ADVANTAGES TO CONVERSION OF LATTICE HEAT CAPACITY TO C_V IN THE RESOLUTION OF EXCESS PROPERTIES[*]
The Ln2S3's as an example

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Abstract

This paper represents a fitting (modeling) of the temperature dependence of the Komada-Westrum characteristic temperature for those γ-, δ- and ε-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 (θ_{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, Ln_2S_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

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[*] 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 δ-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, θ_{KW}, must be specified. This fitting parameter – relatable to the Debye characteristic temperature, θ_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(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(tot) as a function of temperature at higher temperatures, anharmonicity effects cause a gradual decrease in the apparent θ_{KW} at higher temperatures. This is a major concern since the constancy of the θ_{KW} has been emphasized as the criterion of goodness of fit of the model. The calculation of θ_{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 γ-Ln_2S_3's resolving heat capacities with the LEM equations were demonstrated in Ref. [3].

The lanthanide sesquisulfides (Ln_2S_3)

As a systematic, more extensive test of the modeling we have selected the polymorphic lanthanide sesquisulfides, Ln_2S_3, which occur in three phases γ(cu-

bic), δ(Al_2O_3-type, hexagonal), and ε (Ho_2S_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 γ-Series, La_2S_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 La_2S_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[a]	Number of formula units per primitive cell
AN	3	Number of anions per formula unit
CN	2	Number of cations per formula unit
M_{avg}	74.802	Arithmetic mean of masses of atoms in formula unit
BL	0.821977[b,c]	Minimum size of first Brillouin zone/equivalent diameter (default value used)
BH	1.16245[b,c]	Minimum size of first Brillouin zone/equivalent diameter (cf. Ref. [8]) (default value used)
RTL	1.61	v_L/v_T; estimated default value used
RH	0.7338	$(M_{avg}/M_h)^{1/2}$
RA	1.527	$(M_{avg}/M_l)^{1/2}$
RL	1.308	Adjusting parameter
ZN	26.66666[a]	Number of atoms in a primitive cell
RV	2.9073[b]	$V^{1/3}$ of primitive cell/minimum interatomic distance
NH	2	Number of heavy atoms per formula unit
N	5	Number of atoms in a formula unit

[a] The parameter Z is fractional because the La atom is missing in every ninth position. The primitive cell in La_3S_4 has Z=4, so that there are 12 La and 16 S per primitive cell. In γ-La_2S_3, however, there are 8/9×12 or 10 2/3 La atoms per primitive cell. Thus Z=(10 2/3)/2=(5 1/3) [4].

[b] 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 La^{3+} crystalline ionic radius of 1.30 Å [6, 7] and the 1.700 Å sulfide (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 γ-La_2S_3 with cell direct dimension equal to the lattice parameter, that is, a=b=c=8.7220 Å.

[c] The original Komada-Westrum theory provided a default for parameters BL and BH to reduce the sensitivity of the theory to crystal stucture — 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 γ-phase lanthanum sesquisulfides, the BL and BH values had been employed by Alan Demlow and gave excellent fits and were then used throughout.

rameters 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: $C_p-C_v=kC_v^2T$ (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 effedts, one may fit experimental C_p data by the equation:

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

For substances (such as members of the Ln_2S_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, θ_{KW}, the temperature dependency of which provides a test of the success of the Komada-Westrum approach. The evaluation of the best value of θ_{KW} can be conveniently achieved by the use of the Microsoft Excel 'Solver' matrix which permits multivariable fitting so that optimum values of θ_{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 La_2S_3 (and hence for any Ln_2S_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 θ_{Debye} and the θ_{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 θ_{KW} representation clearly shows the superiority of the Komada-Westrum model compared to the Debye model.

The 4d compound Y_2S_3, although not a lanthanide, has the same structure as the three δ-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 θ_{KW} from that of the δ-lanthanide sesquisulfides.

