

Thermophysical properties of the lanthanide sesquisulfides. I. Schottky functions and magnetic and electronic properties of γ - La_2S_3 , γ - Ce_2S_3 , γ - Nd_2S_3 , and γ - Gd_2S_3

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Heat capacity measurements of four lanthanide sesquisulfides La_2S_3 , Ce_2S_3 , Nd_2S_3 , and Gd_2S_3 , prepared in the γ phase, have been obtained between 6 and 350 K by adiabatic calorimetry. The total heat capacity has been resolved into lattice, electronic, magnetic, and Schottky components. The Schottky contributions agree well with the calculated values based on the observed splitting of the ground-state manifold of the rare earth ions occupying sites of S_4 symmetry in the Th_3P_4 structure. The observed splitting is obtained from an analysis of the hot bands in the absorption spectrum and from direct observation of the Stark levels in the far infrared. The Stark levels (all doublets) for Ce_2S_3 ($^2F_{5/2}$) are 0, 185, and 358 cm^{-1} ; for Nd_2S_3 ($^4I_{9/2}$), they are 0, 76, 150, 180, and 385 cm^{-1} . For La_2S_3 , which has no Schottky or magnetic contributions to the heat capacity, the thermal data can be extrapolated to 0 K. The entropy for La_2S_3 at 298.15 K (as S^0/R) is 19.51. Schottky and magnetic ordering at lower temperatures in Ce_2S_3 , Nd_2S_3 , and Gd_2S_3 preclude such extrapolation techniques. Therefore the entropy at 298.15 K for these compounds $\{S^0 - S^0(7\text{ K})\}/R$, is 21.34, 22.38, and 20.05, respectively.

I. INTRODUCTION

Lanthanide sesquisulfides (Ln_2S_3)—as a consequence of their $4f^n$ states—manifest unusual magnetic and electronic behavior.¹⁻²¹ The $4f$ electrons are localized in the inner shell of the lanthanide ions, but the polarization of the $5d$ conduction electrons is known to give ferro- and antiferromagnetic interactions in lanthanide alloys due to indirect exchange of the RKKY type. Moreover, the Th_3P_4 structure, to which the γ phase of the lanthanide sesquisulfides belongs, allows considerable variation of the composition. One-ninth of the positions of the Ln cation are randomly unoccupied in Ln_2S_3 . They can be filled with excess Ln up to the composition Ln_3S_4 thereby providing additional free electrons that profoundly change the physical properties of the compound. This property makes them suitable materials in which the number of conduction electrons can be adjusted at will to the required physical properties. One finds a whole range of ferro- and antiferromagnetic ordering, insulators, semiconductors, and superconductors associated with these materials. They are found as components in solar energy absorbers, in efficient solar photovoltaic cells, or in infrared parametric oscillators.^{2,7,20}

The materials we study in this series of papers belong to the limiting composition Ln_2S_3 , in which, ideally, there are no nonlocalized electrons. They are insulators and we can extract the physical properties that depend on the lattice structure and single ion properties. The crystal field surrounding the lanthanide ions acts as a small perturbation on the localized electrons. The field splits the ground state into sublevels called Stark levels. Hence, thermophysical effects are expected when the higher-energy Stark levels of the lanthanide ions are depopulated on lowering the temperature. Specifically, the heat capacity shows Schottky contributions manifesting the magnitude of the splitting and degeneracy of the Stark levels of the ground state. These phenomena revealed by calorimetric,⁵⁻¹⁸ spectroscopic,^{1-4,19} and magnetic techniques^{13,15,20,21} provide elucidation and resolution of the energetic spectra. The infrared and Raman spectra, the magnetic susceptibility, and analysis of the crystal-field splitting of these compounds enable one to make an interpretation of the observed heat-capacity values and thermophysical functions, and resolved Schottky contributions. Moreover, subsequent comparison made with crystal-field lattice-sum calculations provides further evidence of the essential validity of this interpretation of the entire gamut of the thermophysical, crystalline electric field (CEF), and related properties as has already been done for the bixbyite sesquioxides.²²

Subambient heat-capacity determinations represent an important technique for study of these materials and their

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Schottky and magnetic contributions. Either of them may be resolved even at moderate temperatures by an essentially volumetric scheme for the estimation of lattice heat capacities.^{23,24}

Heat-capacity data on lanthanide sesquisulfides of different preparations, compositions, and crystal structures obtained between 0.3 and 20 K are available in the literature.⁷⁻¹³ Systematic studies also exist for the lanthanide monosulfides and for the Ln_3S_4 compounds, but are of relevance here in only a few respects.^{6,15,25,26} Heat capacities of Ln_3Ch_4 ($\text{Ch} = \text{Se}, \text{Te}, \text{etc.}$) and sesquisulfide systems (e.g., mixed rare earth with S, Se, or Te), and the binary systems $\text{Ln}_3\text{Ch}_4\text{-Ln}_2\text{Ch}_3$ have interesting thermophysical properties. For example, T_c in La_3S_4 (7 K) drops essentially to 0 K in La_2S_3 . In fact, treatment of the lanthanide sulfides (LnS_x) as a homologous series provides useful correlation of thermophysical values for device applications.²⁷

Many of the heat capacity values reported for Ln_2S_3 do not extend to temperatures sufficiently high to enable one to determine the Schottky contribution due to the crystal-field splitting of the ground-state manifold of the tripositive rare earth ion. Furthermore, the samples investigated were not well characterized. Our purpose here is to detail stoichiometric sample preparation and crystal structure of the Ln_2S_3 compounds we investigated. We report heat capacity measurements between 6 and 350 K which can be resolved into lattice, magnetic, and Schottky components. In this first paper, we compare the experimental Schottky contribution obtained for Ce_2S_3 and Nd_2S_3 with the calculated contribution based on the crystal-field splitting of the ground-state manifold as deduced from optical spectra. Overall agreement indicates that the volumetric method of analysis described earlier^{23,24} is a useful approach to these systems.

