

# ADVANTAGES TO CONVERSION OF LATTICE HEAT CAPACITY TO $C_V$ IN THE RESOLUTION OF EXCESS PROPERTIES\*

## The $\text{Ln}_2\text{S}_3$ 's as an example

A. R. Demlow<sup>1</sup>, D. V. Eldred<sup>2</sup>, D. A. Johnson<sup>2</sup> and  
E. F. Westrum, Jr.<sup>3</sup>

<sup>1</sup>Department of Mathematics, Cornell University, Ithaca, NY 14853

<sup>2</sup>Department of Chemistry, Spring Arbor College, Spring Arbor, MI 49283

<sup>3</sup>Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, USA

## Abstract

This paper represents a fitting (modeling) of the temperature dependence of the Komada-Westrum characteristic temperature for those  $\gamma$ -,  $\delta$ - and  $\epsilon$ -phase lanthanide sesquisulfides for which the total heat capacities, including internal degrees of freedom (e.g., Schottky and magnetic contributions), were connected to the residue of only lattice vibrations yielding lattice heat-capacity contributions. These characteristic temperatures ( $\theta_{KW}$ ) at 298.15 K are seen to behave smoothly (nearly linearly) as a function of (cationic) atomic number within the region of stability of each phase as does the density. The trends between the phases also show some consistency but not predictability of one from the other.

**Keywords:**  $C_p$ ,  $C_v$ , entropies,  $\text{Ln}_2\text{S}_3$ , phonon dispersion

## Introduction

In obtaining a resolution of the electronic (Schottky) and magnetic excess modes in experimental data by the evaluation of the lattice heat capacity for a material, one recognizes the failure in the constancy of the Debye characteristic temperature and turns to a more accurate representation of the lattice heat capacity – e.g., the Komada-Westrum approach which is, likewise, a single fitted parameter model but one which takes prior significant input of molecular and crystalline parameters characteristic of the Born von Kármán model [1]. Thus, one takes into account the longitudinal and transverse acoustical branches as well as

\* Key lecture.

the corresponding optical branches, so that for  $C_v$ , the heat capacity at constant volume is simply a summation

$$C_{v,m} = \sum (C_v)_i$$

over these branches. Using parabolic acoustical modes (and neglecting dispersion) leads to the familiar Debye model; using Dirac  $\delta$ -functions to represent contributions from molecular ions [2] yields the Einstein model. In the Komada-Westrum approach for modeling the experimental heat-capacity of a substance, the input parameters (or their default values) and the K-W characteristic temperature,  $\theta_{KW}$ , must be specified. This fitting parameter – relatable to the Debye characteristic temperature,  $\theta_D$  – renders this a single parameter theory [1]. Unlike the Debye theory, however, the Komada/Westrum characteristic temperature is usually remarkably constant up to temperatures where the anharmonicity contributes significantly to the measured heat capacity [e.g., 1, 2, 3].

In the *ab initio* generation of a heat capacity expression for a crystalline or vitreous phase, the Komada-Westrum model does indeed yield  $C_v$  data. However, in the resolution of the total heat capacity of a condensed phase into a contribution from the lattice and the internal degrees of freedom, it is often assumed that an adequately good resolution (essentially a ‘differential’ effect) can be obtained by operating on the available measured  $C_p(\text{tot})$  data rather than the often theoretically preferred but essentially immeasurable condensed phase  $C_v$ . This may be effective at a temperature low enough to insure the absence of vibrational anharmonicity, but in the need to determine  $C_p(\text{tot})$  as a function of temperature at higher temperatures, anharmonicity effects cause a gradual decrease in the apparent  $\theta_{KW}$  at higher temperatures. This is a major concern since the constancy of the  $\theta_{KW}$  has been emphasized as the criterion of goodness of fit of the model. The calculation of  $\theta_{KW}$  can readily be achieved by use of a program designated LEM-1, lattice heat capacity estimation program, from a  $(C_v, T)$  data set and the parameters provided by the underlying model [1].

