Thermophysical properties of the lanthanide sesquisulfides. II. Schottky contributions and magnetic and electronic properties of γ-phase Pr$_2$S$_3$, Tb$_2$S$_3$, and Dy$_2$S$_3$

John B. Gruber
Department of Physics, San Jose State University, San Jose, California 95192

Ramón Burriel
Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Edgar F. Westrum, Jr., W. Plautz, G. Metz, and Xiao-Xia Ma
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

B. J. Beaudry and P. E. Palmer
Ames Laboratory, Iowa State University, Ames, Iowa 50011

Heat-capacity measurements by adiabatic equilibrium calorimetry are reported for γ-phase Pr$_2$S$_3$, Tb$_2$S$_3$, and Dy$_2$S$_3$ between 5 and 350 K. Highly purified samples were prepared and their composition verified by chemical analysis. Precision lattice parameters were determined for each compound and are compared with literature values. The total heat capacity has been resolved into lattice, magnetic, and Schottky components by a volumetric approach. The experimental Schottky contributions accord with the calculated curves based on the crystal-field splitting of the $^{2S+1}L_J$ ground state of the lanthanide ions occupying sites of S$_4$ symmetry in the Th$_3$P$_4$ lattice. The individual crystal-field electronic energy levels have been obtained in part from an analysis of the hot-band data observed in the absorption spectra of Pr$_2$S$_3$, Tb$_2$S$_3$, and Dy$_2$S$_3$, and from a calculated splitting in which the crystal-field parameters B_{km}, were determined from a lattice-sum calculation. Molar thermodynamic properties are reported for all three compounds. The entropy at 298.15 K $\{S^0 - S^0 (7 \text{ K})\}$, is 22.78$R$, 22.93$R$, and 23.36$R$, for γ-phase Pr$_2S_3$, Tb$_2S_3$, and Dy$_2S_3$, respectively.

I. INTRODUCTION

In the first paper of this series (referred to as I) we presented the thermophysical properties of four lanthanide sesquisulfides having the Th$_3$P$_4$ (γ-phase) structure, namely La$_2$S$_3$, Ce$_2$S$_3$, Nd$_2$S$_3$, and Gd$_2$S$_3$.[1] Interest in these materials arises from their success as components in solar energy absorbers and photovoltaic cells.[1-6] The defect structure of the material allows one to explore a range of electronic transport phenomena as the solid-solution between R$_2$S$_3$ and R$_3$S$_4$ involves a change from insulating to semimetallic characteristics without a change in phase.[7-14]

In this paper we extend the analyses given in I to other lanthanide sesquisulfides that can be prepared in the same phase. These compounds include γ-phase Pr$_2$S$_3$, Tb$_2$S$_3$, and Dy$_2$S$_3$. The compound Sm$_2$S$_3$ is a special case that we reserve for discussion in a later paper. Literature heat-capacity values for γ-phase Pr$_2$S$_3$, Tb$_2$S$_3$, and Dy$_2$S$_3$, do not extend to sufficiently high temperatures to determine the Schottky contribution due to the crystal-field electronic energy levels associated with the $^{2S+1}L_J$ ground-state manifold of the tripositive lanthanide ion.[13] Moreover, their samples were not well characterized as to their chemical composition.

In this paper we include additional details of the sample preparation, and verify the crystal structure of samples investigated.[7] We report heat-capacity measurements between 5 and 350 K resolved into lattice, magnetic, and Schottky components for γ-phase Pr$_2$S$_3$, Tb$_2$S$_3$, and Dy$_2$S$_3$, based on the crystal-field electronic energy levels of the ground-state manifold of Pr^{3+} ($^3H_4$),Tb^{3+} ($^7F_6$), and Dy^{3+} ($^6H_{15/2}$). A detailed analysis of the crystal structure of the γ phase of these sesquisulfides indicates that the lanthanide ions occupy sites of S_4 symmetry.[15-21] We conclude that the volumetric method used to determine the Schottky contribution represents a valid approach to the analysis of molar heat-capacity data for all γ-phase Ln$_2$S$_3$ compounds.[1,20,22]

II. SAMPLE PREPARATION

The Pr$_2$S$_3$, Tb$_2$S$_3$, and Dy$_2$S$_3$ samples were prepared by direct combination of the pure elements in a manner similar to that described earlier.[23] The lanthanide metals were prepared in the Ames Laboratory and had the chemical analyses typical of the highly purified metals produced in that laboratory.[24] Sublimed sulfur (99.999%) was contained from ASARCO.[25]

After the synthesis was carried out in sealed quartz ampoules; the material was not melted as it had been in a previous study.[23] Instead, the quartz ampoules were opened and the sulfide ground and sieved to 200 mesh powder. The powder was cold pressed into pellets 3 mm thick by 15 mm diameter. The pressed pellets of Pr$_2$S$_3$ were heated to 1500 °C under a dynamic H$_2$S atmosphere for 9 h. The Tb$_2$S$_3$ and Dy$_2$S$_3$ pellets were heated to 1450 °C for 48 h under flowing H$_2$S.

Debye–Scherrer x-ray patterns taken at 295 K con-

TABLE I. Lattice parameters and analyzed compositions of γ-phase Pr_2S_3, Tb_2S_3, and Dy_2S_3.

| Sesquisulfide | Lattice parameter/Å | | Analyzed mole ratio S/Ln | Sample mass m/g | Molar mass M/g mol^{-1} | Color |
	Present study	Reference 7				
Pr_2S_x	8.5748 ± 0.0003	8.573	1.500 ± 0.006	27.719	378.007	Dark green
Tb_2S_x	8.3334 ± 0.0003	8.333	1.496 ± 0.002	34.093	414.043	Grey green
Dy_2S_x	8.3006 ± 0.0002	8.292	1.499 ± 0.001	53.573	421.192	Yellow green

tained only lines of the γ-phase structure. Precision lattice parameters were determined 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.[7] The final composition was determined by chemical analysis. The sesquisulfides were dissolved in 4.8 M hydrochloric acid and the evolved hydrogen sulfide gas was collected in a solution of sodium hydroxide and hydrogen peroxide. The sulfate which formed was determined as barium sulfate. The lanthanide ions in solution were quantitatively analyzed by titrating with EDTA. An additional test, which was the most sensitive to the presence of trace oxysulfide impurities, was to dissolve the sulfide in 6N HCl and observe the clarity of the solutions. A clear solution indicates the absence of oxysulfide. All samples used in this study gave clear solutions on dissolution.

