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Low-temperature heat capacities of yttrium, lanthanum, and lutetium sesquisulfides

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The heat capacities of δ-$YS_{1.491}$, α-La_2S_3, β-La_2S_3, and ϵ-Lu_2S_3 were measured from 1.2 to 20 K and that of δ-$YS_{1.497}$ from 0.3 to 20 K. The heat capacities of the two La_2S_3 samples and the Lu_2S_3 sample exhibited only a T^3 dependence, i.e., the electronic specific constant γ was found to be zero within ± 0.02 mJ/g-at. K^2. This indicates that these materials are insulators or semiconductors. The temperature dependence of the heat capacity of the two substoichiometric δ-YS_x samples exhibited both T and T^3 dependences. The small γ values indicated that some conduction electrons were present, and that the stoichiometric δ-Y_2S_3 would be a semiconductor or insulator.

I. INTRODUCTION

The rare-earth sesquisulfides have received considerable attention over the past decade because of their diversity of structural types and their interesting physical properties that suggest potential device applications.[1–5] According to the literature, for many of the rare earths the R_2S_3 ($RS_{1.5}$)$-$$R_3S_4$ ($RS_{1.33}$) region has a single crystalline high-temperature phase persisting through the indicated composition range.[6–10] Increasing the metal content from stoichiometric $RS_{1.5}$ changes the material from an insulator or semiconductor to a semimetal and finally to a metallic substance.[5,10–15] Increasing the metal content also leads to superconductivity in the $LaS_{1.5}$$-$$LaS_{1.33}$ system and magnetic ordering in most of the remaining rare-earth systems which have an unfilled $4f^n$ subshell.[16–23]

Low-temperature heat-capacity measurements provide an important method to study many of these interesting physical changes.[24–26] Over the last few years we have carried out extensive calorimetric measurements on nearly all rare-earth sesquisulfides or their metal-rich analogs analyzing the Schottky and magnetic contributions to the heat capacity. However, to properly understand the data one needs information concerning the basic heat-capacity contributions due to the lattice (C_L) and the electrons at the Fermi surface (C_E). As a practical approach, we have made heat-capacity measurements on the δ form of $YS_{1.5}$, the α, β forms of $LaS_{1.5}$, and the ϵ form of $LuS_{1.5}$ for comparative purposes. The crystal structure and lattice parameters are given in Refs. 1, 6, 8, 9, and 27–31. The results reported here are a starting point toward a more quantitative understanding of the Schottky and magnetic effects in the remaining rare-earth sesquisulfides for which we also have magnetic susceptibility and optical data to present at a later date.

II. SAMPLE PREPARATION

The rare-earth sulfides were prepared by direct combination of the elements. The rare-earth metals, see Table I, were prepared at the Ames Laboratory by the calcium reduction of the corresponding trifluoride.[32,33] Sublimed sulfur (99.999% pure) was obtained from ASARCO.[34]

Electropolished strips of lanthanum and sublimed sulfur were carefully weighed to give the desired stoichiometry and placed in a previously outgassed quartz tube that was then evacuated, backfilled with helium to 650 Torr, and fused close with a flame. The sealed tube was heated from room temperature to 600±10 °C in about six hours. The reaction took place over a three day period giving a reddish-brown colored powder. After all the free sulfur had reacted the furnace temperature was raised to approximately 900 °C and the sample

TABLE I. Chemical analyses of the starting rare-earth metals[a] (in atomic ppm).

	Rare-earth metal			
Impurity	Y (12875)	Y (12979-W)	La	Lu
H	352	880	412	866
C	148	282	92	233
N	19	25	545	25
O	322	411	304	327
F	14	98	180	<27
Al		6		
Si			<2	1.1
Cl	5	2	10	
Sc	3.7			
Cr	1.3			
Fe	13	17	4	47
Ni		2		2
Cu	7.5	4	1.8	16
Zr		<2		
Ba			<3	
La		1.5		
Ce	<6	2.4		
Pr	1.5			
Nd				2.5
Gd		<20		3
Tb	2.3			
Yb		<4		
Lu		2		
Hf		<2		
Ta		2	2	
W	12	40	<2	16

[a] Only impurity levels greater than 1 atomic ppm are listed.

was heated again for about a week after which the reddish-brown color had turned to maroon.

α-La_2S_3 has been reported to be a line compound[3,31] and does not exhibit a range of compositions as do the β and γ forms. This observation has been confirmed in the present study. The materials weighed into the capsule gave $LaS_{1.500}$ while quantitative chemical analysis gave $LaS_{1.500\pm0.004}$ as the final composition.[35] Debye-Scherrer patterns of the maroon colored sulfide were the same as that reported for α-La_2S_3.[27,29,31] The powder was then compressed under 345 MPa (50 000 psi) to produce pellets for heat-capacity measurements.