II. EXPERIMENTAL

A. Sample provenance and characterization for heat-capacity studies

The four sulfide 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.*¹¹ The rare earth metals were also prepared in the Ames Laboratory²⁸ and had the chemical analyses typical of the highly purified metals reported earlier.²⁸ Sublimed sulfur (99.999%) was obtained from ASARCO.²⁹ After synthesis of Ln_2S_3 was achieved in sealed quartz ampoules, the samples were not melted as they had been in a previous study.¹⁴

Instead, the quartz ampoules were opened and the sulfide ground and sieved to 200 mesh powder. The powder was cold pressed into pellets 4 mm thick by 15 mm diameter. The pressed pellets of La_2S_3 , Ce_2S_3 , and Nd_2S_3 were heated to 1500 °C under a dynamic H_2S atmosphere for 48 h. The Gd_2S_3 was heated to 1450 °C for 24 h under dynamic H_2S treatment.

Debye Scherrer x-ray patterns contained only lines of the γ -phase bcc structure of Th_3P_4 . Lattice parameters determined in this study are given in Table I along with the literature values.³⁰ The final compositions were determined by G. V. Austin and R. Z. Bachman, Analytical Services Group, Ames Laboratory, Iowa State University, using the following procedures: 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 gravimetrically as barium sulfate. The lanthanide cations in solution were quantitatively analyzed by titrating with EDTA. A sensitive test used to determine the presence of trace oxysulfide impurities was performed by dissolving the sulfide in 6N HCl and observing the clarity of the solution. All samples used in this study gave clear solutions when dissolved; this showed the absence of oxysulfides.³⁰

B. Automated adiabatic calorimetry

The data were taken in the Mark X calorimetric cryostat, an improved (by addition of a guard shield surrounding the adiabatic shield)³¹ version of the Mark II cryostat previously described together with the relevant operating techniques. The acquisition of heat-capacity data from about 6 to 350 K was computer assisted.³² After being programmed for a series of determinations, the computer recorded: (i) drift readings of the calorimeter temperature (including the first and second derivatives) over a suitable length of time before and after each energy input to determine the equilibrium temperature and drift; and (ii) during each energy input, current and potential of the heater and the duration of the heating period. Information was recorded on the initial, final, and mean temperatures, on the energy input, and on the resistance of the heater, together with the apparent heat capacity of the system (including the calorimeter, heater, thermometer, and sample).

A gold-plated, oxygen-free, high-conductivity copper calorimeter (laboratory designation W-61) especially equipped with a pair of perforated copper spring-loaded sleeves soldered to the heater-thermometer well to hold the

TABLE I. Lattice parameters and analyzed compositions of the γ -lanthanide sulfides used in this study.

Sesquisulfide	Lattice parameter (Å)		Analyzed mole ratio S/Ln	m/g	M/g mol ⁻¹	Color
	Present study	Reference 30				
La_2S_3	8.7220 ± 0.0007	8.731	1.497 ± 0.005	37.8289	374.003	Yellow-green
Ce_2S_3	8.636 ± 0.0002	8.630	1.500 ± 0.001	38.1789	376.432	Dark gray
Nd_2S_3	8.5248 ± 0.0002	8.527	1.500 ± 0.006	36.3252	384.66	Yellow-blue
Gd_2S_3	8.3779 ± 0.0003	8.387	1.503 ± 0.003	36.1260	410.692	Yellow

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 % tin and indium) solder. Relevant adjuvant quantities (sample mass, molar masses, lattice constants, etc.) used in computer reduction of the data are also given in Table I. The mole used throughout this paper is based on the formula written as Ln_2S_3 and thus involves 2 mol of lanthanide metal. Temperatures were measured on an ASL-7 induction bridge with a Leeds and Northrup platinum-resistance thermometer sensor calibrated by the National Institute of Standards and Technology. All other accurate experimental quantities are referred to standards and calibrations provided by NIST.

C. Optical spectroscopy: Samples and technique

The spectra of γ -phase single crystal Ce_2S_3 and Nd_2S_3 were first observed by Henderson *et al.*^{1,2} They prepared the material by passing purified H_2S over finely divided oxide powder in graphite boats at temperatures between 850 and 1300 °C. The powders were used to grow single crystals by the Bridgman method.¹ The x-ray crystallographic patterns of pieces of the crystals indicated that Ce_2S_3 and Nd_2S_3 were grown in the γ phase.

Chemical analysis of the crystals indicated the materials were stoichiometric ($\text{LnS}_{1.500 \pm 0.002}$).¹⁻⁴

Infrared spectra on powdered mull samples of La_2S_3 , Ce_2S_3 , and Nd_2S_3 were recorded between 2.5 and 40 μ using a Perkin-Elmer 301 spectrophotometer. The infrared spectra between 10 and 200 μ of single crystals were recorded using a Beckman FS-720 Fourier interference spectrophotometer. Samples were cooled to 15 and 90 K using a conduction dewar filled sequentially with liquid helium and liquid nitrogen. The measurements were performed by Henderson, Muramoto, and Gruber.¹⁻³

III. RESULTS

A. Calorimetric determinations

The values for the heat capacity of La_2S_3 presented in Table II in energy-dimensionless units are in chronological sequence, so that the temperature increments can usually be deduced from the sequential temperatures. Corresponding values for the other three compounds are given in Table II. The data were smoothed at the lowest temperatures by use of a C_p/RT vs T^2 plot. From such a plot, we obtained for La_2S_3 a Debye temperature $\theta_0 = 284$ K, and an electronic coefficient $\gamma = 0 \pm 0.0002$ RK. The temperature range of our measurements did not permit the estimation of a more accurate value for γ .

TABLE II. Molar heat capacities of lanthanide sesquisulfides ($R = 8.3144$ J K⁻¹ mol⁻¹).

