

A Method of Nano-Size Intermetallic Compounds and Heusler Phases Entropy Estimation

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Abstract

A new approach to predict the standard entropy of crystal intermetallic compounds and Heusler phases with fairly good accuracy was developed. In the conjunction with Jiang and Yang's equation which links the entropy of nano-sized materials with crystal ones, this approach allows to make estimations for nano-intermetallic materials and nano-Heusler phases. The approach is based on the Grimvall and coworkers' idea that the difference in the atomic masses accounts for almost all differences in the entropy among chemically similar compounds. This idea was implemented through the correlation equations between natural logarithm of the entropy of binary intermetallic compounds and the reduced mass of a pair of interacting atoms in the compound. The regularities that link together fitting constants of the correlation equations for different groups of similar compounds have been revealed. Based on the obtained correlations, simple and well-defined predictive schemes were developed. The constituent additivity method as an expression of the additivity principle for entropy has been successfully applied for the standard entropy prediction of complex (M_mX_n , $n \geq 2$) intermetallic compounds and Heusler phases. The mean deviations of the standard entropy estimations from experimental and/or tabulated data with the use of the obtained correlations are in the range of ± 1 -5%. In the conjunction with the Debye theory of heat capacity, the proposed schemes provide the assessment of the temperature dependences of intermetallic compounds and Heusler phases entropy.

Keywords: Nano-particles, Entropy, Correlation equations, Intermetallic compounds, Heusler phases

Introduction

Intermetallic compounds and Heusler phases are of heightened interest due to their current and potential applications, such as hydrogen storage materials [1], battery electrodes [2], electrocatalysts [3], thermoelectric materials [4], semi- and superconductors [4], ferromagnetic and spintronic materials [4].

Thermodynamic calculations are a powerful tool for prediction of the phase stability and chemical behavior of compounds in different environments, and their thermal stability during thermal

processing. The fundamental thermodynamic relationship for macroscopic systems at equilibrium is [5]

$$dU = TdS - PdV + \mu dN \quad (1)$$

where U , T , S , P , V , μ and N denote the internal energy, the absolute temperature, the entropy, the pressure, the volume, the chemical potential and the number of components, respectively. The link between nano- and classical thermodynamics is made by introducing the additional term in Eq. (1) [5]

$$dU = TdS - PdV + \mu dN + \gamma dA \quad (2)$$

where γ and A are the interfacial energy and the interfacial surface, respectively. The different approaches for the extension of the classical thermodynamics to nano-meter scale have been proposed [6-8]. Thus, Avramov and Michailov [6], in the framework of the Lindemann model of melting, extended the Einstein model for heat capacity of solids to nano-crystals. Zhang and Banfield [7] elaborated a model to predict the dependence of excess heat capacity of solid nano-particles (with respect to macroscopic size crystals). Jiang and Yang [8] developed an extension of the classical thermodynamics to nano-meter scale on the basis of the Lindemann's criterion for solid melting, Mott's expression for vibrational melting entropy and Shi's model for size-dependent melting temperature. In particular, according to his theory, the molar entropy of nano-sized material, $S_m(r)$, can be determined using the following expression:

$$\frac{S_m(r)}{S_m(\infty)} = 1 - 1/\left[\frac{r}{r_0} - 1\right] \quad (3)$$

where $S_m(\infty)$ denotes the vibrational entropy at melting point of a bulk crystal of a compound, r is the size of a nano-particle and r_0 is the parameter of the theory. As can be seen from Eq. (3), to calculate the molar entropy of a nano-intermetallic compound, the entropy of a bulk compound should be also known. Existing thermodynamic database resources [9-13] provide a rather limited set of the data on standard entropy of crystal intermetallic compounds and these data can be often uncertain. The experimental determination of the entropy of materials is difficult and time demanding. Entropies of solids are calculated as integrals of the measured heat capacities over the temperature