III. AUTOMATED ADIABATIC CALORIMETRY

The heat-capacity data were taken in the Mark X calorimetric cryostat, an improved version of the Mark II cryostat previously described (by addition of a guard shield surrounding the adiabatic shield) together with the relevant operating techniques.[26] The acquisition of heat-capacity data from about 5 to 350 K was computer assisted.[27] A gold-plated oxygen-free high-conductivity copper calorimeter (laboratory designation W-61) specially equipped with a pair of perforated copper spring-loaded sleeves soldered to the heater-thermometer well to hold the sulfide pellets was employed for all measurements. After loading the calorimeter was evacuated and about 2.0 kPa (at 300 K) helium gas added to facilitate thermal equilibration. The calorimeter seal-off tip was closed with Cerroseal (50 mass percent tin and indium) solder. Temperatures were measured on an ASL-7 induction bridge with a Leeds and Northrup platinum-resistance thermometer sensor calibrated by the National Bureau of Standards (now called NIST). All other accurate experimental quantities are referred to standards and calibrations provided by NBS.

IV. CALORIMETRIC MEASUREMENTS

Table II presents the molar heat capacities for γ-phase Pr_2S_3, Tb_2S_3, and Dy_2S_3. Relevant adjuvant quantities (sample mass, molar masses, lattice constants, etc.) used in computer reduction of the data are given in Table I. The mole used throughout the paper is based on the formula written as Ln_2S_x and thus involves two moles of lanthanide (Ln) ca-

tions. The data, in energy-dimensionless units, are given in chronological sequence so that the temperature increments can usually be deduced from differences in adjacent temperatures. Data were obtained between 5 and 350 K and are represented in Fig. 1. They are compared with the results for La_2S_3 that has no excess contribution to the "lattice" C_p. The low temperature detail of Fig. 1 represents a plot of C_p vs T for Pr_2S_3, Tb_2S_3, and Dy_2S_3 up to 20 K. The open symbols are data obtained in the present study; the solid symbols represent the results reported by Ho *et al.*[13] The results for Dy_2S_3 and Pr_2S_3 are in reasonable agreement, whereas the results for Tb_2S_3 are lower than the values reported by Ho *et al.*[13] The difference may be due to the difference in stoichiometry between the two Tb_2S_3 samples. Additionally there is a small peak in our data of unknown origin at 12.4 K without any relevant feature in the susceptibility measurements.[28]

Although no evidence is found for magnetic ordering in Pr_2S_3 above 1 K neither from magnetic susceptibility[28] nor from heat-capacity measurements, Dy_2S_3 shows antiferromagnetic ordering around 3 K, and Tb_2S_3 has low lying levels below 10 K. This precludes determination of the Debye characteristic temperature at 0 K. For Pr_2S_3 our data accord well with the values of Ho *et al.*[13] which extend to lower temperatures (Fig. 1).

The thermodynamic properties of γ-phase Pr_2S_3, Tb_2S_3, and Dy_2S_3 between 7 and 350 K are summarized in Tables III–V. The accuracy is characterized by $<0.1\%$ standard deviation above 15 K. Below this temperature, standard deviations of the heat-capacity gradually increase until they attain an uncertainty of about two percent at the lowest temperatures.

V. DETERMINATION OF SCHOTTKY HEAT-CAPACITY CONTRIBUTIONS

The presence of Schottky contributions to the heat capacities of γ-phase Pr_2S_3, Tb_2S_3, and Dy_2S_3 is evident upon comparison with the La_2S_3 and Gd_2S_3 curves reported in I. The volume-weighted lattice heat capacity approximation technique has been used successfully in several other groups of lanthanide compounds (sesquioxides, halides, trihydroxides, etc.) to deduce the vibrational lattice contribution.[29,30] Of the γ-phase lanthanide sesquisulfides, only La_2S_3, has not excess contribution in the heat capacity. After subtraction of the low-temperature magnetic contribution in the γ-phase Gd_2S_3, its lattice heat capacity was used in I together with that of La_2S_3 to interpolate the values for the other isostructural lanthanide sesquisulfides with this technique. This

TABLE II. Molar heat capacities of lanthanide sesquisulfides ($R = 8.3144$ J K^{-1} mol^{-1}).

