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Heat Capacity of Rare Earth Sesquisulfides

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Abstract - Heat capacity measurements between about 2 and 20 K have been made on a series of nearly stoichiometric rare earth sesquisulfides $RS_{1.5}$ with R = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, or Lu. No magnetic ordering was observed. Extra heat capacity contributions beyond those due to the lattice and conduction electrons occur in all cases except in the La and Lu compounds. Such contributions are mostly of the Schottky type associated with crystal field effects.

Résumé - On a effectué des mesures de la capacité de chaleur, entre 2 et 20 K environ, sur une série presque stoïchiométrique de sesquisulfures de terres rares, $RS_{1.5}$, avec R = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, ou Lu. Aucune disposition magnétique n'a été remarquée. Des contributions supplémentaires à la capacité de chaleur, au delà de celles dûes aux électrons de matrix et de conduction, sont présentes dans tous les cas sauf dans les composés à La et à Lu. Pour la plupart, de telles contributions sont du type Schottky en association avec des effets de champ du cristal.

1. Introduction - In this paper we are concerned with a study of low temperature heat capacity of the refractory semiconducting R_2S_3 ($RS_{1.5}$) phases. The compounds, where R = La through Dy, crystallize with the bcc Th_3P_4 defect-type structure and are generally called the γ-phase.[1] The compounds $HoS_{1.5}$ through $TmS_{1.5}$ have the "δ" or the monoclinic δ-Dy_2S_3 type structure, $YbS_{1.5}$ and $LuS_{1.5}$ have "ε" or the rhombohedral α-Al_2O_3 type

structure. The resulting materials are often semiconducting or semimetallic in nature, and have received increasing attention in recent years with particular interest centered on their transport, optical, and magnetic properties.[2] To help elucidate, among others, their crystal fields and magnetic behaviors, low temperature heat capacity data should be most useful, but only very limited studies have so far been reported. This work was therefore initiated as a preliminary survey over the almost entire set of rare earth elements.

2. Experimental - Listed below are eleven RS_x samples with their chemically analysed compositions (±0.01 in x for compositions given to three significant figures or ±0.005 in x for compositions given to four significant figures):

R	La	Ce	Pr	Nd	Gd	Tb	Dy	Ho	Er	Tm	Lu
x	1.499	1.457	1.471	1.45	1.47	1.496	1.49	1.48	1.491	1.470	1.494

While those with R = Nd, Gd, and Dy are 1-2 g single crystals grown by flame fusion in an argon plasma or by Bridgman techniques,[3] others were prepared by direct combination of the elements between 600 and 900°C and grown as 10-20 g crystals or ingots from the melt (1700-2200°C). X-ray powder patterns confirm the crystal structures reported by Flahaut et al.[1] and as noted above. The Th_3P_4 structure thus obtained appears stable against any phase transformations down to liquid helium temperatures.

Heat capacity measurements by adiabatic calorimetry were made between about 2 and 20 K. Pulsed heating and germanium thermometry were used. Overall uncertainties of the heat capacity values associated mainly with addenda corrections were estimated to be within 1 or 2%, depending on the size and the magnitude of heat capacity of a given sample.

3. Results and Discussion - Figure 1 shows the linear dependence of C/T versus T^2 for $LaS_{1.499}$ and $LuS_{1.494}$ typical for normal solids at low

enough temperatures. The different Debye temperatures of 320 K and 265 K, respectively, are not consistent with the mass difference between La and Lu, a Debye temperature of 293 K for $LuS_{1.494}$ would be expected relative to that for $LaS_{1.499}$ if the lattice stiffness were only dependent on the lanthanide mass. The lower observed Debye temperature for $LuS_{1.494}$ is probably due to the fact that the compounds have different crystal structures. Whereas $LuS_{1.494}$ behaves as an insulator, the non-zero electronic heat capacity of $LaS_{1.499}$ is unexpected and not understood. At present time we can not rule out a deviation from the stoichiometric composition or compositional inhomogeneity.

Figure 2 summarizes the experimental data. There is no indication of any magnetic ordering below 20 K in the heat capacity data and this has been confirmed by magnetic susceptibility results. Without any unpaired 4f electron, $LaS_{1.499}$ and $LuS_{1.494}$ should have only the lattice and electronic heat capacity. Indeed, the observed temperature dependence of heat capacity is monotonic, and can be used as base lines (i.e., the lattice and electronic heat capacity) for other compounds with various degrees of anomaly. Even though some of the samples are known to become magnetically ordered at higher temperatures[4] and have therefore magnetic contributions to the total heat capacity, the observed features of temperature dependence with broad peaks and inflection points suggest that the extra heat capacities in the temperature range being considered here are mostly of the Schottky type caused by crystal field effects. Such effects occur when the crystal field removes the degeneracy of the ground J-multiplet, splitting it into a ground state and one or more excited states, all of which may or may not be degenerate. The magnitude of this Schottky contribution to heat capacity therefore depends on the crystal structure in terms of the symmetry about the rare earth ions and

the strength of the crystal field. While no center of symmetry exists in the Th_3P_4 structure,[5] optical studies have shown that one can approximate the point group symmetry of the rare earth ions with the symmetry group O_h. Crystal field parameters can also be obtained from optical spectra. For $NdS_{1.45}$ and $DyS_{1.49}$ good agreement between the heat capacity data and the calculated values based on such an approach has been previously reported.[4] Optical studies on other compounds would be useful for further comparisons. Heat capacity measurements extended to lower temperatures on some of them, e.g., Ce, Er, and Tm, thus to generate more complete Schottky anomalies would also be desirable in this respect.

