

SCHOTTKY LEVELS AND THERMODYNAMIC CONTRIBUTIONS OF LIGHT LANTHANIDE SESQUISULFIDES HAVING THE Th_3P_4 STRUCTURE*

JOHN B. GRUBER

Departments of Physics and Chemistry, Portland State University, Portland, OR 97207 (U.S.A.)

R. BURRIEL and EDGAR F. WESTRUM, JR.

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109 (U.S.A.)

P. E. PALMER and B. J. BEAUDRY

Ames Laboratory, Iowa State University, Ames, IA 50011 (U.S.A.)

(Received March 3, 1983)

Summary

Heat capacity measurements were made by adiabatic calorimetry over the range 7–350 K on γ phase preparations of four lanthanide sesquisulfides, and the heat capacities were resolved into lattice, magnetic, Schottky and other components. The entropy at 298.15 K for La_2S_3 which is written as S°/R is 19.51 while values of $S^\circ - S^\circ(7\text{ K})$ for Ce_2S_3 , Nd_2S_3 , Gd_2S_3 and Dy_2S_3 are 21.34, 22.38, 20.05 and 22.58 respectively. IR and visible optical spectra of La_2S_3 , Ce_2S_3 , Nd_2S_3 and Dy_2S_3 and lattice sum crystal field splitting calculations for Nd_2S_3 , Ce_2S_3 and Dy_2S_3 are compared with Raman scattering data and Schottky contributions derived from calorimetry.

1. Introduction

The lanthanide sesquisulfides Ln_2S_3 manifest unusual magnetic and electronic behavior as a consequence of their $(4f)^n$ states [1–3]. The study of these phenomena by calorimetric, spectroscopic and magnetic techniques leads to an elucidation and resolution of their energetic spectra. To date relatively few heat capacity data have been reported [4–7] and they have not been interpreted in specific detail between 20 and 300 K other than to establish the possible occurrence of magnetic ordering or structural phase transitions. A successful interpretation of the observed phenomena taking account of crystal

* Paper presented at the Sixteenth Rare Earth Research Conference, The Florida State University, Tallahassee, FL, U.S.A., April 18–21, 1983.

field effects and available lower temperature heat capacity data [7, 8] has permitted evaluation of the thermodynamic functions and resolution of the Schottky contributions together with correlation with IR and Raman scattering data presented here and in the literature [8–11].

2. Experimental details

2.1. Sample provenance and characterization for heat capacity studies

The sulfides were prepared at the Ames Laboratory, Iowa State University, by direct combination of high purity elements produced in the Laboratory in a manner similar to that described by Gschneidner *et al.* [12]. The quartz ampoules containing the reacted elements were opened and the sulfide was ground and sieved to 200 mesh powder, cold pressed into pellets and heated under a dynamic H₂S atmosphere for 24–48 h at 1450–1500 °C.

Debye–Scherrer X-ray patterns contained only lines of the γ phase b.c.c. Th₃P₄ structure. The final compositions were determined by chemical analysis to be stoichiometric within the experimental uncertainty. The clarity of the solution in 6 N HCl indicates the absence of trace oxysulfide impurities. All samples used in this study gave clear solutions when dissolved.

2.2. Automated adiabatic calorimetry

The data were obtained using the mark X calorimetric cryostat, which is an improved (by the addition of a guard shield surrounding the adiabatic shield) version of the mark II cryostat described in ref. 13 where the relevant operating techniques were also given. The operation of the instruments and the acquisition of heat capacity data from about 7 to 350 K was computer assisted. Temperatures and other accurate experimental quantities are referred to standards provided by the National Bureau of Standards.

2.3. 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 heat capacity volume-weighted lattice approximation technique employed for Ce₂S₃, Nd₂S₃ and Dy₂S₃ has been used successfully for several other groups of lanthanide compounds [14] and involves linear interpolation between diamagnetic La₂S₃ and Gd₂S₃ with the magnetic contribution deleted. It should be noted that the mole throughout is based on the formula written as Ln₂S₃ or 2 mol of lanthanide.

2.4. Optical spectroscopy: samples, technique and measurements

Samples used in the investigation of the IR spectra were prepared by passing purified H₂S gas over graphite boats containing finely ground Ln₂O₃ powder (minimum purity, 99.99%) at 850–1300 °C. Analysis of the X-ray crystallography patterns revealed that the dark red–brown to black powders had the high temperature γ phase Th₃P₄ b.c.c. structure. Chemical analysis of the powder indicated that the material was stoichiometric.

IR spectra of powdered mull samples were recorded between 250 and 2500 cm^{-1} using a Perkin-Elmer 301 spectrometer. Samples were cooled to 15 K and to 90 K using a conduction Dewar filled with liquid helium and liquid nitrogen respectively. The measurements were performed by J. R. Henderson, M. Muramoto and J. B. Gruber between 1967 and 1970 as part of a comprehensive research project to investigate the optical, magnetic and electrical properties of the lanthanide sesquisulfides. Only part of these investigations has been reported [3, 9, 10].