Praseodymium sesquisulfide (Pr$_2$S$_3$)

T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R
Series I		25.48	2.105	75.88	7.787	211.69	14.059
7.26	0.455	26.80	2.235	79.81	8.208	216.87	14.100
7.62	0.471	28.08	2.377	84.24	8.679	222.05	14.185
8.11	0.501	29.42	2.525	89.16	9.136	227.22	14.248
8.58	0.537	30.82	2.682	94.11	9.530	232.40	14.295
9.05	0.576	32.29	2.853	99.09	9.905	237.58	14.322
9.54	0.612	33.83	3.028	104.09	10.283	242.76	14.386
10.02	0.646	35.44	3.213	109.10	10.628	247.93	14.458
10.51	0.684	37.14	3.404	114.14	10.966	253.12	14.501
10.99	0.717	38.91	3.615	119.19	11.280	258.30	14.500
11.49	0.760	40.77	3.826	124.25	11.562	263.49	14.582
12.05	0.804	42.73	4.047	129.33	11.821	268.66	14.574
12.64	0.849	44.78	4.284	134.42	12.068	273.84	14.608
13.25	0.900	46.93	4.549	139.51	12.296	279.02	14.629
13.89	0.952	49.19	4.801	144.62	12.524	284.20	14.656
14.57	1.017	51.79	5.107	149.87	12.675	289.40	14.677
15.27	1.079	54.67	5.434	154.87	12.850	294.62	14.645
16.01	1.145			160.00	13.021	299.81	14.737
16.78	1.213	Series II		165.14	13.155	304.98	14.808
17.59	1.289	51.40	5.057	170.28	13.300	310.15	14.801
18.44	1.367	54.04	5.362	175.43	13.410	315.34	14.838
19.32	1.452	56.93	5.694	180.58	13.526	320.51	14.869
20.25	1.544	59.83	6.033	185.81	13.632	325.68	14.902
21.22	1.643	62.74	6.390	190.97	13.709	330.83	14.931
22.24	1.748	65.62	6.711	196.15	13.812	335.99	14.967
23.30	1.864	68.75	7.035	201.32	13.918	341.16	15.020
24.41	1.980	72.19	7.406	206.51	13.964	346.33	15.051

Terbium sesquisulfide (Tb$_2$S$_3$)

T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R
Series I		13.14	0.839	59.45	6.374	184.76	13.313
7.10	0.678	13.40	0.852	62.35	6.720	189.91	13.426
7.77	0.654	13.88	0.875	65.40	7.051	195.07	13.522
8.30	0.652	14.72	0.938	68.29	7.348	200.23	13.612
8.83	0.656	15.67	1.010	70.85	7.585	205.40	13.668
9.32	0.675	16.62	1.090	74.38	7.929	210.57	13.733
9.79	0.684	17.56	1.173	78.05	8.286	215.74	13.806
10.28	0.708	18.51	1.264	81.92	8.659	220.91	13.874
10.79	0.724	19.46	1.360	85.89	9.031	226.08	13.962
11.32	0.758	20.41	1.460	87.89	9.125	231.26	14.011
11.88	0.792	21.38	1.569	90.44	9.399	236.44	14.066
12.45	0.841	22.40	1.690	95.46	9.744	241.62	14.094
13.07	0.831	23.46	1.812	100.45	10.063	246.78	14.190
13.73	0.864	24.57	1.955	105.46	10.387	251.96	14.229
14.40	0.908	25.67	2.905	110.48	10.690	257.14	14.261
15.10	0.964	26.82	2.241	115.53	10.959	263.33	14.309
15.83	1.022	28.09	2.407	120.60	11.241	267.51	14.325
16.59	1.086	29.42	2.581	125.68	11.505	272.69	14.388
17.39	1.158	30.82	2.770	130.77	11.728	277.87	14.406
18.23	1.235	32.29	2.964	135.86	11.944	283.06	14.468
19.10	1.323	33.82	3.171	140.97	12.121	288.24	14.493
		35.43	3.390	146.09	12.308	293.43	14.520
		37.12	3.614	151.21	12.478	298.61	14.535
Series II		38.90	3.851			303.79	14.578
10.00	0.692	40.76	4.088	Series III		308.98	14.616
10.51	0.717	42.72	4.342	149.59	12.426	314.17	16.675
11.00	0.737	44.77	4.608	154.72	12.564	319.35	14.722
11.50	0.772	46.93	4.879	159.86	12.703	324.55	14.753
11.88	0.789	49.19	5.166	165.00	12.865	329.74	14.807
12.12	0.819	51.57	5.458	170.13	12.997	334.92	14.864
12.37	0.853	54.07	5.753	174.44	13.103	340.11	14.900
12.62	0.846	56.69	6.058	179.61	13.201	345.29	14.984
12.88	0.822						

Dysprosium sesquisulfide (Dy$_2$S$_3$)

T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R
Series I		158.75	13.334	320.29	15.095	29.44	2.347
61.77	6.758	163.89	13.443	325.48	15.074	30.83	2.549
64.82	7.156	169.04	13.559	330.68	15.088	32.31	2.741
67.99	7.523	174.18	13.690	335.86	15.141	33.84	2.964
71.33	7.902	179.34	13.767	341.06	15.156	35.45	3.197
74.84	8.286	185.13	13.862	346.25	15.189	37.15	3.419
78.53	8.683	189.15	13.943			38.92	3.682

TABLE II. (*continued*).

