220\pm0.0005$[a]	6.722	1.499 ± 0.005	71.315	6.2556	33.434	446.12	Greyish white
	$c_0=18.154\pm0.001$	18.160						

[a]Hexagonal.
[b]V=molar volume.
[c]m=sample mass.
[d]ρ=x-ray density.

sulfur (99.999%) was obtained from ASARCO.[15] After completion of the reaction in the sealed fused silica ampoules, the Lu_2S_3 was further purified by reaction with H_2S. The ampoules were opened in a helium-filled glove box. The as-formed Lu_2S_3 was ground to 200 mesh powder, cold pressed into pellets at 2.1×10^8 Pa (3×10^4 lbs/in^2), and heated to 1275 °C for 50 h under a dynamic H_2S atmosphere. A Debye–Scherrer x-ray diffraction pattern only gave lines of the ϵ Lu_2S_3 structure. All of the Lu_2S_3 dissolved readily in a 1:1 HCl:H_2O solution indicating that oxysulfide was not present.

In the preparation of Yb_2S_3, stoichiometric quantities of Yb metal and sulfur were sealed into two separate fused silica ampoules. The ampoules were heated slowly to 575 °C and maintained there until all free sulfur had reacted. The temperature was then slowly increased—over three days—to 850 °C, held there for ten days, and then raised to and held at 900 °C for two more days. Both ampoules contained hard chunks of yellow-gold colored ϵ-phase Yb_2S_3 at the end of this process. Heating Yb_2S_3 under H_2S was not required. Chemical analysis of a random sample gave $YbS_{1.5\pm0.003}$, indicating the intended composition of $YbS_{1.500}$ had been achieved within the accuracy of the analysis. A complete description of the chemical analysis method is given in the first paper of this series. An x-ray diffraction pattern gave only lines of ϵ-phase Yb_2S_3. No acid insoluble residue remained after treatment with 1:1 HCl:H_2O. Precision lattice parameters were determined for both ϵ-Lu_2S_3 and ϵ-Yb_2S_3 from Debye–Scherrer x-ray patterns taken at 295 K by measuring the theta values of the doublets in the back reflection and applying a Nelson–Riley extrapolation function to the data. Lattice parameters determined in this study are given in Table I along with literature values.[16]

B. Automated adiabatic calorimetry

Two gold-plated, oxygen-free, high-conductivity (OFHC) copper calorimeters (laboratory designation W-61 and W-AB) were employed in the two measurements. The Lu_2S_3 sample was determined in the W-61 calorimeter, which is especially equipped with two pairs of perforated, spring-loaded, copper sleeves soldered to the heater–thermometer well to hold the sample pellets. The heat capacity of the Yb_2S_3 (Ref. 16) sample was determined in the W-AB calorimeter. After loading (and for Lu_2S_3, soldering the cover in place), the calorimeters were evacuated and approximately 2.0 kPa (at about 300 K) helium gas was added to facilitate rapid thermal equilibration (see also Table I). The data were taken in the Mark X calorimetric cryostat, an improved version of the Mark II cryostat described elsewhere, together with relevant operating techniques.[17,18] Data acquisition was computer assisted. The temperatures were measured with a Leeds and Northrup platinum resistance thermometer calibrated at the National Bureau of Standards (NBS). All other crucial measurements were similarly referenced to NBS calibrations.

C. Optical spectroscopy

The material used to obtain the absorption spectrum of Yb_2S_3 was prepared by the method of Henderson *et al.*[19] The samples contained less than 100 ppm atomic oxygen and displayed the Debye–Scherrer x-ray pattern for ϵ-phase Yb_2S_3. Based on wet chemical analysis, the compounds can be represented as $YbS_{1.5\pm0.003}$. We had no success in growing $YbS_{1.5}$ single crystals from the melt. Even with an appreciable sulfur vapor pressure within sealed capsules, it was not possible to keep some of the trivalent ytterbium from being reduced. The melted ingots were black with very small crystallites found scattered throughout the highly fractured material.