$T(\text{K})$	C_p/R	$T(\text{K})$	C_p/R	$T(\text{K})$	C_p/R	$T(\text{K})$	C_p/R
Lanthanum sesquisulfide (La_2S_3)							
Series I		Series II		Series IV		19.72	0.493
180.08	12.521 ^a	71.98	6.406	40.93	2.759	21.43	0.630
185.09	12.735	74.77	6.710	42.57	2.926	23.33	0.780
190.23	12.847	78.14	7.032	44.62	3.198	25.31	0.976
195.38	12.969	81.66	7.425	46.75	3.456	27.14	1.171
200.54	13.091	85.69	7.802	48.98	3.732	28.93	1.355
205.70	13.169	89.94	8.207	51.32	4.016	31.00	1.579
210.86	13.252	94.41	8.543	53.79	4.320	33.32	1.845
216.02	13.385	99.12	8.907	56.38	4.626	35.90	2.149
223.76	13.493	104.03	9.293	59.10	4.963	38.76	2.489
228.88	13.560	122.14	10.439	61.96	5.302	41.94	2.862
234.03	13.638	129.82	10.854	64.97	5.673		
239.20	13.715	134.93	11.081	68.13	5.999	Cerium sesquisulfide (Ce_2S_3)	
244.38	13.770	140.01	11.293	71.47	6.359		
249.55	13.836	145.11	11.510	74.96	6.732		
254.73	13.896	150.21	11.722	78.65	7.115	Series I	
259.91	13.915	155.32	11.919	82.52	7.521	148.74	12.896
265.08	13.986	160.26	12.083			153.68	13.088
270.26	14.070	165.22	12.274	Series V		158.81	13.251
275.44	14.091	170.37	12.350	65.71	5.751	163.92	13.384
282.03	14.154	175.51	12.528	69.02	6.094	169.03	13.514
287.20	14.202	180.65	12.663	72.38	6.457	174.17	13.658
292.38	14.254	185.81	12.750	75.94	6.759	179.31	13.786
297.57	14.279	190.95	12.893	83.59	7.611	184.46	13.876
302.76	14.301	196.11	12.991			189.61	13.990
307.94	14.361			Series VI		194.78	14.080
313.12	14.415	Series III		7.72	0.022	199.95	14.164
318.30	14.489	105.22	9.357	8.30	0.029	205.11	14.232
323.49	14.533	110.25	9.709	9.11	0.038	210.27	14.293
328.68	14.564	121.12	10.378	10.35	0.057	215.42	14.370
333.87	14.598	126.10	10.645	12.76	0.116	220.59	14.441
339.06	14.611	131.18	10.894	13.71	0.150	225.76	14.517
344.25	14.660	136.26	11.153	14.81	0.198	230.94	14.549
		141.35	11.362	18.19	0.386	236.12	14.625

TABLE II (continued).

$T(K)$	C_p/R	$T(K)$	C_p/R	$T(K)$	C_p/R	$T(K)$	C_p/R
241.19	14.640	36.84	2.423	10.28	0.144	Series I	
246.37	14.732	38.89	2.687	10.77	0.149	56.64	4.666
251.66	14.770	41.20	2.992	11.27	0.164	59.53	4.972
256.84	14.785	43.78	3.334	11.80	0.176	62.42	5.285
262.02	14.834	46.38	3.691	12.35	0.196	65.45	5.617
267.19	14.864	51.37	4.364	12.92	0.218	68.64	5.928
272.36	14.885	53.39	4.628	13.52	0.248	72.01	6.253
277.52	14.933	56.28	5.025	14.09	0.278	75.54	6.598
282.71	14.948	59.15	5.436	14.69	0.319	79.26	6.980
287.89	14.983	62.05	5.834	15.36	0.367	83.16	7.346
293.05	14.994	65.42	6.289	16.06	0.422	87.27	7.737
298.16	14.989	69.28	6.773	16.79	0.486	91.59	8.099
303.33	15.047	73.14	7.246	17.55	0.558	95.90	8.404
308.50	15.045	77.04	7.709	18.35	0.641	100.49	8.741
313.70	15.080			19.18	0.733	105.50	9.099
318.91	15.114	Neodymium sesquisulfide (Nd ₂ S ₃)		20.06	0.837	110.51	9.419
324.10	15.138			20.97	0.955	115.54	9.765
329.28	15.186			21.93	1.084	120.59	10.032
334.47	15.225	Series I		22.93	1.225	125.66	10.341
339.65	15.251	117.69	11.270	23.99	1.380	130.72	10.566
344.84	15.289	121.32	11.449	25.09	1.549	135.79	10.830
348.76	15.315	125.12	11.633	26.25	1.726	140.88	11.094
		130.14	11.840	27.47	1.925	145.98	11.316
		135.23	12.069	28.67	2.119	151.09	11.530
Series II		140.33	12.255	29.94	2.321	156.21	11.714
76.68	7.659	145.44	12.447	31.34	2.555	161.34	11.866
80.05	8.075	150.56	12.622	32.81	2.792	166.47	12.042
84.00	8.535	155.68	12.764	34.36	3.053	171.60	12.210
88.15	8.992	160.81	12.929	35.98	3.313	176.74	12.344
92.53	9.393	165.95	13.034	37.68	3.585	181.88	12.483
97.15	9.777	171.08	13.160	39.47	3.864	187.04	12.622
102.00	10.188	176.19	13.273	41.35	4.146	192.19	12.732
106.99	10.575	181.31	13.366	43.32	4.465	197.35	12.859
112.02	10.941	186.46	13.468	45.40	4.752	202.51	12.943
117.06	11.304	191.62	13.556	47.59	5.069	207.67	13.052
122.11	11.607	196.78	13.638	49.88	5.373	212.83	13.169
127.18	11.912	201.94	13.706	52.29	5.697	217.99	13.254
137.66	12.450	207.10	13.784	54.83	6.015	223.16	13.358
142.71	12.678	212.27	13.838	57.50	6.351	228.33	13.422
147.82	12.889	217.44	13.927	60.30	6.695	233.50	13.513
152.94	13.074	222.62	13.987	63.25	7.044	238.68	13.588
		227.80	14.046	66.35	7.383	243.85	13.679
Series III		232.96	14.119			249.02	13.724
6.84	0.163	238.13	14.142	Series III		254.20	13.787
7.55	0.133	243.31	14.236	24.00	1.375	259.38	13.843
8.41	0.116	248.48	14.270	39.79	3.918	264.55	13.906
9.18	0.111	253.66	14.321	71.97	7.938	269.73	13.972
9.92	0.110	258.85	14.355	75.44	8.279	274.90	14.011
10.64	0.116	264.03	14.405	83.15	9.022	280.07	14.076
11.45	0.127	269.21	14.437	87.18	9.381	285.23	14.107
12.35	0.146	274.39	14.486	91.64	9.768		
13.23	0.170	279.58	14.513	96.65	10.056	Series II	
14.10	0.202	284.76	14.545	101.66	10.368	276.68	14.020
14.98	0.241	289.93	14.593	106.69	10.646	281.79	14.053
15.82	0.282	295.11	14.602	111.72	10.926	286.88	14.110
16.68	0.328	300.28	14.648	116.77	11.234	291.95	14.156
17.57	0.384	305.45	14.685	117.51	11.261	297.01	14.207
18.46	0.445	310.62	14.707	121.60	11.451	302.05	14.249
19.45	0.517	315.79	14.781	125.73	11.651	307.08	14.291
20.53	0.600	320.95	14.797	130.82	11.900	312.10	14.326
21.60	0.693	326.12	14.841	135.92	12.113	317.13	14.382
22.77	0.802	331.29	14.904	141.02	12.305	322.13	14.437
24.03	0.924	336.48	14.931	146.15	12.478	327.11	14.501
25.29	1.052	341.66	14.985	151.27	12.630	332.08	14.510
26.66	1.197	346.85	15.022	156.41	12.791	337.03	14.543
28.11	1.357			161.54	12.931	342.03	14.612
29.57	1.524	Series II		166.68	13.050	346.91	14.663
31.13	1.708	8.24	0.138	171.82	13.171		
32.78	1.907	8.76	0.133				
33.54	2.001	9.29	0.135	Gadolinium sesquisulfide (Gd ₂ S ₃)		Series III	
35.03	2.192	9.79	0.138			290.01	14.128