T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R
82.40	9.123	194.04	14.012	Series V		40.78	3.930
86.48	9.532	199.43	14.074	6.59	0.517	42.74	4.206
90.77	9.888	204.60	14.155	6.92	0.523	44.79	4.496
95.30	10.238	209.77	14.228	7.33	0.476	46.95	4.797
100.07	10.582	214.94	14.279	7.72	0.475	49.21	5.092
105.02	10.928	220.11	14.330	8.12	0.472	51.59	5.416
110.06	11.255	225.29	14.393	8.56	0.451		
115.10	11.551	230.46	14.435	9.27	0.452	Series VII	
120.14	11.836	235.64	14.485	10.21	0.460	5.93	0.66
125.21	12.082	240.82	14.536	11.21	0.489	6.97	0.52
130.30	12.288	245.99	14.605	12.16	0.525	8.18	0.459
135.38	12.513	251.17	14.620	13.10	0.571	9.59	0.452
140.45	12.643	256.36	14.662	14.03	0.632	11.07	0.482
145.55	12.924	261.54	14.681	14.96	0.700	12.46	0.538
		266.72	14.713	15.89	0.773	13.81	0.613
Series II		271.90	14.751	16.83	0.850	15.14	0.710
79.86	8.821	277.09	14.780	17.76	0.938	18.21	0.976
82.75	9.143	282.27	14.828	18.69	1.030	19.80	1.144
86.87	9.562	287.45	14.847	19.88	1.152		
91.20	9.935	292.62	14.907	21.06	1.283	Series VIII	
95.75	10.275	297.80	14.951	22.05	1.400	45.62	4.608
100.37	10.586	302.98	14.999	23.09	1.524	47.98	4.928
105.18	10.930	308.15	15.043	24.17	1.660	50.84	5.316
				25.31	1.811	53.70	5.703
Series III		Series IV		26.51	1.962	58.26	6.300
51.64	5.426	191.06	14.014			62.69	6.892
54.57	5.815	196.20	14.089	Series VI		67.42	7.476
57.20	6.157	201.20	14.157	5.55	0.75	77.04	8.556
59.99	6.531	206.21	14.219	6.53	0.55	81.91	9.072
62.91	6.918	211.39	14.277	7.81	0.471	86.81	9.583
65.99	7.291	216.57	14.338	8.95	0.446	91.75	9.999
69.22	7.666	221.75	14.390	9.98	0.460	96.74	10.370
72.63	8.054	226.93	14.440	10.97	0.480	101.75	10.710
79.97	8.848	232.11	14.466	11.93	0.517	106.77	11.066
83.92	9.266	237.30	14.504	12.88	0.560		
88.08	9.674	242.49	14.537	13.82	0.615		
92.47	10.031	247.67	14.572	14.75	0.682		
97.09	10.358	252.87	14.602	15.68	0.758		
101.95	10.720	258.06	14.661	16.61	0.831		
106.05	11.049	263.24	14.711	17.54	0.916		
109.83	11.220	268.43	14.757	18.47	1.006		
112.81	11.425	273.62	14.796	19.41	1.108		
117.89	11.727	278.80	14.824	20.35	1.203		
122.96	11.983	283.99	14.856	21.31	1.308		
128.04	12.228	289.18	14.888	22.31	1.429		
133.13	12.462	294.37	14.933	23.36	1.577		
138.24	12.664	299.56	14.935	24.46	1.710		
143.42	12.858	304.75	15.023	25.63	1.841		
148.50	13.007	309.93	15.002	26.84	2.007		
153.63	13.170	315.11	15.035	28.11	2.166		

principle is followed quite accurately in isostructural compounds in which only the cation is changed.

For example, the lattice heat capacity of γ-phase Ln_2S_3 may be represented as

$$C_p(Ln_2S_3, \text{ lattice}) = xC_p(Gd_2S_3, \text{ lattice})$$
$$+ (1 - x)C_p(La_2S_3)$$

in which x is the fractional increment in the molar volume V and is given by the expression

$$x = \{V(Ln_2S_3) - V(La_2S_3)\}/$$
$$\{V(Gd_2S_3) - V(La_2S_3)\}.$$

The qualification lattice attached to Gd_2S_3 is a reminder that the cooperative magnetic contribution—insignificant above 50 K—has been subtracted. The excess heat capacities (Schottky contributions) have been obtained for γ-phase Pr_2S_3, Tb_2S_3, and Dy_2S_3 after subtracting the calculated lattice contributions and are displayed by continuous curves in Figs. 2–4.
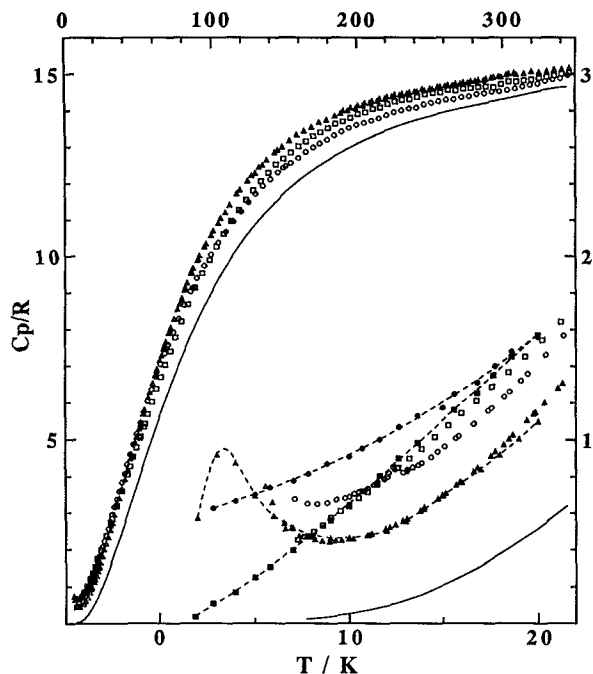
FIG. 1. Molar heat capacities of γ-phase Pr_2S_3, ($\square$), Tb_2S_3, ($\bigcirc$), and Dy_2S_3, ($\triangle$) from 5 to 350 K. The continuous line represents the "lattice" heat capacity for γ-phase La_2S_3 (Ref. 1). Lower right corner: Molar heat capacities up to 20 K; open symbols represent present study, solid symbols are taken from Ref. 13.