β-La_2S_3 was prepared by heat treating α-La_2S_3 or γ-La_2S_3 (Ref. 23) for several weeks at approximately 1100 °C. The temperature range of stability of the β phase is reported to be between 900 and 1350 °C.[1,3,28] We have observed that conversion of the α form to the β form is complete at 1000 °C after 2.5 weeks, but the product is a powder. The γ form slowly reverts to the β form when heat treated at 1100 °C; the reaction is only 70% completed after ten days.

A crystalline form of the β phase was prepared by slowly cooling a 50-gm sample of γ-La_2S_3 composition from the liquid state. The outside of the ingot was a blue-black slightly metal-rich γ phase while the interior was a clear pale yellow β phase. The γ phase was separated mechanically from the sample. Visual inspection showed that less than 5% of the γ phase remained in the β-phase ingot. A Debye-Scherrer pattern showed the clear phase to have the structure reported for β-La_2S_3.[1,3,28] The composition was calculated to be $LaS_{1.499\pm0.001}$ as based on weighed in quantities and weight lost during melting.

Preparation of Lu_2S_3 and Y_2S_3 by direct combination of the elements is more difficult than the preparation of La_2S_3. The sulfide does not spall as it is formed, but remains on the surface of the metal as a tightly adhering coat. The reaction proceeds at a slow rate at 600 °C. Above this temperature the sulfur vapor pressure is high enough to break the quartz tube. To offset this problem longer tubes were used having one end at about 300 °C and the other end, which contains the metal, at temperatures near 900 °C. Under this arrangement approximately 20 to 30 grams of the sulfide were made over a time period of nine days for Lu_2S_3 and six days for Y_2S_3. The lutetium sample was melted under vacuum in a graphite crucible at 1800 °C. Chemical analysis[35] of part of the ingot gave a final value of $LuS_{1.494\pm0.006}$. The yttrium sulfides were similarly melted in a tungsten crucible under vacuum. Chemical analyses[35] of the two samples gave compositions of $YS_{1.491\pm0.003}$ and $YS_{1.497\pm0.005}$. The former sample was prepared from yttrium stock 12875 and the latter from 12979-W, see Table I. Debye-Scherrer patterns were taken of all samples and found to agree with the respective structures reported in the literature, see Table II.

III. CALORIMETRY MEASUREMENTS

The heat capacity of δ-$YS_{1.491}$ (3.1315 g), α-$LaS_{1.500}$ (2.3028 g), β-$LaS_{1.499}$ (2.1875 g), and ϵ-$LuS_{1.494}$ (5.1866 g) were measured from 1.2 to 20 K using standard adiabatic calorimetry. At the lowest temperatures, <2 K, there was a systematic tendency of the C/T values to rise above the straight line established at higher temperatures in the standard C/T vs T^2 plot. This tendency is primarily due to the low-heat capacity of the samples at these temperatures. In order to verify this systematic error and to obtain a more reliable value for the electronic specific-heat constant, the measurements on δ-$YS_{1.497}$ (1.1641 g) were extended down to lower temperatures (0.3 K) by making a second set of measurements on a ^{3}He calorimeter.

The sample temperature determinations were based on the electrical resistance of a Cyro-Cal germanium resistance thermometer. Pulsed Joule heating was obtained by passing a current through a Pt-W alloy wire which, along with the thermometer, was thermally anchored to the sample. The heat capacity of the thermometer-heater assembly was separately measured for addenda corrections. The performance of the calorimeter was checked by measuring the heat capacity of a 1965 Calorimetry Conference standard copper sample. The data were in good agreement with the literature values.[36] Uncertainty in the measurements of the sulfides is 1% over the temperature range reported.

IV. RESULTS

The heat capacities at the lowest temperature are shown in Figs. 1–5 in the standard C/T vs T^2 plots, and the smoothed data are summarized in one degree steps from 2 to 20 K in Table III. The data clearly show that for the two δ-YS_x samples (Figs. 1 and 2) that the intercept, γ is positive and nonzero. This indicates that there are conduction electrons present as would be suggested from the stoichiometries and the valence of the two constituents. A plot of these γ values versus the S:Y ratio indicates that δ-Y_2S_3 ($x=1.500$) would have $\gamma=0$. Thus δ-Y_2S_3 would behave just as the other R_2S_3 sulfides, see below.