To obtain the absorption spectrum of Yb_2S_3, stoichiometric powder was mixed with an optically transparent inert gel to produce "mull" samples. The spectra were observed with a Cary Model 14R at 90 K and room temperatures. Hot bands of the $^2F_{5/2}$ multiplet manifold observed at 1.0 μm indicate that the ground state $^2F_{7/2}$ has crystal-field electronic energy levels at 0, 155, 285, and 380 cm^{-1}. Each level is twofold degenerate. Since there are more crystal-field parameters associated with C_2 symmetry than experimental energy levels associated with the $^2F_{7/2}$ and $^2F_{5/2}$ multiplet manifolds, we were not able to obtain a

TABLE II. Experimental heat capacities of ϵ-phase Yb_2S_3 and Lu_2S_3 (R=8.3144 J K^{-1} mol^{-1}).

T/K	$C_{p,m}/R$
ϵ-phase ytterbium sesquisulfide (Yb_2S_3, M=442.26 g mol^{-1})	
Series I	
251.148	14.729
256.469	14.785
262.683	14.864
268.898	14.927
275.112	14.981
281.318	15.204[a]
287.552	15.084
293.769	15.158
299.989	15.228
306.195	15.265
312.412	15.276
318.636	15.308
324.855	15.315
331.071	15.339
337.313	15.348
343.567	15.349
Series II	
129.513	12.045
132.764	12.239
137.875	12.445
142.978	12.637
148.096	12.862
153.210	13.050
158.340	13.197
163.477	13.348
168.621	13.475
173.756	13.609
178.908	13.721
184.061	13.836
189.209	13.929
194.377	14.042
199.545	14.116
204.706	14.188
209.879	14.240
215.042	14.307
220.207	14.385
225.380	14.443
230.555	14.496
235.743	14.555
240.920	14.611
246.098	14.660
251.280	14.718
6.650	0.309
7.059	1.924
9.101	0.552
11.320	0.486
12.339	0.501
Series III	
13.320	0.518
14.271	0.567
15.288	0.620
16.386	0.695
17.482	0.768
18.575	0.865
19.671	0.962
20.772	1.066

TABLE II. (*Continued.*)

T/K	$C_{p,m}/R$
Series IV	
7.109	0.996
8.598	0.558
10.000	0.508
11.071	0.484
12.095	0.497
13.069	0.511
14.023	0.554
14.961	0.603
15.981	0.666
17.080	0.742
18.174	0.827
Series V	
6.743	0.675
7.573	0.653
8.169	0.636
8.539	0.645
8.821	0.560
10.192	0.502
12.468	0.501
14.458	0.578
16.314	0.691
18.152	0.826
19.641	0.959
21.124	1.101
22.552	1.247
23.990	1.399
25.443	1.563
26.907	1.731
28.382	1.904
30.041	2.100
31.877	2.311
33.721	2.558
35.601	2.647[a]
37.498	3.223[a]
39.575	3.321
41.949	3.609
44.311	3.873
46.670	4.187
49.270	4.539
49.087	4.512
51.794	4.863
54.653	5.227
57.526	5.597
60.421	5.968
63.566	6.363
66.958	6.785
70.361	7.198
73.793	7.527[a]
77.239	7.977
80.941	8.392
84.897	8.805
88.862	9.210
92.848	9.570
97.099	9.923
101.614	10.253
106.138	10.600
110.669	10.918
115.209	11.245
119.770	11.527

TABLE II. (*Continued.*)