VI. ANALYSIS OF OPTICAL SPECTRA

We compared the Schottky heat-capacity curves (Figs. 2–4) with the Schottky contributions based on the experi-

mental crystal-field energy levels for Pr^{3+} ($^3H_4$), Tb^{3+} ($^7F_6$), and Dy^{3+} ($^6H_{15/2}$) in the sesquisulfide lattice. The levels were determined from an analysis of the absorption spectra reported earlier for each compound.[2,10,16–19]

The Schottky heat capacity has been developed using the partition function Z for a general system of n energy levels of energies E_i and degeneracies g_i

$$Z = \sum_{i=0}^{n} g_i \exp(-E_i/RT)$$

and taking $E_0 = 0$, the average energy of such a system is given by

$$\overline{E} = Z^{-1} \sum_{i=0}^{n} g_i E_i \exp(-E_i/RT).$$

Hence, the electronic heat capacity is given by

$$C_{\text{Sch}} = (d\overline{E}/dT)$$

$$= \frac{d}{dT}\left(RT^2 \frac{d\ln Z}{dT}\right)$$

$$= Z^{-2}R^{-1}T^{-2}\left\{Z\sum_{i=1}^{n} g_i E_i^2 \exp(-E_i/RT)\right.$$

$$\left. - \left[\sum_{i=1}^{n} g_i E_i \exp(-E_i/RT)\right]^2\right\}.$$

The crystals used in those measurements were shown to have a stoichiometry and structure similar to the materials used in the present study and reported in Table I. Further details regarding sample preparation, crystal growth, and optical transmission characteristics of those crystals are given in Refs. 31–33.

TABLE III. Molar thermodynamic properties of γ-phase Pr_2S_3 ($R = 8.3144$ J K^{-1} mol^{-1}).

T/K	C_p/R	$\{S^0 - S^0(7)\}/R$	$\{H^0 - H^0(7)\}/R$ K	$-\{G^0 - G^0(7)\}/RT$
7	0.499	0.0	0.0	0.0
10	0.643	0.127	1.140	0.013
15	1.053	0.463	5.353	0.106
20	1.521	0.828	11.764	0.240
25	2.041	1.223	20.650	0.397
30	2.593	1.643	32.226	0.569
40	3.735	2.545	63.84	0.949
50	4.898	3.503	107.01	1.363
60	6.061	4.500	161.82	1.802
70	7.175	5.518	228.06	2.260
80	8.210	6.545	305.06	2.732
90	9.147	7.567	391.92	3.212
100	9.978	8.575	487.64	3.698
120	11.328	10.519	701.4	4.675
140	12.310	12.344	938.3	5.641
160	13.009	14.036	1191.9	6.586
180	13.510	15.60	1457.4	7.502
200	13.879	17.04	1731.4	8.385
220	14.158	18.38	2011.9	9.233
240	14.368	19.62	2297.3	10.048
260	14.526	20.78	2586.3	10.829
280	14.645	21.86	2878.1	11.579
298.15	14.739	22.78	3144.7	12.233
300	14.749	22.87	3172.0	12.298
320	14.864	23.83	3468.1	12.989
350	15.08	25.17	3917.2	13.976

TABLE IV. Molar thermodynamic properties of γ-phase Tb_2S_3 ($R = 8.3144$ J K^{-1} mol^{-1}).

T/K	C_p/R	$\{S^0 - S^0(7)\}/R$	$\{H^0 - H^0(7)\}/R$ K	$-\{G^0 - G^0(7)\}/RT$
7	0.693	0.000	0.0	0.0
10	0.701	0.236	1.989	0.037
15	0.961	0.566	6.096	0.159
20	1.418	0.900	11.955	0.302
25	2.010	1.278	20.493	0.459
30	2.658	1.701	32.143	0.630
40	3.991	2.650	65.43	1.014
50	5.253	3.678	111.75	1.443
60	6.440	4.742	170.29	1.904
70	7.519	5.817	240.18	2.386
80	8.474	6.885	320.25	2.882
90	9.310	7.933	409.27	3.385
100	10.035	8.952	506.1	3.891
120	11.209	10.890	719.1	4.898
140	12.089	12.688	952.5	5.884
160	12.745	14.347	1201.2	6.840
180	13.228	15.88	1461.1	7.760
200	13.587	17.29	1729.4	8.643
220	13.865	18.60	2004.1	9.490
240	14.093	19.82	2283.7	10.300
260	14.283	20.95	2567.5	11.076
280	14.435	22.02	2854.8	11.820
298.15	14.551	22.93	3117.8	12.469
300	14.563	23.02	3144.8	12.533
320	14.709	23.96	3437.4	13.218
350	15.03	25.29	3883.4	14.197

Analysis of the crystal structure indicates that the lanthanide ions occupy sites of S_4 symmetry in the γ-phase Ln_2S_3 lattice.[6,7] In S_4 symmetry the ground state of Pr^{3+} ($^3H_4$) is split by the crystalline electric field into five nondegenerate and two doubly degenerate crystal-field electronic energy levels. Since the overall symmetry of the crystal is cubic, it is not possible to carry out the usual polarization experiments to establish the symmetry label for individual levels. However, an analysis of the hot bands made by comparing the absorption spectra observed at 10, 80, and 300 K establish

TABLE V. Molar thermodynamic properties of γ-phase Dy_2S_3 ($R = 8.3144$ J K^{-1} mol^{-1}).