Our only previous use of  $C_v$  data was in the resolution of the minute thermal effect of electronic delocalization near 225 K in deerite (a hydrous ferrous ferric sulfate). Conversion to  $C_v$ , was essential in this case because relatively large anharmonicities exist in the vibrational motion even at 225 K compared to the minute heat capacity contribution (ca. 0.6%) of the delocalization itself [2]. The general advantages of the  $C_v$  approach on the  $\gamma$ - $\text{Ln}_2\text{S}_3$ 's resolving heat capacities with the LEM equations were demonstrated in Ref. [3].

### The lanthanide sesquisulfides ( $\text{Ln}_2\text{S}_3$ )

As a systematic, more extensive test of the modeling we have selected the polymorphic lanthanide sesquisulfides,  $\text{Ln}_2\text{S}_3$ , which occur in three phases  $\gamma$ (cu-

bic),  $\delta$  ( $\text{Al}_2\text{O}_3$ -type, hexagonal), and  $\epsilon$  ( $\text{Ho}_2\text{S}_3$ -type, monoclinic) with cationic symmetries of  $S_1$ ,  $C_1$ , and  $C_2$ , respectively, and thus allow comparison of the effect of different crystal structures and arrangements.

As an illustration of the parameters utilized from molecular and crystalline data, consider the quantities listed in Table 1 for the first (diamagnetic) member of the  $\gamma$ -Series,  $\text{La}_2\text{S}_3$ , which has no excess (or internal) heat-capacity contributions; the measured heat capacity is entirely 'vibrational' or 'lattice' [2]. The pa-

**Table 1** Input parameters for  $\text{La}_2\text{S}_3$

Parameter	Value chosen	Explanation
$M_h$	138.905	Mass of heavier atom (La)
$M_l$	32.066	Mass of lighter atom (S)
$Z$	5.33333 <sup>a</sup>	Number of formula units per primitive cell
$AN$	3	Number of anions per formula unit
$CN$	2	Number of cations per formula unit
$M_{\text{avg}}$	74.802	Arithmetic mean of masses of atoms in formula unit
$BL$	0.821977 <sup>b,c</sup>	Minimum size of first Brillouin zone/equivalent diameter (default value used)
$BH$	1.16245 <sup>b,c</sup>	Minimum size of first Brillouin zone/equivalent diameter ( <i>cf.</i> Ref. [8]) (default value used)
$RTL$	1.61	$v_L/v_T$ ; estimated default value used
$RH$	0.7338	$(M_{\text{avg}}/M_h)^{1/2}$
$RA$	1.527	$(M_{\text{avg}}/M_l)^{1/2}$
$RL$	1.308	Adjusting parameter
$ZN$	26.66666 <sup>a</sup>	Number of atoms in a primitive cell
$RV$	2.9073 <sup>b</sup>	$V^{1/3}$ of primitive cell/minimum interatomic distance
$NH$	2	Number of heavy atoms per formula unit
$N$	5	Number of atoms in a formula unit

<sup>a</sup>The parameter  $Z$  is fractional because the La atom is missing in every ninth position. The primitive cell in  $\text{La}_3\text{S}_4$  has  $Z=4$ , so that there are 12 La and 16 S per primitive cell. In  $\gamma\text{-La}_2\text{S}_3$ , however, there are  $8/9 \times 12$  or  $10 \ 2/3$  La atoms per primitive cell. Thus  $Z=(10 \ 2/3)/2=(5 \ 1/3)$  [4].

<sup>b</sup>The lattice parameter ( $V^{1/3}$ , where  $V$  is the volume of the primitive cell) has a value of 8.7220 Å [5]. The minimum interatomic distance is estimated to be 3.00 Å based on a  $\text{La}^{3+}$  crystalline ionic radius of 1.30 Å [6, 7] and the 1.700 Å sulfide ( $\text{S}^{2-}$ ) ionic radius [6]. Thus  $RV=8.7220/3.00=2.9073$ . The parameters  $BL$  and  $BH$  were calculated on the assumption of a cubic lattice for  $\gamma\text{-La}_2\text{S}_3$  with cell direct dimension equal to the lattice parameter, that is,  $a=b=c=8.7220$  Å.