3. Results and discussion

3.1. Spectroscopic properties

The IR spectra between 250 and 2500 cm^{-1} contain a number of very strong bands which are broad even at 15 K (25–50 cm^{-1}). Tracings of these recordings have appeared earlier [3, 9]. There is a band with structure near 270 cm^{-1} in La_2S_3 and near 275 cm^{-1} in Ce_2S_3 . A second band is found at 300 cm^{-1} and at 310 cm^{-1} for La_2S_3 and Ce_2S_3 respectively. A relatively narrow peak of moderate strength (half the absorbance of bands found lower in energy) is observed at approximately 358 cm^{-1} in Ce_2S_3 . This peak, which is not found in the La_2S_3 spectrum, may be due to an electronic (magnetic dipole) 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 R_2S_3 lattice is S_4 , the ground state manifold $J = \frac{5}{2}$ is split into three Kramers doublets. Earlier measurements and interpretation of magnetic susceptibility confirm the ground state level to be a doublet in Ce_2S_3 [15, 16]. Absorption above 380 cm^{-1} is too broad for any structure to be identified.

The spectra of powdered mull samples were investigated between 30 and 300 cm^{-1} using a Beckman FS-720 Fourier interference spectrophotometer and a conduction Dewar filled with liquid nitrogen. Bands approximately 15–25 cm^{-1} wide at half-maximum absorption were obtained at 60 (63) cm^{-1} , 120 (123) cm^{-1} , 170 (175) cm^{-1} , 230 (235) cm^{-1} and 270 (275) cm^{-1} for La_2S_3 (Ce_2S_3). The 80 K spectrum of Ce_2S_3 at 185 cm^{-1} shows a 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 roughly the same with the Ce_2S_3 spectrum shifted slightly to the high energy side of the La_2S_3 spectrum. Both the IR and the Raman spectral data are summarized in Table 1, and the data for Ce_2S_3 are compared graphically in Fig. 1 with those derived from the calorimetric data of Fig. 2. An equally excellent correlation obtains for Nd_2S_3 .

3.2. Thermophysical properties

The calorimetrically derived Schottky contribution to the heat capacity of Ce_2S_3 is displayed as the full curve in Fig. 1. The entropy at 298.15 K for La_2S_3 , which is written as S°/R , is 19.51 while values of $S^\circ - S^\circ(7\text{ K})$ for Ce_2S_3 , Nd_2S_3 , Gd_2S_3 and Dy_2S_3 are 21.34, 22.38, 20.05 and 22.58 respectively.

Recent reports by various Russian groups, including the results of room

TABLE 1
IR and Raman spectra for several lanthanide sesquisulfides

La_2S_3		Ce_2S_3	Nd_2S_3	
IR (cm^{-1})	Raman (cm^{-1})	IR (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})
60 ^a	65 ^b	63 ^a	64 ^a	—
—	85 ^b	—	76 ^{a,c}	80 ^b
120 ^a , 127 ^d	122 ^b	123 ^a	124 ^a	—
—	—	—	140 ^{a,c} , 150 ^{a,c}	—
170 ^a , 180 ^d	185 ^b	175 (185) ^a	180 ^{a,c} , 200 ^d	192 ^b
230 ^a , 230 ^d	232 ^b	235 ^a	235 ^a , 240 ^d	237 ^b
270 ^a , 270 ^d	273 ^b	275 ^a	278 ^d	287 ^b
300 ^d	300 ^d	310 ^a	—	—
—	—	358 ^a	385 ^a	—

^a From ref. 17 (spectra recorded at 90 K).

^b From ref. 11 (spectra recorded at room temperature).

^c From ref. 18 (spectra recorded at 90 K).

^d From ref. 19 (spectra recorded at room temperature).

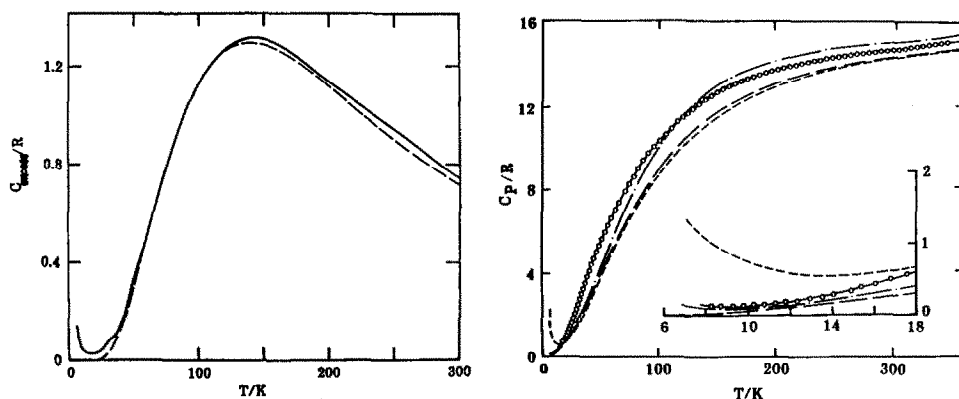


Fig. 1. Comparison of the calorimetric Schottky contributions, i.e. $C_p(Ce_2S_3) - \{0.39C_p(Gd_2S_3, \text{corrected for magnetic ordering}) - 0.61C_p(La_2S_3)\}$ (—) with spectroscopic contributions calculated from the Stark levels (0, 185 and 358 cm^{-1}) (---).