As seen in Figs. 3–5 the extrapolation of the C/T vs T^2 data for α- and β-La_2S_3 and ϵ-Lu_2S_3 approaches zero within the uncertainty of the data (±0.02 mJ/g-at. K^2). This indicates that no conduction electrons are present, and that these materials are semiconductors or insulators, as one would surmise from the chemical valences of the components which make up the compounds.

The results on the ϵ-Lu_2S_3 sample warrants a special comment. The chemical analyses gave a

TABLE II. Lattice parameters of δ-$YS_{1.491}$, α-La_2S_3, β-La_2S_3, and ϵ-$LuS_{1.494}$.

Compound	a (Å)	b (Å)	c (Å)	β (°)	Ref.
δ-$YS_{1.491}$	17.51 $\pm$0.09	4.02 $\pm$0.02	10.14 $\pm$0.07	98.7 $\pm$0.5	a,b
Y_2S_3	17.520	4.019	10.170	98.64	9
α-La_2S_3	7.587$\pm$0.007	4.149$\pm$0.002	15.863$\pm$0.004		a
α-La_2S_3	7.584	4.144	15.860		9
β-La_2S_3	15.65$\pm$0.04		20.64$\pm$0.06		a
β-La_2S_3	15.62		20.62		28
ϵ-$LuS_{1.494}$	6.724$\pm$0.003		18.131$\pm$0.006		a
Lu_2S_3	6.722		18.160		39

[a] This paper.

[b] Based on front reflection lines.

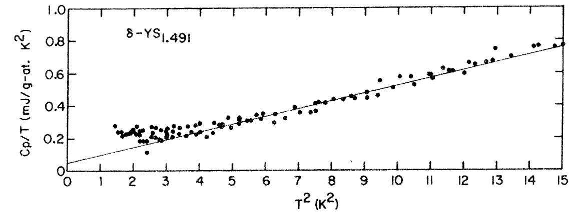

FIG. 1. Heat capacity of δ-$YS_{1.491}$ from 1.2 to 3.9 K.

S:Lu ratio of 1.494±0.006, and on the basis of this average value and the results obtained on δ-YS_x and γ-LaS_x (Refs. 14 and 23) one might have expected a nonzero value for γ. The fact that $\gamma=0$ for our lutetium sulfide indicates that either the heat-capacity sample had a composition of $LuS_{1.500}$ (which is consistent with the upper limit of the experimental uncertainty of the chemical analyses), or more likely, the Lu_2S_3 exists as a line compound and that even though our sample had a slight excess of lutetium, the major contribution to the heat capacity was that of Lu_2S_3 and the presence of a second phase had no measurable effect on the observed γ value. The presence of a small amount of second phase (probably Lu_3S_4 or Lu_2O_2S) was verified by metallographic examination of the sample. This behavior is in contrast to that observed in the γ-LaS_x (Refs. 14 and 23) and δ-YS_x alloys, where a solid solution region exists, and the electronic specific-heat constant varies with the S:R ratio.

V. DISCUSSION

In Table IV we report the coefficients of the T and T^3 terms of the normal temperatures dependences of the heat capacity. Also included in this table is the Debye temperature Θ_D, which is calculated from the coefficient of the T^3 on lattice term β,

$$\beta=(\tfrac{12}{5})\pi^4 Nk(\Theta_D)^{-3} ,$$

where N and k are Avogadro's number and Boltzmann's constant, respectively, and β is expressed in units of mJ/g-at. K^4. Above 4 or 5 K ($\sim\Theta_D/60$) the lattice heat capacity deviates from the T^3 dependence as expected. This is especially evident for α- and β-La_2S_3 (see Figs. 3 and 4). The other materials also exhibit such departures, but since the plots do not include the high-temperature data, such departures are not seen in Figs. 1, 2, and 5.

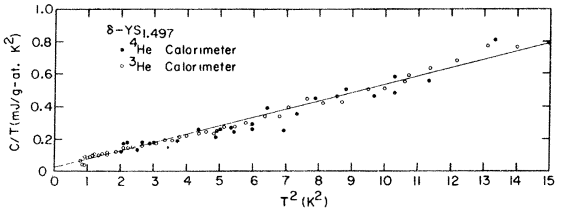

FIG. 2. Heat capacity of δ-$YS_{1.497}$ from 0.8 to 3.9 K.