<sup>c</sup>The original Komada-Westrum theory provided a default for parameters  $BL$  and  $BH$  to reduce the sensitivity of the theory to crystal structure—the values used are default parameters recommended in the Komada thesis (*cf.* for example, page 319, Ref. [1]). These values are adequate for the present evaluation, but for more demanding purposes actual Brillouin zone data can be introduced. For  $\gamma$ -phase lanthanum sesquisulfides, the  $BL$  and  $BH$  values had been employed by Alan Demlow and gave excellent fits and were then used throughout.

parameters in Table 1 are defined such that phonon modes are collectively approximated rather than individually determined as in the Born von Kármán model [1].

## The evaluation process

The difference between  $C_p$  and  $C_v$ , according to Lord, Ahlberg, and Andrews [9], may be approximated as:  $C_p - C_v = kC_v^2 T$  (provided the anharmonicity is small), where  $k$  is a constant characteristic of the substance. Thus, assuming that the experimental heat capacity is completely described only by lattice and anharmonic effects, one may fit experimental  $C_p$  data by the equation:

$$C_p(T, \theta_{KW}) = C_v(T, \theta_{KW}) + kC_v(T, \theta_{KW})^2 T$$

For substances (such as members of the  $\text{Ln}_2\text{S}_3$  series) which include electronic (usually Schottky) and/or magnetic contributions, these internal excess contributions must first be removed from the measured heat capacity and the remaining (lattice) heat capacity converted to  $C_v$ .

Insight into the provision of input LEM parameters may be seen in Table 2 which includes definition, symbolism, and constancy throughout the series as well as those which are cation dependent, and finally,  $\theta_{KW}$ , the temperature dependency of which provides a test of the success of the Komada-Westrum approach. The evaluation of the best value of  $\theta_{KW}$  can be conveniently achieved by the use of the Microsoft Excel 'Solver' matrix which permits multivariable fitting so that optimum values of  $\theta_{KW}$  could be selected by iteration and reiteration over the entire temperature range of measurement with selective weighting. Further discussion and explanation of this approach is provided in a NAPS document [10]. The experimental data used in this paper were determined in our laboratory [3, 11–14].

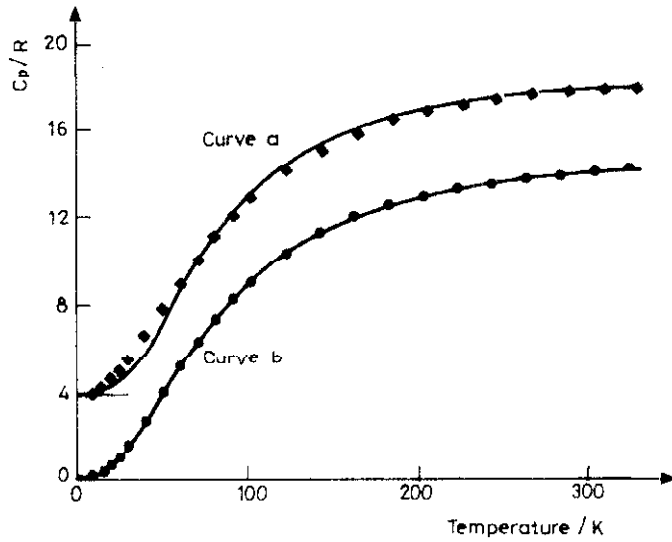
An instructive comparison for  $\text{La}_2\text{S}_3$  (and hence for any  $\text{Ln}_2\text{S}_3$ ) is shown in curves a and b in Fig. 1 which compare the lattice  $C_p$  calculated from experimental data  $C_p$  with the fits obtained from  $\theta_{\text{Debye}}$  and the  $\theta_{KW}$  [1]. In each case the  $C_v$ -data calculated from measured  $C_p$ -data using the equation of Lord, Ahlberg and Andrews [9] was used for the fitting process. The efficacy of the  $\theta_{KW}$  representation clearly shows the superiority of the Komada-Westrum model compared to the Debye model.