Table 2 Physical parameters for LEM program fitting

Constans for all γ-Ln$_2$S$_3$[a]			Determined by fitting				
Name	Explanations	Value	RV	RA	RH	θ$_{KW}$/K	Cpd.
			$(M_{avg}/M_H)^{1/2}$	$(M_{avg}/M_L)^{1/2}$	$V^{1/3}/d_{min}$		
			For γ-phase Ln$_2$S$_3$				
AN	Number of anions per formula unit	3	2.907	1.527	0.733	94.00	La$_2$S$_3$[b]
CN	Number of cations per formula unit	2	2.898	1.532	0.733	94.15	Ce$_2$S$_3$
Z	Number of formula units per primitive cell	5 1/3	2.891	1.535	0.732	94.35	Pr$_2$S$_3$
BL	Min. size of first Brillouin zone/equivalent diameter	0.822	2.891	1.549	0.730	94.52	Nd$_2$S$_3$
BH	Max. size of first Brillouin zone/equivalent diameter	1.162	–	–	–	94.60	Pm$_2$S$_3$[c]
NH	Number of heavy atoms per formula unit	2	2.894	1.574	0.727	94.75	Sm$_2$S$_3$
K	Anharmon. Corr. Consts., $C_P-C_V=kTC_V$	7.80×10^{-6}	–	–	–	94.90	Eu$_2$S$_3$[d]
RTL	V_l/V_T	1.61	2.896	1.600	0.723	95.05	Gd$_2$S$_3$[e]
RL	Adjusting parmeter	1.308	2.894	1.607	0.722	95.20	Tb$_2$S$_3$
			2.895	1.621	0.720	95.30	Dy$_2$S$_3$
			For δ-phase Ln$_2$S$_3$[f]				
		3	3.279	1.307	0.785	114.0	Y$_2$S$_3$[h]
		2	3.271	1.630	0.719	89.2	Ho$_2$S$_3$
		5	3.271	1.639	0.718	89.4	Er$_2$S$_3$
		0.822	3.269	1.645	0.717	89.7	Tm$_2$S$_3$
		1.162					
		2					
		4.0×10^{-6}					
		1.741					
		0.250					
			For ε-phase Ln$_2$S$_3$[g]				
		3	3.378	1.661	0.715	81.5	Yb$_2$S$_3$
		2	3.378	1.668	0.714	81.9	Lu$_2$S$_3$[i]
		6					
		0.822					
		1.162					
		2					
		4.1×10^{-6}					
		1.741					
		0.714					