TABLE II (continued).

$T(K)$	C_p/R	$T(K)$	C_p/R	$T(K)$	C_p/R	$T(K)$	C_p/R
295.06	14.186	291.72	14.156	Series VII		24.10	1.134
300.09	14.250	296.70	14.188	6.05	1.957	25.23	1.245
305.10	14.272	301.67	14.229	6.36	1.791	26.49	1.369
310.09	14.328	306.61	14.288	6.73	1.655	27.72	1.495
315.08	14.382	314.00	14.358	7.14	1.347	29.02	1.621
320.05	14.437	321.37	14.429	7.62	1.200	30.38	1.761
325.00	14.461	326.26	14.468	8.16	1.063	31.80	1.928
329.94	14.504	331.15	14.517	8.78	0.928	33.29	2.083
334.88	14.543	336.03	14.554	9.45	0.824	34.86	2.269
339.80	14.594	340.90	14.575	10.25	0.708	36.51	2.444
344.72	14.627	345.77	14.507	11.08	0.626	38.23	2.630
				11.97	0.579	40.05	2.833
Series IV		Series VI		12.89	0.552	41.95	3.045
323.05	14.424	6.02	2.037	13.80	0.540	43.95	3.260
330.25	14.489	6.98	1.455	14.68	0.548	46.04	3.499
337.44	14.556	8.45	0.976	15.59	0.570	48.25	3.740
342.21	14.592	9.87	0.742	16.55	0.600	50.56	3.994
346.98	14.639	11.12	0.625	17.50	0.643	52.99	4.263
		12.26	0.568	18.44	0.695	55.54	4.533
Series V		13.32	0.543	19.39	0.753	58.23	4.813
271.64	13.930	14.34	0.545	20.33	0.815	61.04	5.141
276.69	13.991	15.32	0.564	21.27	0.891	64.00	5.476
281.72	14.043	16.29	0.590	22.21	0.964	67.12	5.775
286.73	14.078	17.24	0.629	23.15	1.045		

^aThis point not used in fitting curve.

The thermodynamic functions for La_2S_3 are summarized in Table III with an occasional extra digit beyond those absolutely significant to facilitate interpolation. Corresponding values for the other three compounds are given in Table IV. It should be noted here that the data for the en-

trophy, enthalpy, and Gibbs energy increments refer to 7 K rather than 0 K. The experimental curves for the four compounds are depicted in Fig. 1. The presence of Schottky contributions to the heat capacities of Nd_2S_3 and Ce_2S_3 are quite evident upon comparison with La_2S_3 and Gd_2S_3 curves

TABLE III. Molar thermodynamic functions of lanthanum sesquisulfide ($R = 8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$).

$T(K)$	C_p/R	S^0/R	$\{H^0 - H^0(0)\}/RK$	$-\{G^0 - H^0(0)\}/RT$
0	0.0	0.0	0.0	0.0
10	0.050	0.017	0.122	0.004
15	0.206	0.061	0.698	0.015
20	0.515	0.159	2.440	0.037
25	0.948	0.319	6.054	0.077
30	1.470	0.537	12.071	0.134
40	2.638	1.117	32.531	0.304
50	3.862	1.837	65.00	0.537
60	5.065	2.648	109.68	0.820
70	6.199	3.515	166.07	1.143
80	7.236	4.412	233.33	1.495
90	8.165	5.319	310.42	1.869
100	8.983	6.222	396.25	2.260
120	10.314	7.983	589.9	3.068
140	11.309	9.652	806.6	3.891
160	12.056	11.213	1040.6	4.709
180	12.629	12.668	1287.7	5.514
200	13.076	14.022	1544.9	6.298
220	13.430	15.29	1810.1	7.058
240	13.713	16.47	2081.6	7.793
260	13.943	17.57	2358.3	8.504
280	14.139	18.61	2639.1	9.189
298.15	14.301	19.51	2897.2	9.790
300	14.317	19.60	2923.7	9.850
320	14.484	20.53	3211.7	10.489
350	14.697	21.83	3649.6	11.406

TABLE IV. Molar thermodynamic functions of lanthanide sesquisulfides ($R = 8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$).