T/K	$C_{p,m}/R$
124.348	11.754
128.939	11.979
133.515	12.280
138.116	12.450
ϵ-phase lutetium sesquisulfide (Lu_2S_3, M=446.12 g mol^{-1})	
Series I	
7.46	0.033
8.04	0.045
8.46	0.055
8.90	0.066
9.35	0.081
9.79	0.095
10.24	0.113
10.64	0.128
11.08	0.148
11.59	0.173
12.11	0.199
12.67	0.228
13.24	0.265
13.85	0.300
14.48	0.352
15.13	0.404
15.83	0.460
16.55	0.522
29.85	1.958
31.25	2.121
32.72	2.293
34.26	2.470
35.89	2.654
37.59	2.845
39.37	3.046
41.24	3.258
43.21	3.475
45.28	3.710
46.89	3.885
49.04	4.111
51.40	4.370
53.88	4.625
56.49	4.901
59.23	5.183
62.10	5.502
65.12	5.798
68.31	6.087
128.42	10.444
133.50	10.689
138.59	10.916
143.69	11.132
148.79	11.327
153.92	11.500
159.04	11.670
164.17	11.864
169.30	12.019
174.45	12.122
179.59	12.285
184.74	12.388
Series II	
170.33	11.986
175.28	12.156
180.42	12.314
185.57	12.454
190.72	12.542
257.87	13.577
263.05	13.658

TABLE II. (*Continued.*)

T/K	$C_{p,m}/R$
268.23	13.729
273.42	13.761
278.60	13.813
283.77	13.870
288.95	13.924
294.13	13.970
299.31	14.005
304.49	14.027
309.67	14.072
314.85	14.134
320.04	14.186
325.22	14.236
330.40	14.291
335.61	14.362
340.83	14.392
346.03	14.419
17.31	0.591
18.11	0.666
18.94	0.748
19.81	0.836
20.73	0.933
21.69	1.036
22.69	1.145
23.75	1.263
24.86	1.389
26.02	1.521
27.23	1.658
28.51	1.807
71.90	6.395
75.81	6.768
79.72	7.151
83.76	7.528
88.31	7.916
93.26	8.247
98.22	8.621
103.19	9.195
108.20	9.278
113.25	9.590
118.30	9.890
123.35	10.173
195.87	12.646
201.00	12.765
206.14	12.865
211.31	12.953
216.48	13.049
221.65	13.130
226.82	13.216
232.00	13.298
237.17	13.361
242.34	13.446
247.52	13.496
252.69	13.551
Series III	
293.43	13.961
298.61	13.982
303.79	14.031
308.98	14.070
314.17	14.124
319.35	14.182
324.55	14.217
329.74	14.273
334.92	14.33
340.11	14.35
345.29	14.425

[a]Not included in values on which smoothed curve (Fig 1) is based.

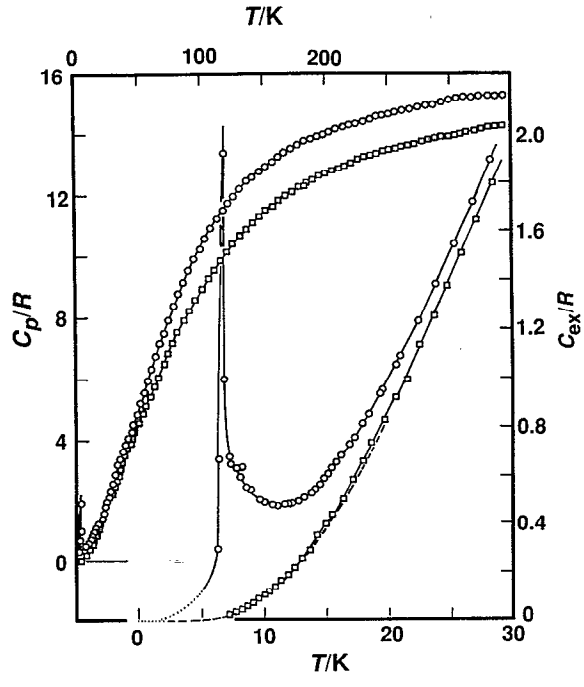

FIG. 1. *Cp* ϵ-phase Yb_2S_3–O–and ϵ-phase Lu_2S_3–⊟–. The data of Gschneidner *et al.* (Ref. 10) are shown as ---.

unique theoretical crystal-field splitting using the lattice-sum method described in Ref. 2.

III. RESULTS AND DISCUSSION

The experimental heat-capacity data for Yb_2S_3 and Lu_2S_3 are presented in Table II and plotted in Fig. 1. Smoothed heat capacities and thermodynamic functions at selected temperatures are presented in Table III. The standard deviation in these measurements is less than ±0.1% above 20 K. Between 6 and 20 K, the deviations decrease gradually from about ±4% to ±0.1% at 20 K.