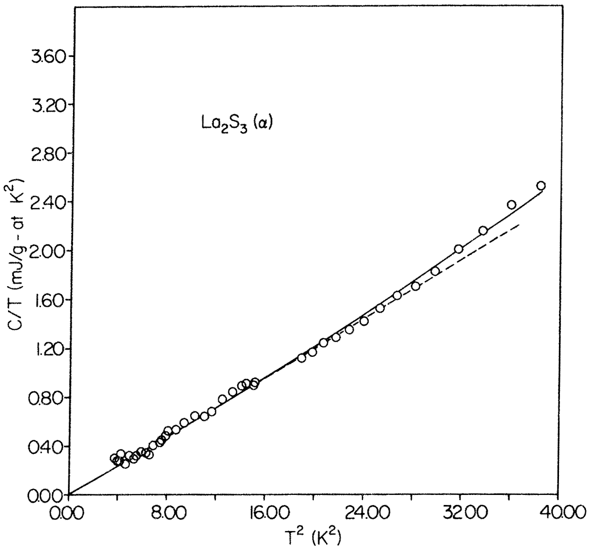

FIG. 3. Heat capacity of α-La_2S_3 from 2 to 6 K.

The zero values for γ of δ-Y_2S_3, α-La_2S_3, β-La_2S_3, and ε-Lu_2S_3 are not surprising and are ex-

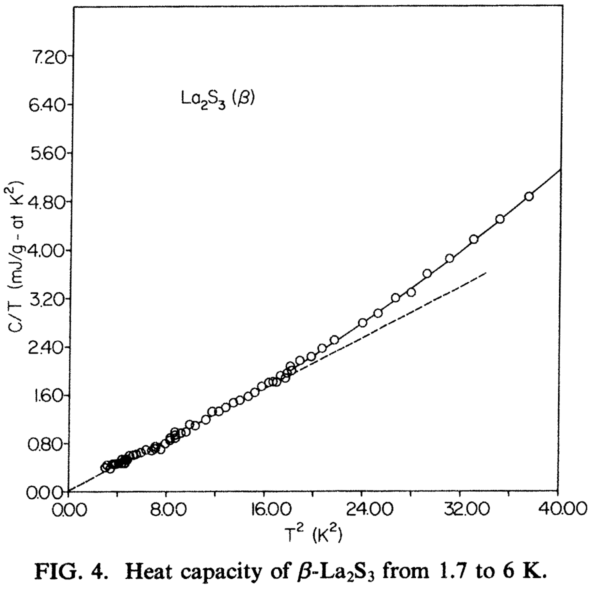

FIG. 4. Heat capacity of β-La_2S_3 from 1.7 to 6 K.

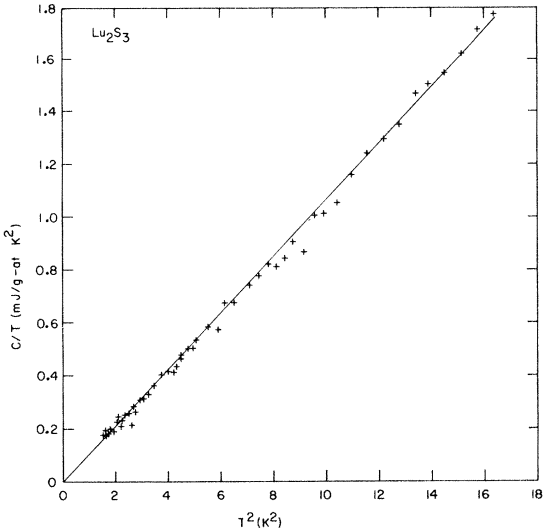

FIG. 5. Heat capacity of ϵ-Lu_2S_3 from 1.2 to 4 K.

pected from the chemical nature of the two components. The nonzero value for γ-La_2S_3, however, is unexpected. Although we have not yet succeeded in preparing stoichiometric γ-La_2S_3, the highest sulfur compositon ($LaS_{1.496}$) (Refs. 14 and 23) is sufficiently close to the stoichiometric composition, that there is little doubt that γ-La_2S_3 will have a nonzero γ value ($\gamma=0.30$ mJ/g-at. K^2 for $LaS_{1.496}$ and 0.47 mJ/g-at. K^2 for $LaS_{1.456}$). These heat-capacity results suggest that there is an overlap between the filled valence band and the empty conduction band (i.e., no energy gap), or if there is an energy gap, it is of the order of 10^{-4} eV. This means that there are always some conduction electrons available and these give rise to a nonzero electronic specific-heat constant.

The variation of the Debye temperatures is quite surprising when considering the small difference between those of δ-Y_2S_3 and α-La_2S_3 (8 K) and the large differences between those of the three La_2S_3 phases (54 and 32 K relative to α-La_2S_3). Although some variation is to be expected because of the variation in the rare-earth mass and the molecular volume and melting point differences of the compounds there appears to be no correlation. For the three La_2S_3 phases the rare-earth mass and the compound melting point differences are eliminated, but still taking account of the molecular volume per formula unit there is no correlation between the observed Debye temperatures. This suggests that the crystal structure has a strong influence on Θ_D. This crystal structure effect becomes more evident when the Lindemann equation[37] is used to analyze these results. This equation relates the mean atomic weight M, the melting point T_m, and the volume per g-at. V, with the Debye tempera-

TABLE III. Smoothed heat-capacity values for the stoichiometric and near-stoichiometric sesquisulfides of yttrium, lanthanum, and lutetium.