$T(\text{K})$	C_p/R	$\{S^0 - S^0(T)\}/R$	$\{H^0 - H^0(T)\}/RK$	$-\{G^0 - H^0(T)\}/RT$
Cerium sesquisulfide (Ce_2S_3)				
7	0.155	0.0	0.000	0.0
10	0.110	0.044	0.363	0.007
15	0.242	0.106	1.156	0.029
20	0.559	0.215	3.088	0.061
25	1.021	0.387	6.990	0.108
30	1.575	0.621	13.451	0.173
40	2.833	1.243	35.369	0.359
50	4.174	2.019	70.40	0.611
60	5.549	2.902	119.01	0.918
70	6.867	3.858	181.17	1.269
80	8.063	4.854	255.94	1.655
90	9.116	5.866	341.95	2.066
100	10.030	6.875	437.79	2.497
120	11.488	8.839	653.7	3.392
140	12.546	10.694	894.7	4.304
160	13.288	12.421	1153.5	5.212
180	13.795	14.017	1424.6	6.103
200	14.153	15.49	1704.3	6.969
220	14.431	16.85	1990.2	7.806
240	14.656	18.12	2281.2	8.613
260	14.822	19.30	2576.0	9.391
280	14.932	20.40	2873.7	10.138
298.15	15.01	21.34	3145.4	10.792
300	15.02	21.43	3173.2	10.857
320	15.12	22.41	3474.5	11.549
350	15.33	23.77	3931.1	12.539
Neodymium sesquisulfide (Nd_2S_3)				
7	0.134	0.0	0.000	0.0
10	0.138	0.050	0.406	0.010
15	0.340	0.134	1.472	0.036
20	0.833	0.293	4.298	0.078
25	1.532	0.551	10.143	0.145
30	2.334	0.900	19.784	0.241
40	3.946	1.796	51.28	0.513
50	5.392	2.835	98.12	0.872
60	6.660	3.933	158.53	1.290
70	7.760	5.044	230.76	1.747
80	8.709	6.144	313.23	2.228
90	9.530	7.218	404.52	2.723
100	10.240	8.260	503.5	3.225
120	11.391	10.233	720.3	4.231
140	12.253	12.057	957.2	5.220
160	12.887	13.737	1208.9	6.181
180	13.346	15.28	1471.5	7.108
200	13.686	16.71	1741.9	7.998
220	13.954	18.02	2018.4	8.850
240	14.181	19.25	2299.8	9.666
260	14.370	20.39	2585.4	10.448
280	14.521	21.46	2874.4	11.197
298.15	14.634	22.38	3139.0	11.850
300	14.646	22.47	3166.0	11.915
320	14.791	23.42	3460.3	12.604
350	15.03	24.76	3908.1	13.589
Gadolinium sesquisulfide (Gd_2S_3)				
7	1.445	0.0	0.000	0.0
10	0.732	0.368	3.034	0.065
15	0.555	0.608	5.969	0.211
20	0.794	0.795	9.235	0.333
25	1.219	1.015	14.215	0.447
30	1.730	1.282	21.564	0.563
40	2.829	1.929	44.333	0.821
50	3.933	2.679	78.14	1.116
60	5.025	3.493	122.96	1.444
70	6.068	4.347	178.47	1.797
80	7.038	5.221	244.08	2.170
90	7.920	6.102	318.94	2.558
100	8.712	6.978	402.18	2.957

TABLE IV. (continued).

$T(K)$	C_p/R	$\{S^0 - S^0(T)\}/R$	$\{H^0 - H^0(T)\}/RK$	$-\{G^0 - H^0(T)\}/RT$
120	10.031	8.688	590.2	3.770
140	11.048	10.315	801.4	4.590
160	11.830	11.843	1030.5	5.402
180	12.437	13.273	1273.4	6.198
200	12.916	14.609	1527.2	6.973
220	13.295	15.86	1789.4	7.725
240	13.597	17.03	2058.4	8.452
260	13.841	18.13	2332.9	9.154
280	14.045	19.16	2611.8	9.833
298.15	14.214	20.05	2868.3	10.428
300	14.230	20.14	2894.6	10.487
320	14.410	21.06	3181.0	11.120
350	14.672	22.36	3617.3	12.028

which are essentially pure lattice heat capacity over this range.

The accuracy of the data is characterized by $<0.06\%$ standard deviation above 15 K. Below this temperature, standard deviations of the heat capacity gradually increase until they attain an uncertainty of about 1% at the lowest temperatures.

B. Schottky heat-capacity contributions

Resolution of Schottky contributions from heat-capacity data on lanthanide compounds requires an accurate determination of the much larger "lattice" contribution. The volume-weighted lattice heat-capacity approximation technique has been used successfully in several other groups of lanthanide compounds (sesquioxides, halides, trihydroxides, etc.)³³⁻³⁸ Of the lanthanide sesquisulfides reported here, only La_2S_3 has no excess contribution in the heat capacity. After subtraction of the low-temperature magnetic contribution in Gd_2S_3 , its lattice heat capacities can be used to interpolate the values for the other isostructural lanthanide sesquisulfides with the volumetric technique.

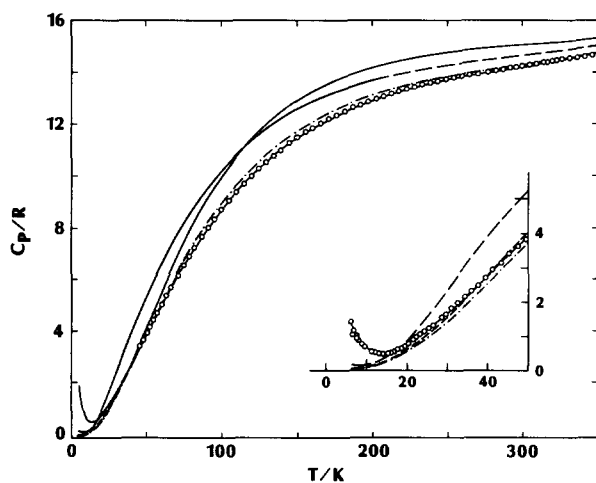


FIG. 1. Molar heat capacities of La_2S_3 (---); Ce_2S_3 (—), and (---); Nd_2S_3 (-, -, -); and Gd_2S_3 (—○—); experimental points shown for Gd_2S_3 to indicate typical density of data points obtained between 6 and 350 K.