The 4d compound  $\text{Y}_2\text{S}_3$ , although not a lanthanide, has the same structure as the three  $\delta$ -phase sesquisulfides. Its crystallographic cell structure is of comparable size to the lanthanide sesquisulfides but the cation/anion mass ratio is only about 50% as great. Although we can fit its lattice heat capacity very well, we do not yet have a firm basis for extrapolating the magnitude of its  $\theta_{KW}$  from that of the  $\delta$ -lanthanide sesquisulfides.

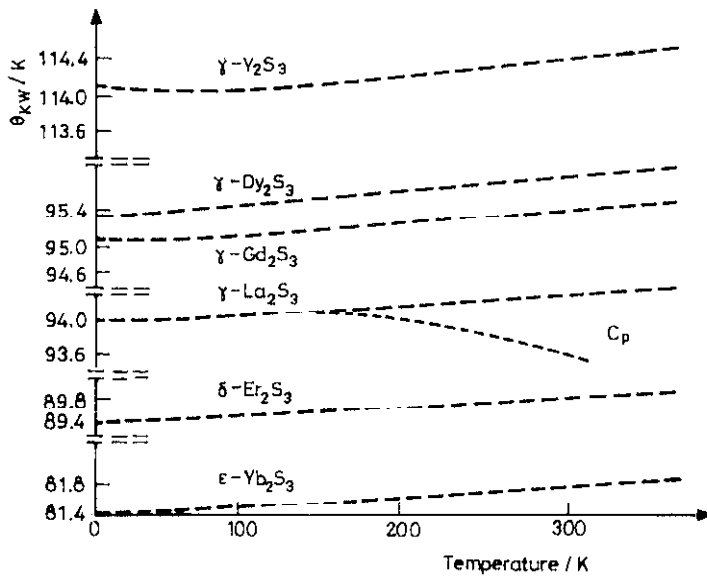
Table 2 Physical parameters for LEM program fitting

Name	Constans for all $\gamma$ -Ln <sub>2</sub> S <sub>3</sub> <sup>a</sup>							Determined by fitting						
	AN	CN	Z	BL	BH	NH	K	RTL	RL	RV	RA	RH	$\theta_{KW}/K$	Cpd.
Value	3	2	5 1/3	0.822	1.162	2	$7.80 \times 10^{-6}$	1.61	1.308	2.907	1.527	0.733	94.00	La <sub>2</sub> S <sub>3</sub> <sup>b</sup>
Explanations	Number of anions per formula unit	Number of cations per formula unit	Number of formula units per primitive cell	Min. size of first Brillouin zone/zone-equivalent diameter	Max. size of first Brillouin zone/zone-equivalent diameter	Number of heavy atoms per formula unit	Anharmon. Ccr. Consts., $C_p - C_v = kTC_v$	$V/V_r$	Adjusting parameter	$(M_{av}/M_r)^{1/2}$	$(M_{av}/M_c)^{1/2}$	$V^{1/3}/d_{min}$		
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	2.898	1.532	0.733	94.15	Ce <sub>2</sub> S <sub>3</sub>
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	2.891	1.535	0.732	94.35	Pr <sub>2</sub> S <sub>3</sub>
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	2.891	1.549	0.730	94.52	Nd <sub>2</sub> S <sub>3</sub>
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	-	-	-	94.60	Pm <sub>2</sub> S <sub>3</sub> <sup>c</sup>
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	2.894	1.574	0.727	94.75	Sm <sub>2</sub> S <sub>3</sub>
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	-	-	-	94.90	Eu <sub>2</sub> S <sub>3</sub> <sup>d</sup>
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	2.896	1.600	0.723	95.05	Gd <sub>2</sub> S <sub>3</sub> <sup>c</sup>
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	2.894	1.607	0.722	95.20	Tb <sub>2</sub> S <sub>3</sub>
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	2.895	1.621	0.720	95.30	Dy <sub>2</sub> S <sub>3</sub>
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	3.279	1.307	0.785	114.0	Y <sub>2</sub> S <sub>3</sub> <sup>h</sup>
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	3.271	1.630	0.719	89.2	Ho <sub>2</sub> S <sub>3</sub>
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	3.271	1.639	0.718	89.4	Er <sub>2</sub> S <sub>3</sub>
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	3.269	1.645	0.717	89.7	Tm <sub>2</sub> S <sub>3</sub>
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	3.578	1.661	0.715	81.5	Yb <sub>2</sub> S <sub>3</sub>
Value	3	2	5	0.822	1.162	2	$4.0 \times 10^{-6}$	1.741	0.250	3.378	1.668	0.714	81.9	Lu <sub>2</sub> S <sub>3</sub> <sup>i</sup>