The Komada–Westrum characteristic temperature (Θ_{KW}) was calculated for ϵ-phase Lu_2S_3 on the assumption that no excess contributions are present in the experimental data.[5] The lattice heat-capacity contribution of ϵ-phase Yb_2S_3 was then calculated with the LEM-3 computer program using input coefficients calculated in the same manner as those for γ-phase compounds, but extrapolating from Lu_2S_3 as a reference point.[2,3,5] Since only one reference point was available in the ϵ phase, it was assumed that the coefficients vary similarly to those in the γ-phase lanthanide sesquisulfides, i.e., that the same dependence on atomic number used for the coefficients in the γ-phase (Fig. 3 of Ref. 3) are used for the ϵ phase.

The variation in Θ_{KW} for Lu_2S_3 (82.3 K) is shown in Fig. 2. The value calculated for Yb_2S_3, Θ_{KW}=89.1 K has been used to obtain the excess heat-capacity contributions to Yb_2S_3 which are shown in Fig. 3 together with the Schottky contribution based on the analysis of the optical

TABLE III. Smoothed heat capacities and derived thermodynamic properties (R=8.3144 J K^{-1} mol^{-1}).

	$C_{p,m}$	$S^0_m-S^0_m(0\ K)$	$H^0_m-H^0_m(0\ K)$	Φ^0_m
T/K	R	R	$R\cdot K$	R
ϵ-phase ytterbium sesquisulfide Yb_2S_3, M=442.26 g mol^{-1}				
0.0	0.0	0.0	0.0	0.0
5.0	0.094	0.022	0.110	0.0
10.0	0.493	0.546	4.74	0.072
15.0	0.609	0.755	7.34	0.266
20.0	0.991	0.977	11.25	0.414
25.0	1.512	1.2528	17.47	0.554
30.0	2.096	1.580	29.26	0.605
35.0	2.715	1.949	38.49	0.849
40.0	3.352	2.353	53.65	1.012
45.0	3.989	2.784	72.00	1.184
50.0	4.625	3.238	93.54	1.367
60.0	5.920	4.195	146.27	1.757
70.0	7.155	5.201	211.66	2.177
80.0	8.294	6.232	289.01	2.619
90.0	9.293	7.268	377.07	3.078
100.0	10.153	8.293	474.41	3.549
110.0	10.890	9.296	579.7	4.026
120.0	11.523	10.271	691.8	4.506
130.0	12.068	11.216	809.9	4.986
140.0	12.534	12.128	932.9	5.464
150.0	12.927	13.006	1060.3	5.937
160.0	13.255	13.851	1191.2	6.406
170.0	13.526	14.663	1325.2	6.868
180.0	13.753	15.443	1461.6	7.323
190.0	13.943	16.20	1600.1	7.778
200.0	14.107	16.92	1740.4	8.218
210.0	14.251	17.61	1882.2	8.647
220.0	14.380	18.27	2025.4	9.064
230.0	14.496	18.92	2169.8	9.486
240.0	14.605	19.53	2315.3	9.883
250.0	14.711	20.13	2461.9	10.282
260.0	14.818	20.71	2609.5	10.673
270.0	14.926	21.27	2758.0	11.054
280.0	15.03	21.82	2908.0	11.434
290.0	15.13	22.35	3058.8	11.802
298.15	15.20	22.77	3182.5	12.096
300.0	15.22	22.86	3210.6	12.158
325.0	15.32	24.08	3592.6	13.026
350.0	15.37	25.22	3976.2	13.859
ϵ-phase lutetium sesquisulfide Lu_2S_3, M=446.12 g mol^{-1}				
0.0	0.0	0.0	0.0	0.0
10.0	0.103	0.033	0.250	0.008
15.0	0.392	0.123	1.399	0.029
20.0	0.857	0.296	4.468	0.073
25.0	1.404	0.545	10.100	0.141
30.0	1.978	0.852	18.551	0.233
40.0	3.115	1.578	44.060	0.476
50.0	4.209	2.390	80.67	0.777
60.0	5.270	3.252	128.11	1.117
70.0	6.259	4.140	185.82	1.485
80.0	7.165	5.036	253.01	1.873
90.0	7.985	5.928	328.83	2.274
100.0	8.724	6.808	412.44	2.683
120.0	9.981	8.514	600.0	3.514
140.0	10.973	10.130	809.9	4.345
160.0	11.733	11.647	1037.3	5.164
180.0	12.303	13.064	1278.0	5.964
200.0	12.738	14.383	1528.6	6.741
220.0	13.091	15.61	1786.9	7.492
240.0	13.392	16.77	2051.8	8.217
260.0	13.645	17.85	2322.3	8.917
280.0	13.841	18.87	2597.3	9.592
298.15	13.987	19.74	2849.7	10.183
300.0	14.001	19.83	2875.6	10.243
320.0	14.162	20.74	3157.2	10.870
350.0	14.507	22.02	3587.0	11.772