The calculation of $C_v^L(T)$ for Gd_2S_3 below 50 K has been done by applying a corresponding-states principle to the heat capacity of La_2S_3 . This principle is followed quite accurately by isostructural compounds in which only one atom has been changed. Hence, their lattice heat capacities can be related by $C_v(\text{Gd}_2\text{S}_3, T) = C_v(\text{La}_2\text{S}_3, T/f)$.

The scaling factor $f = 0.96$ has been determined in the temperature range where there are no anomalous contributions.

The other two sesquisulfides have broad Schottky anomalies in the whole temperature range, so that the scaling factor cannot be calculated in any temperature range.

Alternatively, the magnetic excess contribution is obtained by use of the single-parameter phonon-distribution approach of Komada and Westrum.³⁹

The lattice heat capacities of γ -type lanthanide sesquisulfides may be expressed as follows:

$$C_p(\text{Ce}_2\text{S}_3, \text{lattice}) = x C_p(\text{Gd}_2\text{S}_3, \text{lattice}) + (1 - x) C_p(\text{La}_2\text{S}_3),$$

in which

$$x = \{V(\text{Ce}_2\text{S}_3) - V(\text{La}_2\text{S}_3)\} / \{V(\text{Gd}_2\text{S}_3) - V(\text{La}_2\text{S}_3)\}$$

where x is the fractional increment in the molar volume V . The qualification "lattice" attached to Gd_2S_3 is a reminder that the cooperative magnetic contribution, insignificant above 50 K, has been subtracted. The calorimetrically derived Schottky contributions to the heat capacities of Ce_2S_3 and Nd_2S_3 are displayed in the form of uninterrupted curves in Figs. 2 and 3.

C. Optical spectroscopic determinations

The infrared spectra between 2.5 and 40 μ contain a number of strong bands which even at 15 K are considered to be broad (20–25 cm^{-1}). There is a band with structure near 270 cm^{-1} in La_2S_3 and Ce_2S_3 . A sharp, narrow band (half-maximum of 8 cm^{-1}) of moderate strength is found at approximately 358 cm^{-1} in Ce_2S_3 . This peak, which is not found in the La_2S_3 spectrum, could be an electronic transition within the ground-state manifold $^2F_{5/2}$ of the Ce^{3+} ($4f^1$) ion. Since the point-group symmetry of Ce^{3+} in the Ln_2S_3

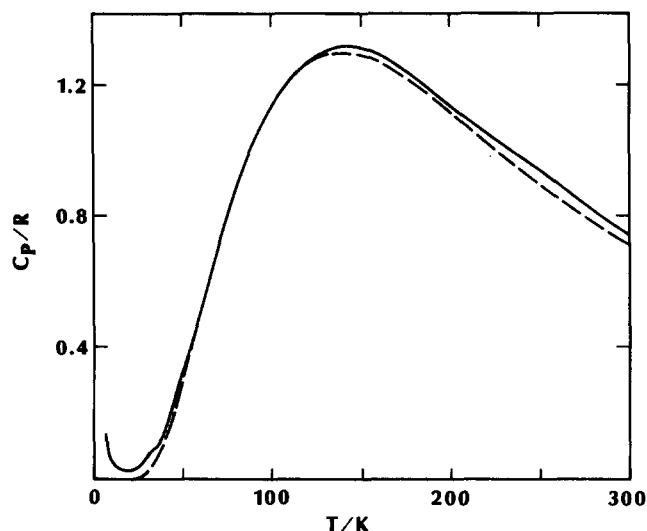


FIG. 2. Schottky contribution to the molar heat capacity of Ce_2S_3 ; solid line represents calorimetric contribution $C_p(\text{Ce}_2\text{S}_3) - [0.29 C_p(\text{Gd}_2\text{S}_3) \text{ lattice} + 0.61 C_p(\text{La}_2\text{S}_3) \text{ lattice}]$; dashed line represents contribution calculated from $\text{Ce}^{3+}(4f^1)^2F_{5/2}, 0(2), 185(2), \text{ and } 358(2)$ in cm^{-1} .

lattice is S_4 , the ground-state manifold $J = 5/2$ is split into three Kramers doublets. Earlier measurements and interpretation of magnetic susceptibility confirm that the ground-state Stark level is a doublet in Ce_2S_3 .¹³ Absorption above 380 cm^{-1} is similar for La_2S_3 and Ce_2S_3 . No analysis was made in the region around 2300 cm^{-1} , where transitions to Stark levels of $^2F_{7/2}$ are expected.

The infrared spectra of La_2S_3 and Ce_2S_3 (Fig. 4) were also investigated between 10 and 200μ with a Beckman FS-720 Fourier interference spectrophotometer using a conduction dewar filled with liquid helium. Bands approximately 20 cm^{-1} wide at half-maximum absorption were obtained at 60, 120, 170, 230, and 270 cm^{-1} for La_2S_3 and 63, 123, 175, 235, and 275 cm^{-1} for Ce_2S_3 . The spectrum of Ce_2S_3 at

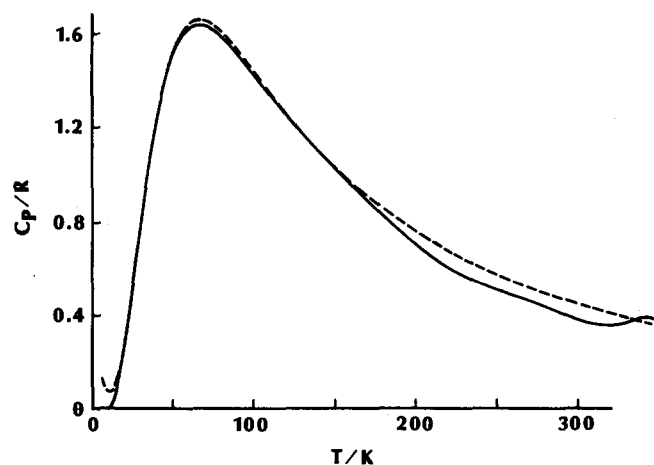


FIG. 3. Schottky contribution to the molar heat capacity of Nd_2S_3 ; solid line represents calorimetric contribution $C_p(\text{Nd}_2\text{S}_3) - [0.62 C_p(\text{Gd}_2\text{S}_3) \text{ lattice} + 0.38 C_p(\text{La}_2\text{S}_3) \text{ lattice}]$; dashed line represents contribution calculated from $\text{Nd}^{3+}(4f^3)^4I_{9/2}, 0(2), 76(2), 150(2), 180(2), \text{ and } 385(2)$, in cm^{-1} .