[a] γ-phase (b.c.c.) cation symmetry=S$_1$; [b] no excess C_p; [c] cation unstable, no C_p measurements; [d] compound relatively unstable to EuS$_2$; [e] only magnetic excess C_p; [f] δ-phase (hexagonal) cation symmetry=C$_1$; [g] ε-phase (monoclinic) cation symmetry=C$_2$; [h] isostructural 4d transition element compound, relative mass of cation (Y/Lu)≈51%; [i] no excess C_p
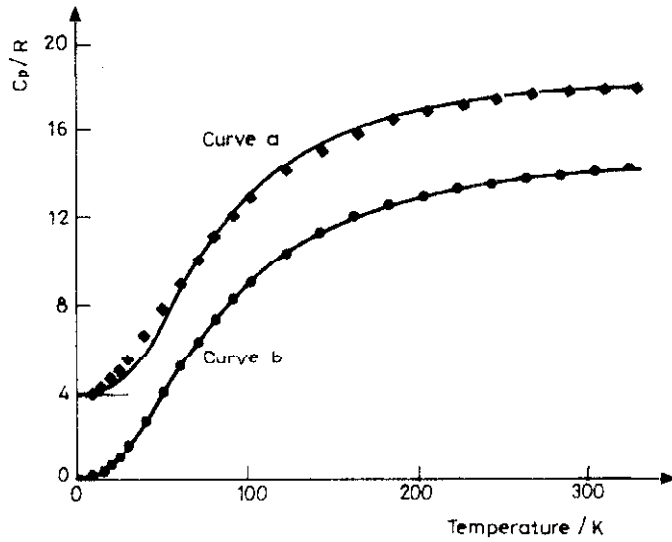
Fig. 1 Curve a: Comparison of C_V/R of La_2S_3 from measured C_p (♦,♦)curve with C_V/R calculated from Debye characteristic temperature value, θ_D, (—); Curve b from measured curve (●, ●) with C_V/R calculated from Komada-Westrum characteristic temperatures (cf. Table 2), C_p (—). Curve a is displaced upwards by 4 C_p/R units
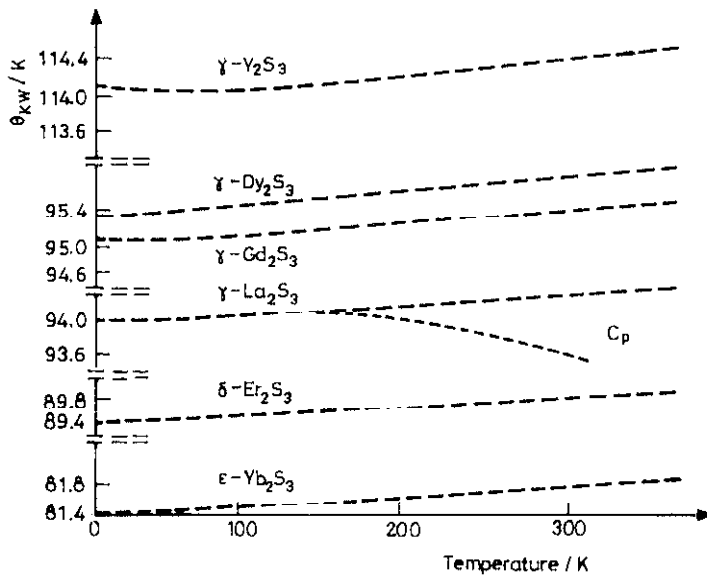

Fig. 2 θ_{KW}/K vs. T/K for some γ-Ln_2S_3 compounds. The deviant short dash line on a γ-Ln_2S_3 shows the trend of θ_{KW} based on C_p values

The samples of the linearity and near constancy of θ_{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.
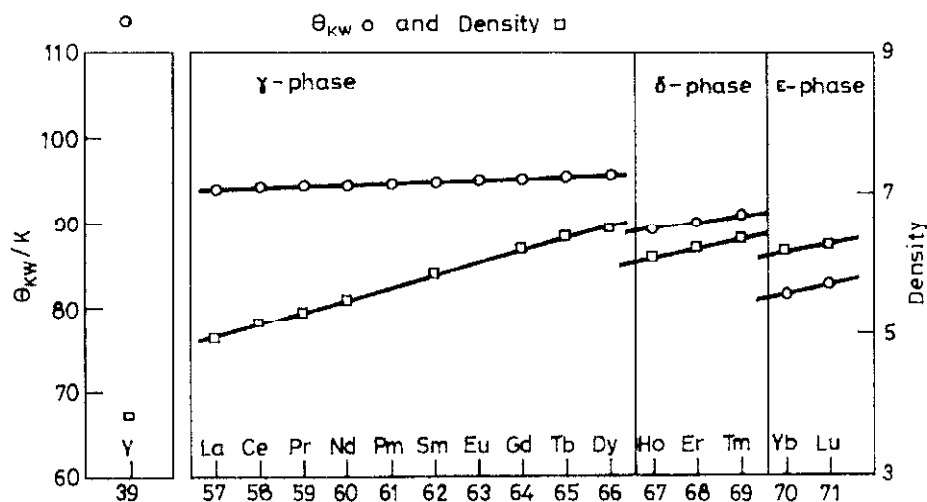

Fig. 3 θ_{KW} *vs.* cationic atomic number for γ-, δ- and ε-phase Ln_2S_3 and Y_2S_3, –o–. (The density of the phases –□ –are also shown with the trends in both variables.)

Moreover, the near linearity of the fitted θ_{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 θ_{KW}=94.60 K and 94.90 K, respectively.

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