<sup>a</sup>  $\gamma$ -phase (b.c.c.) cation symmetry= $S_1$ ; <sup>b</sup> no excess  $C_p$ ; <sup>c</sup> cation unstable, no  $C_p$  measurements; <sup>d</sup> compound relatively unstable to EuS<sub>2</sub>; <sup>e</sup> only magnetic excess  $C_p$ ; <sup>f</sup>  $\delta$ -phase (hexagonal) cation symmetry= $C_1$ ; <sup>g</sup>  $\epsilon$ -phase (monoclinic) cation symmetry= $C_2$ ; <sup>h</sup> isostructural 4d transition element compound, relative mass of cation (Y/Lu)  $\approx$  51%; <sup>i</sup> no excess  $C_p$



**Fig. 1** Curve a: Comparison of  $C_v/R$  of  $\text{La}_2\text{S}_3$  from measured  $C_p$  ( $\blacklozenge, \blacklozenge$ ) curve with  $C_v/R$  calculated from Debye characteristic temperature value,  $\theta_D$ , (---); Curve b from measured curve ( $\bullet, \bullet$ ) with  $C_v/R$  calculated from Komada-Westrum characteristic temperatures (cf. Table 2),  $C_p$  (—). Curve a is displaced upwards by  $4 C_p/R$  units



**Fig. 2**  $\theta_{KW}/K$  vs.  $T/K$  for some  $\gamma\text{-Ln}_2\text{S}_3$  compounds. The deviant short dash line on a  $\gamma\text{-Ln}_2\text{S}_3$  shows the trend of  $\theta_{KW}$  based on  $C_p$  values

The samples of the linearity and near constancy of  $\theta_{KW}$ 's vs. temperature up to 350 K in Fig. 2 and near linearity within the stability regions of the three phases in Fig. 3 are also strong vindications of success of the modeling process.