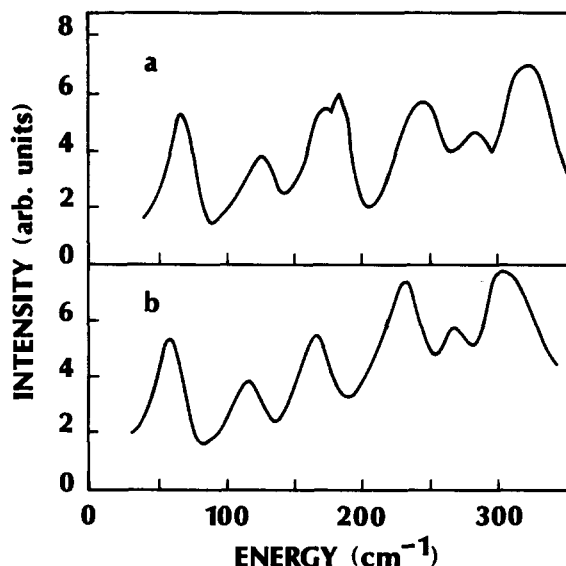


FIG. 4. Observed infrared absorption spectra of (a) Ce_2S_3 , and (b) La_2S_3 obtained between 40 and 350 cm^{-1} at 15 K; intensity is in arbitrary units.

185 cm^{-1} shows a distinct shoulder not observed in the La_2S_3 spectra which may be due to a second electronic transition within the $^2F_{5/2}$ manifold. Otherwise, both spectra appear similar—except that the Ce_2S_3 spectrum is shifted slightly to the high-energy side of the La spectrum.

Recent reports by various Russian groups,^{40,41} including the results of 300 K Raman scattering spectra of La_2S_3 , appear to be in agreement with an analysis of the vibrational spectra observed by Henderson, Muramoto, and Gruber.^{1,42}

The absorption spectra of clear yellow-blue insulating crystals of Nd_2S_3 recorded between 0.3 and 1.0μ at 300, 80, and 10 K were reported earlier by Henderson *et al.*⁴ Recently, the crystal-field splitting of the electronic $[SL]J$ energy levels of Nd^{3+} in Nd_2S_3 was published along with a lattice-sum calculation for the crystal-field parameters.¹⁹ This paper makes use of the reported experimental Stark levels for the ground-state manifold $J = 9/2$ ($^4I_{9/2}$) as well as the predicted splitting based on an effective point-charge model for the γ - Nd_2S_3 lattice. In summary, Table V includes crystal-

TABLE V. Infrared and Raman spectra of Ln_2S_3 .

La_2S_3		Ce_2S_3	Nd_2S_3	
IR (cm^{-1}) ^a	Raman (cm^{-1}) ^b	IR (cm^{-1}) ^a	IR (cm^{-1}) ^c	Raman (cm^{-1}) ^b
60	...	63	64	...
...	85	...	76	80
120,127 ^b	122	123	124	...
...	150	...
170,180 ^b	185	175(185)	180,200 ^b	192
230,230 ^b	232	235	235,240 ^b	237
270,270 ^b	273	275	278 ^b	287
300,300 ^b	300	310
...	...	358	385	...

^a Reference 42.

^b References 41 and 40.

^c References 4 and 19.

field doublet levels for Nd^{3+} at 0, 76, 150, 180, and 385 cm^{-1} and for Ce^{3+} at 0, 185, and 358 cm^{-1} , along with the infrared and Raman spectra reported by Zhuze and his co-workers.^{40,41} Analysis of the vibronic spectra observed in the visible region agrees with the reported infrared and Raman spectra.

IV. DISCUSSION AND CONCLUSIONS

Figure 5 compares the heat capacity data (C_p/R) up to 20 K obtained in the present study with values reported by Ho *et al.*¹⁰ for γ phase La_2S_3 , Ce_2S_3 , Nd_2S_3 , and Gd_2S_3 . Only in the instance of La_2S_3 do our results tally closely. The range below 10 K is that over which we have the least accuracy; yet the consistency and smoothness of our values attest to the reproducibility of these values. Our agreement with Ho *et al.*¹⁰ for La_2S_3 suggests concordance in calibration, etc. The Ce_2S_3 trends are reasonably close, but in Nd_2S_3 considerable divergence exists, and for Gd_2S_3 our data suggest the presence of a transition with a peak below 7 K. The differences in all instances are probably attributable to the high quality—with respect to both stoichiometry (cf. Table I, at worst 1.500 ± 0.006) and homogeneity—of the samples prepared for the present study in contrast with the dubiety of the earlier preparations.¹⁰

Another contrast concerns the data at higher temperatures in the subambient region as depicted on a deviation plot (Fig. 6). Deviation curves for literature values of Nd_2S_3