Fig. 2. Molar heat capacities: experimental points are shown for La_2S_3 (—) to indicate their approximate density for all samples; the curves for Ce_2S_3 (-·-·-), Nd_2S_3 (— — —) and Gd_2S_3 (- - -) are shown without the experimental data to avoid confusion.

temperature Raman scattering spectra of La_2S_3 and Dy_2S_3 [11], are in agreement with the vibrational spectra observed in the unpublished work of Gruber *et al.* [10]. While assignments of vibrational and electronic transitions to the spectra are difficult to ascertain from the optical data alone, it is hoped that future crystal field splitting calculations and the interpretation of unpublished magnetic susceptibility data will further clarify the details of the Stark splitting of the ground state manifolds of all rare earth ions in the sesquisulfide lattice.

Acknowledgments

We wish to thank R. Hofer and R. Z. Bachman, Analytical Services Group, Ames Laboratory, Iowa State University, for the chemical analyses of samples used to make heat capacity measurements, and J. R. Henderson and D. Johnson, McDonnell Douglas Astronautics Company, Santa Monica, CA, for preparing samples used to make the IR spectra measurements. We thank Professor Magda El-Fass, Xiao-Xia Ma and W. A. Plautz for assisting in the evaluation of the heat capacities and thermodynamic functions.

The portion of this work done at the University of Michigan was supported in part by the Structural Chemistry and Chemical Thermodynamics Program of the National Science Foundation under Grant CHE-8007977.

References

- 1 G. H. Dieke, *Spectroscopic Properties of Rare Earth Ions*, Wiley-Interscience, New York, 1965.
- 2 B. R. Judd, *Operator Techniques in Atomic Spectroscopy*, McGraw-Hill, New York, 1963.
- 3 J. R. Henderson, M. Muramoto, E. Loh and J. B. Gruber, *J. Chem. Phys.*, **47** (1967) 3347.
- 4 E. G. King and W. W. Weller, Low temperature heat capacities and entropies at 298.15 K of cerium monosulfide, cerium sesquisulfide and thorium disulfide, *Rep. USMB-R1-5485*, 1959 (U.S. Bureau of Mines).
- 5 V. V. Nogteva, I. E. Paukov and E. I. Yarembash, *Russ. J. Phys. Chem.*, **43** (1969) 1312.
- 6 V. V. Tikhonov and I. A. Smirnov, *Sov. Phys.—Solid State*, **13** (1972) 2296.
- 7 J. C. Ho, S. M. A. Taher, G. B. King, J. B. Gruber, B. J. Beaudry and K. A. Gschneidner, Jr., *J. Phys. (Paris), Colloq. C6*, **8** (1978) 840.
- 8 S. M. A. Taher, J. C. Ho and J. B. Gruber, *J. Chem. Phys.*, **76** (1982) 609.
- 9 J. R. Henderson, M. Muramoto, J. B. Gruber and R. Menzel, *J. Chem. Phys.*, **52** (1970) 2311.
- 10 J. B. Gruber, J. R. Henderson and M. Muramoto, *Rep. DAC-59368P*, October 1966; *Rep. DAC-605317R*, June 1968 (McDonnell Douglas Astronautics Company, Santa Monica, CA) (unpublished).
- 11 T. G. Arkatova, V. P. Zhuze, M. G. Kariss, A. A. Kamarzin, A. A. Kukharskiï, B. A. Mikhailon and A. I. Skelykh, *Sov. Phys.—Solid State*, **21** (1979) 1979.
- 12 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** (1981) 7187.
- 13 E. F. Westrum, Jr., *J. Chem. Educ.*, **39** (1962) 443.
E. F. Westrum, Jr., G. T. Furukawa and J. P. McCullough, in J. P. McCullough and D. W. Scott (eds.), *Experimental Thermodynamics*, Vol. 1, Butterworths, London, 1968, Chap. 4, p. 133.
- 14 E. F. Westrum, Jr., *J. Chem. Thermodyn.*, **15** (1983), in the press.
- 15 A. T. Starovoitov, V. I. Ozhogin, G. M. Loginov and V. M. Sergeeva, *Zh. Eksp. Teor. Fiz.*, **57** (1969) 791 (*Sov. Phys.—JETP*, **30** (1970) 433).
- 16 G. Becker, J. Feldhaus, K. Westerholt and S. Methfessel, *J. Magn. Magn. Mater.*, **6** (1977) 14.
- 17 J. A. Henderson, M. Muramoto and J. B. Gruber, unpublished data, 1969.
- 18 J. R. Henderson, M. Muramoto, J. B. Gruber and R. Menzel, *J. Chem. Phys.*, **52** (1970) 2311.
- 19 V. P. Zakharov and G. V. Lashkarev, *Preparation and Investigation of the Properties of Rare Earth Compounds*, Soviet Physics Publishers, Kiev, 1975, p. 82.