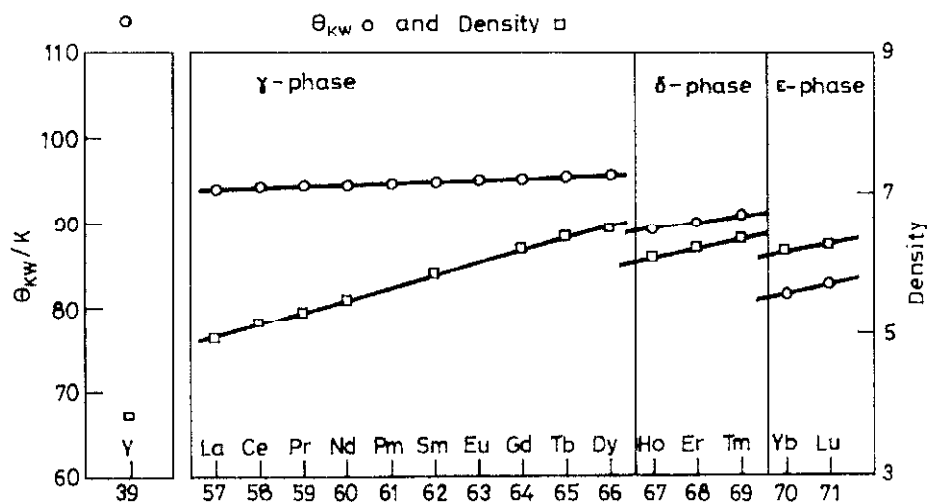


Fig. 3  $\theta_{KW}$  vs. cationic atomic number for  $\gamma$ -,  $\delta$ - and  $\epsilon$ -phase  $Ln_2S_3$  and  $Y_2S_3$ ,  $-o-$ . (The density of the phases  $-\square-$  are also shown with the trends in both variables.)

Moreover, the near linearity of the fitted  $\theta_{KW}$ 's with atomic number suggests the validity of the interpolation for values for the (nuclearly unstable) compound  $Pm_2S_3$  and for  $Eu_2S_3$  (which is so chemically unstable with respect to  $EuS_2$  that we were unable to produce a pure sesquisulfide). For these two unmeasured sesquisulfides, the best estimates of the  $C_{v,lat}$  of  $Pm_2S_3$  and  $Eu_2S_3$  are  $\theta_{KW}=94.60$  K and  $94.90$  K, respectively.

\* \* \*

We thank the University of Michigan program, Communities in Chemical Research, for financial support during 1995–96. Finally, the authors gratefully acknowledge the persistence and endeavors beyond the call of duty of an anonymous referee in enhancing the quality and clarity of presentation of this endeavor.

## References

- 1 N. Komada and E. F. Westrum, Jr., *J. Chem. Thermodyn.*, 29 (1997) 311.
- 2 N. Komada, E. F. Westrum, Jr., B. S. Hemingway and L. M. Anovitz, *J. Chem. Thermodyn.*, 27 (1995) 1097.
- 3 A. R. Demlow, Honors Thesis, Spring Arbor College, Spring Arbor, MI 49283, 1996, pp. 31.
- 4 E. F. Westrum, Jr., R. Burriel, J. B. Gruber, P. E. Palmer, B. J. Beaudry and W. A. Plautz, I., *J. Chem. Phys.*, 91 (1989) 4838.

- 5 A. Sleight and C. Prewitt, *Inorg. Chem.*, 7 (1968) 2282.
- 6 W. Porterfield, *Inorganic Chemistry: A Unified Approach*, 2nd Ed., Academic Press, San Diego 1993, pp. 84.
- 7 R. D. Shanon, *Acta Cryst.*, A32 (1976) 751.
- 8 W. Cochran, *The Dynamics of Atoms in Solids*, Edward Arnold Publishers Limited, London 1973.
- 9 R. Lord, J. Ahlberg and D. Andrews, *J. Chem. Phys.*, 5 (1937) 649.
- 10 See NAPS document No. 07696 for 42 pages, 7 tables, and 18 figures of supplementary material. This is not a multi-article document. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163-3513. Remit in advance \$9 for either microfiche copy or photocopy. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling, for the first 20 pages, and \$1.20 for additional 10 pages of material; \$1.75 for postage of microfiche orders.
- 11 J. B. Gruber, R. Burriel, E. F. Westrum, Jr., W. Plautz, G. Metz, X-X. Ma, B. J. Beaudry and P. E. Palmer, II., *J. Chem. Phys.*, 95 (1991) 1964.
- 12 R. Shaviv, E. F. Westrum, Jr., J. B. Gruber, B. J. Beaudry and P. E. Palmer, III, *J. Chem. Phys.*, 96 (1992) 6149.
- 13 J. B. Gruber, R. Shaviv, E. F. Westrum, Jr., R. Burriel, B. J. Beaudry and P. E. Palmer, IV., *J. Chem. Phys.*, 98 (1993) 1458.
- 14 R. Burriel and E. F. Westrum, Jr., V., *J. Chem. Phys.*, (to be submitted, 1998).