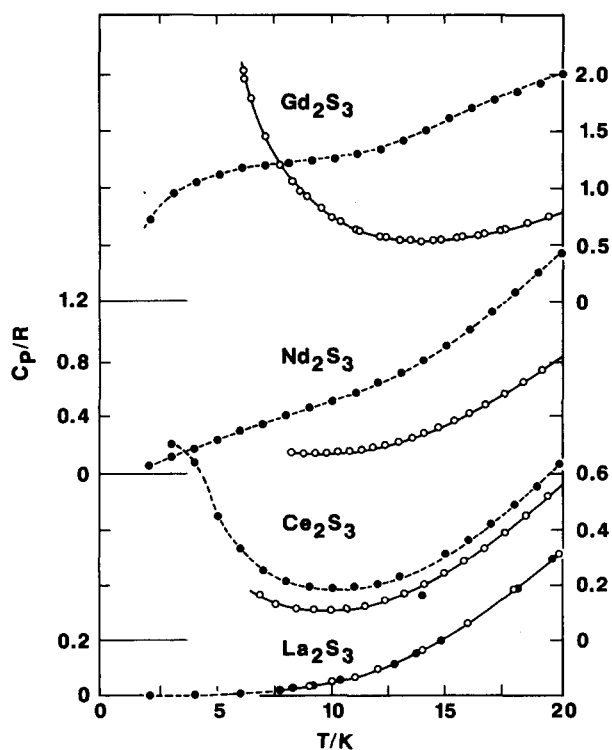


FIG. 5. Molar heat capacities as a function of temperature; present study (—○—○—○—); Ref. 10 (—●—●—●—); ordinates are left (La_2S_3), right (Ce_2S_3), left (Nd_2S_3), and right (Gd_2S_3).

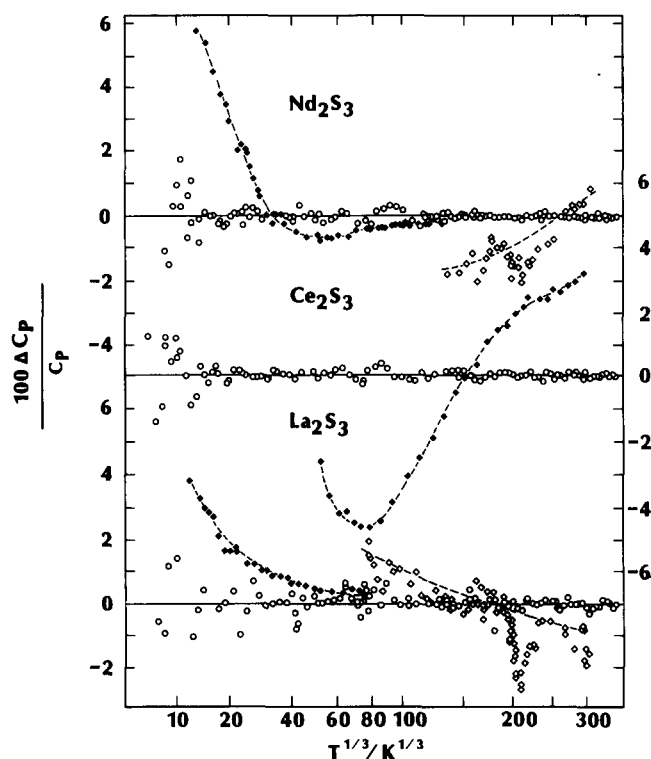


FIG. 6. Percent deviation from the smoothed curve of molar heat capacity vs temperature; ordinates are, left (La_2S_3), right (Ce_2S_3), left (Nd_2S_3), present study (open circles); Ref. 9 (black squares); Ref. 17 (open squares).

below about 130 K and La_2S_3 below about 80 K have been plotted against a percent scale an order of magnitude greater than that indicated—and used—for the other points. Note that Fig. 6 represents a variation in composition over γ phases.

The Nd_2S_3 values of a sample of α and β phases¹⁷ deviate significantly from our values on the γ phase. The Ce_2S_3 sample of King and Weller⁹ is not identified by its phase. The deviations suggest that the Schottky contributions present in their phase differ significantly from those in the γ phase.

The measurements of β - La_2S_3 of Nogteva *et al.*¹⁷ show a significant deviation below 130 K from our values on γ - La_2S_3 roughly similar to their deviation on the Nd_2S_3 data. Moreover, their values are several percent lower than ours near 200 and 300 K. The newer data by the same authors¹⁸ on a γ - La_2S_3 sample are in such remarkable accord with our data, that to avoid confusion on a figure already dense with points, we have elected only to note that our smoothed curves are in coincidence from 20 to 300 K by amounts well within $\pm 0.2\%$. Their sample had a composition of $\text{La}_{1.000 \pm 0.001} \text{S}_{1.481 \pm 0.005} \text{O}_{0.019 \pm 0.005}$ and consisted of light yellow, optically clear crystals several mm on each edge. Above 40 K, the mean deviation of the experimental points was $< 0.06\%$. Their 298.15 K value of $S^0 = 19.47 R$ corresponds to our value of 19.51 R. The trend of the data indicates that their significant deviation from stoichiometry is compensated for by the oxygen present.

For the calculation of the spectroscopic Schottky con-

tributions to the heat capacity, we adopted the levels (and degeneracies) from Table V as follows:

for Nd_2S_3 , 0(2), 76(2), 150(2), 180(2), and 385(2) cm^{-1} ,
for Ce_2S_3 , 0(2), 185(2), and 358(2) cm^{-1} .

Hence, comparison with Fig. 1 shows that Schottky levels make significant contributions to the heat capacity (for Ce_2S_3 and Nd_2S_3 —about 6% and 3% at 300 K) and consequently to the thermophysical functions. On the other hand, it is evident that such small deviations as appear between spectroscopic and heat-capacity curves (cf. Figs. 2 and 3) are well within the experimental errors of heat-capacity and spectroscopic determinations.

From the analysis of the heat capacities of the four lanthanide sesquisulfides, we have been able to calculate the lattice contribution and hence resolve the excess contribution in excellent accord with the interpretation of the spectra of La_2S_3 , Ce_2S_3 , and Nd_2S_3 . The Schottky heat-capacity contributions that result from the population of the Stark levels compare well with the excess experimental heat capacity over the lattice contribution and preclude the existence of any other possible contribution to the heat capacities between 20 and 350 K. Hence, any magnetic transitions in these samples must take place below 7 K. Magnetic transition temperatures reported in the literature between 25 and 39 K for Gd_2S_3 and between 10 and 36 K for Nd_2S_3 are a consequence of deviations from the ideal sesquisulfide stoichiometry of the compounds.

Future research on heat capacities below 4 K and magnetic susceptibility measurements within the whole temperature range would be desirable to clarify the long-range magnetic order and complement the analyses done so far.

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