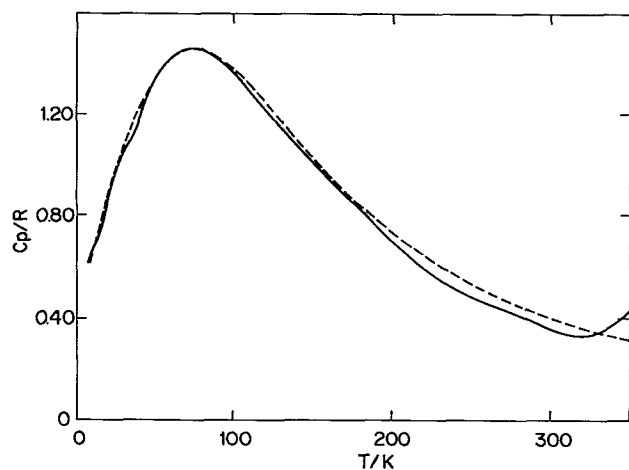| T/K	C_p/R	$\{S^0 - S^0(7)\}/R$	$\{H^0 - H^0(7)\}/R$ K	$-\{G^0 - G^0(7)\}/RT$
7	0.510	0.0	0.0	0.0
10	0.458	0.255	1.965	0.058
15	0.699	0.476	4.734	0.160
20	1.167	0.737	9.331	0.271
25	1.764	1.060	16.620	0.395
30	2.430	1.440	27.086	0.537
40	3.826	2.330	58.35	0.871
50	5.212	3.333	103.56	1.261
60	6.531	4.401	162.34	1.695
70	7.760	5.501	233.88	2.160
80	8.863	6.611	317.12	2.647
90	9.817	7.711	410.65	3.149
100	10.619	8.790	513.0	3.659
120	11.829	10.838	738.2	4.687
140	12.686	12.730	983.8	5.703
160	13.338	14.468	1244.3	6.691
180	13.827	16.07	1516.2	7.645
200	14.155	17.54	1796.3	8.563
220	14.360	18.90	2081.6	9.442
240	14.518	20.16	2370.4	10.283
260	14.680	21.33	2662.4	11.088
280	14.828	22.42	2957.5	11.859
298.15	14.922	23.36	3227.5	12.531
300	14.931	23.45	3255.1	12.598
320	15.08	24.42	3555.0	13.307
350	15.22	25.78	4010.2	14.318
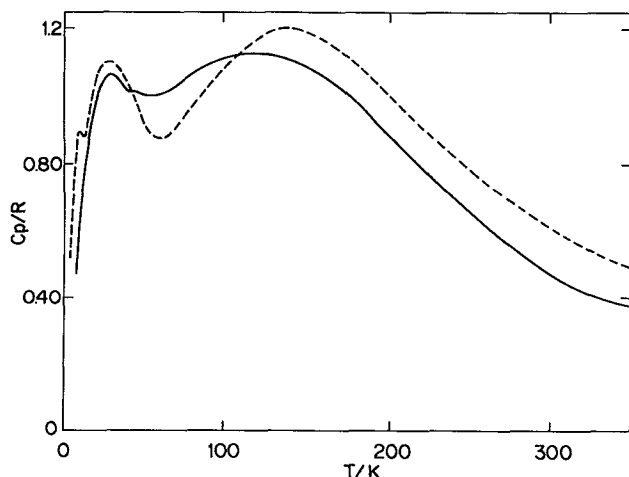
FIG. 2. Schottky contribution to the molar heat capacity of γ-phase Pr_2S_3; solid line represents calorimetric contribution based on volumetric method; dashed line represents contribution based on crystal-field splitting deduced from the optical spectra.
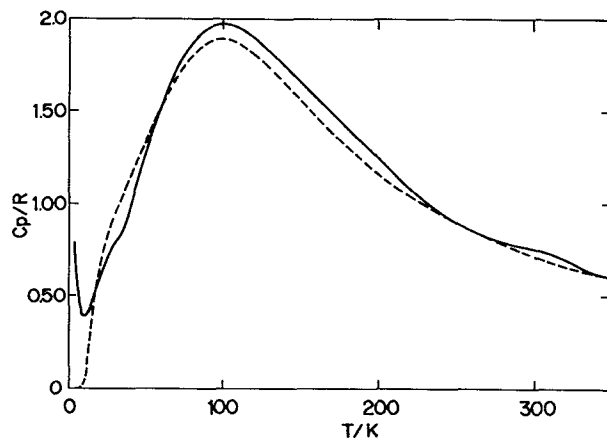

FIG. 4. Schottky contribution to the molar heat capacity of γ-phase Dy_2S_3; solid line represents calorimetric contribution based on volumetric method; dashed line represents contribution based on crystal-field splitting deduced from the optical spectra.

levels above the ground state level at 12, 56, 165, 265, 280, an 300 cm^{-1}.[10,16] The isolated excited states $^3P_0$ (20 400 cm^{-1}) and $^3P_1$ (split into two crystal-field electronic energy levels at 20 900 and 20 950 cm^{-1}) provide the best series of hot-bands in the absorption spectra from which we were able to obtain the splitting of the ground state $^3H_4$. Analysis of the magnetic susceptibility data indicates that the crystal field electronic ground-state level is nondegenerate.[16,28] In the presence of a magnetic field hot-bands from levels 56 and 265 cm^{-1} showed pronounced broadening in the absorption spectrum indicating a Zeeman effect due to twofold degeneracy of these levels.[10] Hot-bands from other electronic energy levels in the $^3H_4$ state did not appear to be affected by the magnetic field. Extension of the analysis of the hot-bands in

FIG. 3. Schottky contribution to the molar heat capacity of γ-phase Tb_2S_3; solid line represents calorimetric contribution based on volumetric method; dashed line represents contribution based on crystal-field splitting deduced from the optical spectra.

the absorption spectra of $^3P_2$ and $^1D_2$ levels await additional experiments to be made on new crystals since the original crystals have deteriorated over the years. A preliminary set of crystal-field electronic energy levels for the $^3H_4$ state is given in Table VI. The number in parentheses gives the degeneracy of the level.

The ground state $^7F_6$ of Tb^{3+} is split into seven nondegenerate and three doubly degenerate crystal-field electronic energy levels when Tb^{3+} ions occupy sites of S_4 symmetry in the sesquisulfide lattice. The excited state $^5D_4$ contains five nondegenerate and two doubly degenerate crystal-field electronic energy levels. Hot-bands observed in the absorption spectra at 10, 80, and 300 K of the two lowest levels of this state at 20 250 and 20 200 cm^{-1} have been analyzed to give the splitting of the $^7F_6$ state as follows: 0, 6, 29, 65, 130, 175, 190, 230, 300, and 310 cm^{-1}. The levels at 6, 300, and 310 cm^{-1} are estimated by analyzing the shoulders found on several of these hot-bands.[16,17] Analysis of the magnetic susceptibility data indicates the electronic ground state level and levels at 6 and 29 cm^{-1} are nondegenerate.[16,17] The three doubly degenerate levels were chosen on the basis of the prediction made by the lattice-sum calculation given in the next section.