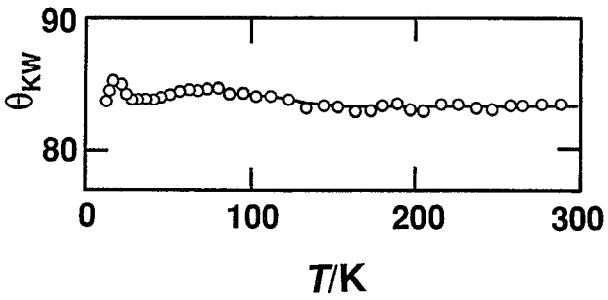

FIG. 2. Θ_{KW} for ϵ-phase Lu_2S_3.

spectra. The agreement shown in Table IV between the calorimetrically determined and the spectroscopically ascertained electronic heat capacity is good. Although an independent evaluation of the lattice contribution might also have been made by the volumetric priority method,[1] the preceding paper in this series[3] has demonstrated convincingly that—despite differences in approach—the agreement is excellent.

In the vicinity of 7 K, a magnetic transition is found. Resolution of the transition indicated a $\Delta_{trs}S^0$ about $0.68R$. This value agrees very well with the entropy for the magnetic ordering of Yb^{3+} with effective spin $S=1/2$ in a crystal-field split ground state that is doubly degenerate.

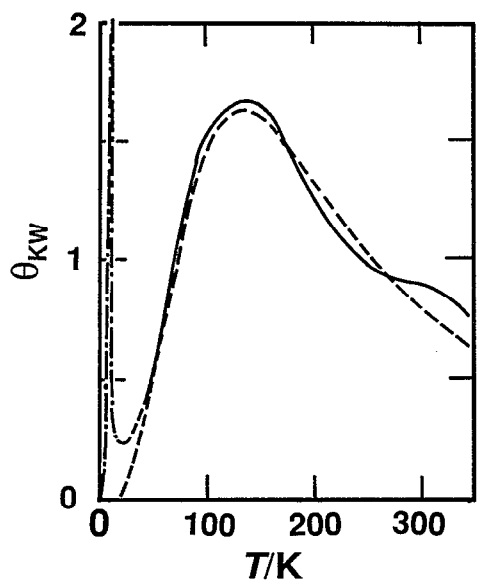

FIG. 3. Excess heat capacities of ϵ-phase Yb_2S_3. Calorimetric—, spectroscopic---, and magnetic- · -contributions.

TABLE IV. Schottky levels, ground state manifold, for ϵ-phase Yb_2S_3.

Compound (term θ_{KW})	Method of determination	Energy (cm^{-1}) and degeneracy (n)
ϵ-Yb_2S_3	Optical spectra	0(2), 155(2), 285(2), 380(2)
$Yb^{3+}(^2F_{7/2})$	Excess C_p (KW)	0(2), 155(2), 285(2), 380(2)
$\theta_{KW}=89.12$		
ϵ-Lu_2S_3, $Lu^{3+}(^1S_0)$, $\theta_{KW}=82.3$		

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