References

1. Flahaut J., Guittard, M., Patrie, M., Pardo M. P., Golabi S. M., and Domange L., Acta Cryst. 19 (1965) 14 and 21 (1966) 431.
2. Taher S. M. A. and Gruber J. B., Phys. Rev. B 16 (1977) 1624, and references therein.
3. Henderson J. R., Muramoto M, Loh E., and Gruber J. B., J. Chem. Phys. 47 (1967) 3347.
4. Taher S. M. A., Gruber J. B., Ho J. C., and Yeh D. C., to be published in the Proceedings of the 13th Rare Earth Research Conference, Oct. 16-20, 1977.
5. Flahaut J. and Laruelle P., Progress in the Science and Technology of the Rare Earths (Pergamon Press, New York) 1968, p. 169.

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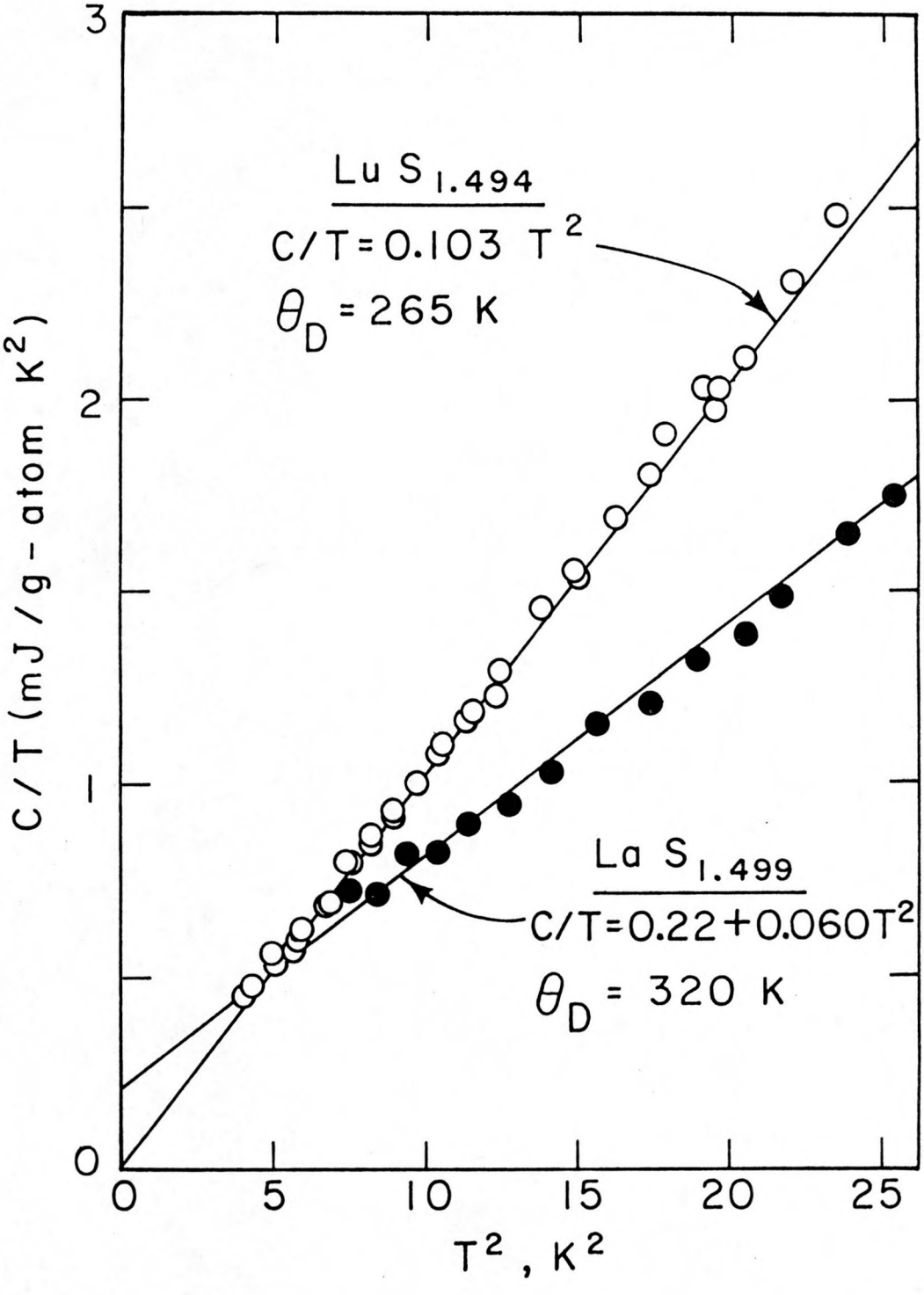