The ground state $^6H_{15/2}$ of Dy^{3+} is split into eight doubly degenerate crystal-field electronic energy levels. Part of the absorption spectra has already been published.[2,18] Subsequent magnetic susceptibility measurements made by Burriel[28] and the heat-capacity measurements reported in Ref. 4 indicate the γ-phase Dy_2S_3 undergoes magnetic ordering around 3 K. Analysis of the hot-band absorption spectra at 10, 80, and 300 K (above the magnetic ordering temperature) establish the splitting of the $^6H_{15/2}$ as 0, 52, 145, 190, 240, 265, and 310 cm^{-1}. The lattice sum calculation given in the next section predicts the eighth electronic energy level at 600 cm^{-1}. The room-temperature absorption spectrum contains a hot-band possibly from an electronic level at 550 cm^{-1}. The peak is broad and weak so that the level reported in Table VI must be considered tentative.

TABLE VI. Crystal-field electronic levels for the ground state, $^{2S+1}L_J$.

Ln_2S_3	Method of determination	Energy (cm^{-1}) and degeneracy (n) of level									
Pr_2S_3	Optical spectra/Mag. suscept.[a]	0(1)	12(1)	56(2)	165(1)	265(2)	280(1)	300(1)			
Pr^{3+} ($^3H_4$)	Lattice sum[b]	0(1)	30(1)	100(2)	180(1)	270(2)	278(1)	282(1)			
Tb_2S_3	Optical spectra/Mag. suscept.[c]	0(1)	6(1)	29(1)	65(2)	130(2)	175(1)	190(1)	230(2)	300(1)	310(1)
Tb^{3+} ($^7F_6$)	Lattice sum[b]	0(1)	5(1)	24(1)	65(2)	130(2)	170(1)	185(1)	235(2)	298(1)	302(1)
Dy_2S_3	Optical spectra/Mag. suscept.[d]	0(2)	52(2)	145(2)	190(2)	240(2)	265(2)	310(2)	550(2)		
Dy^{3+} ($^6H_{15/2}$)	Lattice sum[b]	0(2)	43(2)	140(2)	190(2)	240(2)	280(2)	360(2)	600(2)		

[a] References 10 and 16.
[b] References 16, 17, 19, and 34–36.
[c] References 16 and 17.
[d] References 2, 18, and 28.

Although the heat-capacity maximum near 3 K reported by Ho *et al.*[13] was interpreted[13,18] as a consequence of a low-energy electronic level of Dy^{3+} on the basis of our analysis in this section it must rather be described as due to magnetic ordering. The eight levels of the ground state $^6H_{15/2}$ of Dy^{3+} provide a good fit to the calorimetric Schottky data of Fig. 4. But if one level is used to fit the 3 K maximum (as an electronic anomaly) the remaining portion of the spectroscopically derived Schottky heat-capacity contribution accounts only for approximately one half of that obtained from calorimetry. This emphasizes the strength of the thermophysical approach.

VII. THEORETICAL SPLITTING OF THE GROUND-STATE MANIFOLD: THE LATTICE SUM APPROACH

A second approach to establishing the energies of the crystal-field electronic energy levels of the ground state of the trivalent lanthanide ion in the sesquisulfide lattice has been to calculate the theoretical splitting using crystal-field parameters B_{km} determined from a lattice-sum calculation. Details of this approach are given by Morrison and Leavitt for Ln^{3+} in an extensive review of the energy levels of lanthanide ions in various host crystals.[34–36] Specifics related to the sesquisulfide lattice are reported by Gruber, Leavitt, and Morrison.[19] Following the method of Morrison and Leavitt[34] a set of B_{km} parameters for Ce^{3+} through Dy^{3+} in γ-phase Ln_2S_3 was generated and used to interpret magnetic susceptibility data. The results were reported at several conferences.[16,17] The parameters generated for Pr^{3+}, Tb^{3+}, and Dy^{3+} (Refs. 16 and 17) were used in this paper to calculate the splitting of the $^{2S+1}L_J$ ground state for each respective ion.

We present the results of each calculation in Table VI. The number in parentheses represents the predicted degeneracy for the electronic energy level. As we pointed out earlier, the assignment of degeneracy of the levels in the $^7F_6$ state of Tb^{3+} is based on the results of the calculation. We were not able to do a Zeeman experiment on the terbium sample due to its poor optical quality. Although only part of the absorption spectra were analyzed, leading us to be cautious regarding these analyses, the results of the theoretical splittings appear to be consistent with our experimental assignments and further suggest that the experimental elec-

tronic energy levels deduced from an analysis of the hot-bands appearing in the absorption spectra are reliable. The experimental levels can be used to calculate the Schottky contributions to the heat capacity displayed in Figs. 2–4. The overall agreement is reasonable.

In summary, papers I and II for the series of γ-phase Ln_2S_3 compounds, where Ln represents La to Dy, describe the thermophysical properties which can be interpreted using the volumetric method of analysis. The lattice contribution to the heat capacity can be systematically subtracted from the total measured heat capacity leaving the remainder due to the Schottky contribution and some low-temperature magnetic anomalies.

ACKNOWLEDGMENTS

[1] E. F. Westrum, Jr., R. Burriel, J. B. Gruber, P. E. Palmer, B. J. Beaudry, and W. A. Plautz, J. Chem. Phys. **91**, 4838 (1989).

[2] J. R. Henderson, M. Muramoto, E. Loh, and J. B. Gruber, J. Chem. Phys. **47**, 3347 (1967).