	C_p(mJ/g-at. K)			
T (K)	δ-$YS_{1.497}$	α-La_2S_3	β-La_2S_3	ϵ-$LuS_{1.494}$
2	0.442	0.464	0.770	0.824
3	1.52	1.600	2.75	2.78
4	3.55	3.89	6.99	6.59
5	4.78	7.85	14.69	13.50
6	8.64	14.08	27.25	24.90
7	11.80	23.26	46.13	43.11
8	21.00	36.18	72.62	70.70
9	32.85	53.69	107.66	108.9
10	49.5	76.73	151.66	158.6
11	71.5	106.3	204.5	225.5
12	86.0	143.4	265.6	310.2
13	127.0	189.0	334.4	403.1
14	165.5	244.1	410.8	511.3
15	217	309.6	495.8	630.1
16	271	386.2	591.5	760.4
17	337	474.1	700.9	901
18	405	572.9	825.2	1062
19	480	680.7	958.9	1243
20	547	793	1080	1450

TABLE IV. Heat-capacity-fit parameters for the stoichiometric and near-stoichiometric sesquisulfides of yttrium, lanthanum, and lutetium.

Sample	γ (mJ/g-at. K^2)	β (mJ/g-at. K^4)	Θ_D (K)
δ-YS$_{1.491}$	0.097 ± 0.005.	0.0416 ± 0.0004	360 ± 1
δ-YS$_{1.497}$	0.025 ± 0.002	0.0527 ± 0.0003	333 ± 2
δ-Y$_2$S$_3$	0[a]	0.0587[a]	321[a]
α-La$_2$S$_3$	0	0.0610 ± 0.0006	317 ± 1
β-La$_2$S$_3$	0	0.1066 ± 0.0007	263 ± 1
γ-La$_2$S$_3$	0.24[a,b]	0.0840[a,b]	285[a,b]
ϵ-Lu$_2$S$_3$	0	0.1037 ± 0.0014	266 ± 1

[a] Values obtained by extrapolation from a property versus composition plot.

[b] Data taken from Ikeda *et al.* (Refs. 14 and 23).

ture as follows:

$$\Theta_D = K\left[\frac{T_m}{M}\right]^{1/2}\left[\frac{1}{V}\right]^{1/3},$$

where K is a constant for closely related, isostructural materials. The melting points used in the present calculation were determined at the Ames Laboratory and found as follows: Y_2S_3 (1650 °C), La_2S_3 (1950 °C), and Lu_2S_3 (1850 °C). From the crystal-structure data reported in the literature, the molecular volume and the number of atoms in the unit cell have been determined. Using Θ_D determined from the heat-capacity results (see Table IV), the following values have been calculated for the constant K: δ-Y_2S_3 (131), α-La_2S_3 (145), β-La_2S_3 (125), γ-La_2S_3 (142), and ϵ-Lu_2S_3 (133). A comparison of the La_2S_3 compounds shows that value of K for β-La_2S_3 is significantly lower than those of the α and γ phases. But when all five compounds are considered, the K value for β-La_2S_3 deviates from the average value (135) as much as the value for α-La_2S_3. The average value and the deviation of 135 ± 10 for K is reasonable considering these materials have different crystal structures, especially when compared with the average value for 59 elements ($K = 145.1 \pm 31.6$).[38]

From these results it is now possible to estimate values of Θ_D for other paramagnetic R_2S_3 compounds by using the Lindemann equation and the appropriate constants M, T_m, and V for the particular rare-earth sesquisulfide and the appropriate K for the corresponding crystal structure. This information will be invaluable for analyzing the heat-capacity results obtained on the paramagnetic R_2S_3 compounds and comparing these results with the magnetic susceptibility and absorption spectra on hand for a continuing and systematic study of the physical properties of the rare-earth sesquisulfides.

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[34] American Smelting and Refining Company, Denver, Colorado.

[35] The chemical analyses were carried out by G. V. Austin and R. Z. Bachman, Analytical Services Group, Ames Laboratory, Iowa State University, according to 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 as a barium sulfate. The rare-earth cations in solution were quantitatively analyzed by titrating with ethylene-diamine-tetra-acetic acid.

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