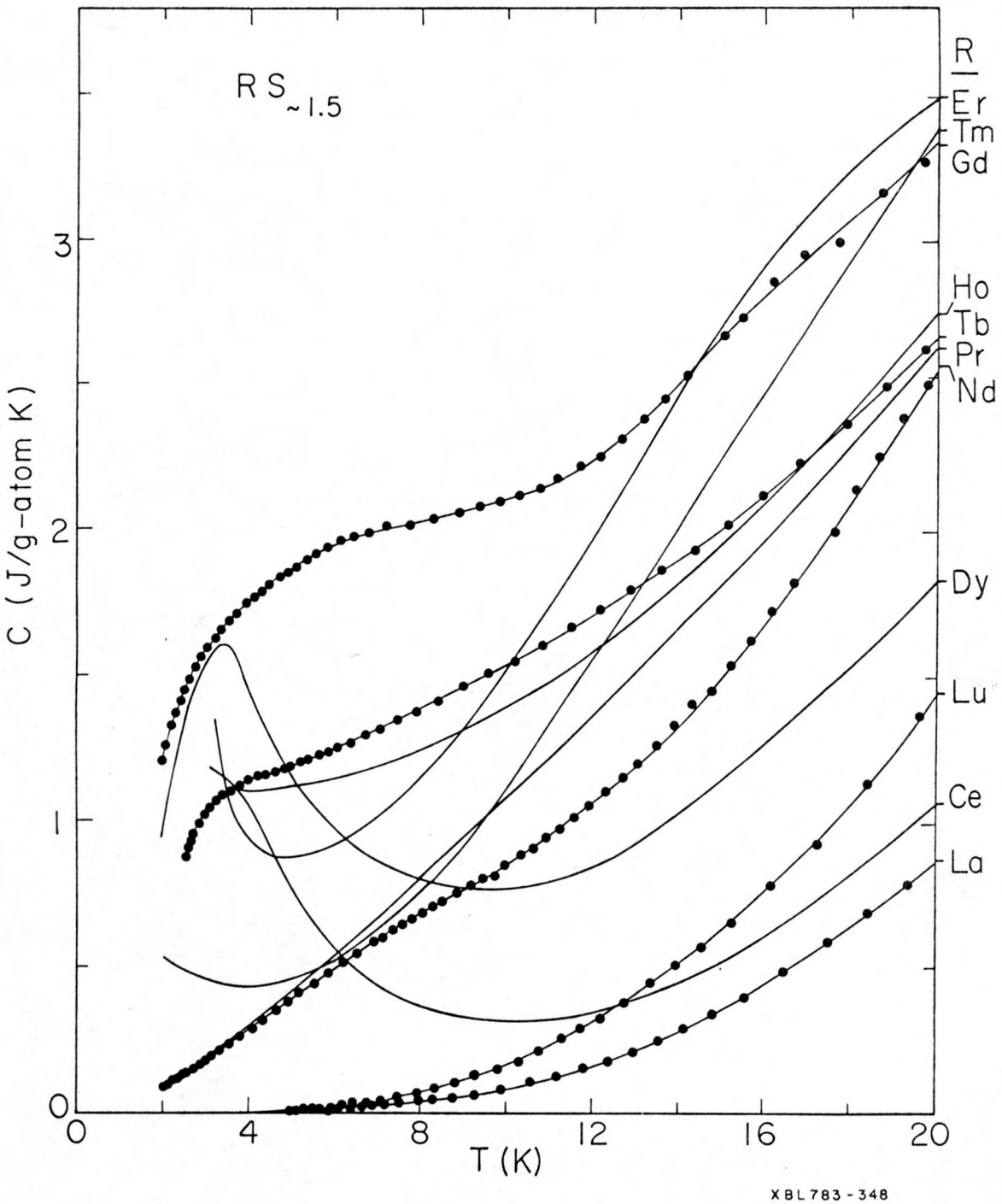
Figure Captions

Figure 1. C/T versus T^2 for $LaS_{1.499}$ and $LuS_{1.494}$. The value of Debye temperature θ_D is calculated from the slope of the straight line fitted to the data.

Figure 2. Heat capacities of various rare earth sesquisulfides between about 2 and 20 K. For clarity most sets of data are represented by smooth curves.


Lu S1.494
C/T = 0.103 T2
θD = 265 K
La S1.499
C/T = 0.22 + 0.060T2
θD = 320 K
C/T (mJ/g-atom K2)
T2, K2
0
1
2
3
0
5
10
15
20
25

XBL783-350


R S ~ 1.5
R
Er
Tm
Gd
Ho
Tb
Pr
Nd
Dy
Lu
Ce
La
C (J/g-atom K)
T (K)
0
1
2
3
0
4
8
12
16
20
XBL783-348