[3] H. J. Goldsmid, in *Applications of Thermoelectricity*, edited by B. L. Worsnop (Methuen, London, 1960), p. 73.

[4] S. M. A. Taher, J. B. Gruber, J. C. Ho, and D. C. Yeh, in *The Rare Earths in Modern Science and Technology*, edited by G. J. McCarthy and J. J. Rhyne (Plenum, New York, 1978), Vol. 1, p. 359.

[5] S. M. Taher and J. B. Gruber, Mater. Res. Bull. **16**, 1407 (1981).

[6] I. A. Smirnov, J. Phys. (Paris) Suppl. C5 **41**, 143 (1980).

[7] J. Flahaut, M. Guittard, M. Patrie, M. P. Pardo, S. M. Golabi, and L. Domange, Acta Crystallogr. **19**, 14 (1965).

[8] V. P. Zhuze, O. A. Golikova, V. M. Sergeeva, and I. M. Rudick, Sov. Phys. Solid State **13**, 669 (1971).

[9] R. M. Bozorth, F. Holtzberg, and S. Methfessel, Phys. Rev. Lett. **14**, 952 (1965).

[10] J. B. Gruber, J. R. Henderson, M. Muramoto, and E. Loh, Bull. Am. Phys. Soc. **14**, 310 (1969).

[11] V. V. Nogteva, O. A. Nabutovskaya, and V. N. Naumov, Russ. J. Phys. Chem. **58**, 1573 (1984).

[12] G. Becker, J. Feldhaus, K. Westerholt, and S. Methfessel, J. Magn. Magn. Mat. **6**, 14 (1977).

[13] J. C. Ho, S. M. A. Taher, G. B. King, J. B. Gruber, B. J. Beaudry, and K. A. Gschneidner, Jr., J. Phys. (Paris) C6 **39**, 841 (1978).

[14] K. A. Gschneider, Jr., T. Takeshita, B. J. Beaudry, O. D. McMasters, S. M. A. Taher, J. C. Ho, G. B. King, and J. B. Gruber, J. Phys. (Paris) Suppl. **40**, 172 (1979).

[15] H. L. Beeler and J. B. Gruber, Chem. Phys. **13**, 359 (1976).

[16] S. M. A. Taher, J. B. Gruber, and B. J. Beaudry, Bull. Am. Phys. Soc. **23**, 401 (1978).

[17] S. M. A. Taher, J. C. Ho, and J. B. Gruber, Bull. Am. Phys. Soc. **26**, 577 (1981).

[18] S. M. A. Taher, J. C. Ho, and J. B. Gruber, J. Chem. Phys. **76**, 609 (1982).

[19] J. B. Gruber, R. P. Leavitt, and C. A. Morrison, J. Chem. Phys. **79**, 1664 (1983).

[20] J. B. Gruber, R. Burriel, E. F. Westrum, Jr., P. E. Palmer, and B. J. Beaudry, J. Less-Common Met. **94**, 227 (1983).

[21] V. P. Zhuze, M. G. Karin, K. K. Sidorin, V. V. Sokolov, and A. I. Shelykh, Sov. Phys. Solid State **27**, 2205 (1986).

[22] E. F. Westrum, Jr., Pure Appl. Chem. **55**, 539 (1983).

[23] K. A. Gschneidner, Jr., B. J. Beaudry, T. Takeshita, S. S. Eucker, S. M. A. Taher, J. C. Ho, and J. B. Gruber, Phys. Rev. B **24**, 7187 (1981).

[24] B. J. Beaudry and K. A. Gschneidner, Jr., in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1978), Vol. 1, p. 173.

[25] American Smelting and Refining Company, Denver.

[26] E. D. West and E. F. Westrum, Jr., in *Experimental Themodynamics*, edited by J. P. McCullough and D. W. Scott (Butterworths, London, 1968), Vol. 1, p. 333.

[27] E. F. Westrum, Jr., in *Thermodynamics and its Applications to Chemical and Biochemical Systems*, edited by M. A. V. Ribeiro da Silva (Reidel, Dordrecht, 1984), p. 745.

[28] R. Burriel, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain (unpublished).

[29] R. D. Chirico and E. F. Westrum, Jr., J. Chem. Thermodyn. **12**, 71, 311 (1980); **13**, 519, 1087 (1981).

[30] R. D. Chirico, E. F. Westrum, Jr., J. B. Gruber, and J. Warmkessel, J. Chem. Thermodyn. **11**, 835 (1979).

[31] J. R. Henderson, D. M. Johnson, and M. Muramoto, "Production of High Purity Rare Earth Sulfides," U. S. Patent No. 3, 748, 095, issued July 24, 1973, owned by McDonnell-Douglas Corp., Long Beach, CA 90846.

[32] J. R. Henderson, M. Muramoto, D. M. Johnson, and E. Loh, "Purification and Growth of Rare Earth Sesquisulfide Semiconductor Crystals," Douglas Paper 4415, Douglas Aircraft Company, Santa Monica, CA, IRAD Program 88001-700 (1967).

[33] J. R. Henderson, J. B. Gruber, D. M. Johnson, and M. Muramoto, "McDonnell-Douglas Corporation Research on Rare Earth Materials, III. Rare Earth Semiconductors, Heterojunctions of GaAs–Ln_2S_3, Infrared Quantum Counters." McDonnell-Douglas Corp. Yearly Report for 1969.

[34] C. A. Morrison and R. P. Leavitt, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, New York, 1982), Vol. 5, p. 461.

[35] C. A. Morrison, D. E. Wortman, and N. Karayianis, J. Phys. C **9**, 191 (1976).

[36] C. A. Morrison, in *Lecture Notes in Chemistry*, edited by G. Berthier (Springer, New York, 1988), Vol. 47, p. 119.