range from 10-15K to ambient temperature. In spite of recent progress in the first-principles of the entropy calculations [14-17], as it was noted in a review [17], they, in many cases, have not reached the level of the successful use in thermodynamic calculations. Correlation methods providing the estimation of the missing entropy values with a reasonable accuracy can fill this gap. A variety of techniques are presently available for the estimation of standard entropy [18-23]. Atomic masses, molar masses, atomic numbers of elements and molar volumes are used as the most accessible physical quantities. One of them, which is still largely used, has been developed by Latimer [24]. He postulated that molar entropy, S_m , of $A_m B_n$ compound is the sum of contributions from each atom:

$$S_m = \frac{3R}{2} (m \ln M_A + n \ln M_B) + R(m + n) s' \quad (4)$$

where R , M_A and M_B , denote the universal gas constant, molar masses of A and B atoms, respectively, and the constant s' was determined empirically by Latimer using the standard entropy of solid KCl. Guosheng *et al.* [25] proposed to estimate standard entropy of intermetallic compounds as the sum of two contributions:

$$S_m = \sum S_{i,j}^{core} + S_{i,j} \quad (5)$$

where $\sum S_{i,j}^{core}$ is the sum of i - and j -core contributions into the entropy and $S_{i,j}$ is the contribution due to the interaction between i and j - atoms. The latter has a character of a correction. The core contribution (a major contribution) into entropy is supposed to be related to the mass of atoms and their electronic structures. The member $S_{i,j}$ is determined as the function of the mean value of principal quantum numbers of the alloying atoms and the difference in their electronegativity. The Debye theory [26,27] presents the entropy as a function of temperature (T/θ_D). There θ_D is the Debye temperature defined as follows:

$$\theta_D = h \nu_D / k_B \quad (6)$$

where h , ν_D and k_B are the Planck constant, the Debye cutoff vibrational frequency and the Boltzmann constant, respectively. At high temperatures ($T \geq 298$ K), where the isobaric heat capacity approaches $3R$, the entropy for monoatomic solids can be calculated [27] by the following equation:

$$S = 3R(\ln T - \ln \theta_D + 1.333) \quad (7)$$

The equation (7) shows that the principal factors affecting entropy are the temperature and Debye temperature. These factors hold also for solids composed of different atoms. The Debye temperature depends on the frequency of atomic vibration and "therefore is proportional to the square root of an interatomic force constant and inversely proportional to the square root of the atomic mass" [27]. According to the simple model of "diatomic approximation" [28], the frequency of atomic vibrations for a solid compound composed of i and j atoms can be estimated by the following equation for harmonic oscillator:

$$\nu = \frac{1}{2\pi} \sqrt{k_s / \mu} \quad (8)$$

In the equation (8), k_s is the force constant for the pair of interacting atoms i and j , and μ is the reduced mass. The reduced mass is calculated by:

$$\mu = \frac{m_i m_j}{m_i + m_j} \quad (9)$$

where m_i and m_j are the atomic masses of i and j atoms. For monoatomic solids, the reduced mass simplifies to the half of the atomic mass ($m_i = m_j$). Grimvall and Rosen [29] showed that the difference in mass is the main reason of distinctions in high temperature entropy for the similar group of chemical compounds. This means that the effect of atomic masses can be separated from the dependence of entropy on interatomic forces. In view of the above mentioned, it is reasonable to suppose the existence of the correlations between the entropy and reduced masses of i - j bonds in binary intermetallic compounds. Undoubtedly, if the missing values of crystal intermetallic compounds can be predicted with good accuracy, calculations (Eq.3) of the entropy of the similar nano-sized materials, with the known size could be performed.

The main purpose of this work is to develop the predictive schemes for the estimation of intermetallic compounds and Heusler phases entropy, based on correlations between the standard entropy and the reduced mass of a pair of interacting atoms i and j in crystal compounds. We have used earlier the reduced mass as a correlation parameter [30] based on the following:

- the Einstein and Debye theories of heat capacity provide a theoretical connection between heat capacity and entropy and give the entropy as a function of temperature;
- the Einstein theory relies on the assumption that a single vibration frequency characterizes all 3N oscillators;
- the frequency of atomic vibrations is proportional to the square root of the reduced mass.

Results and discussion

Binary intermetallic compounds forming homologous series

One should keep in mind that two factors, namely, the "mass effect" and the force constant restraining atomic motion found to be important [27,29], affect the entropy. It is not easy to obtain numerical values for the force constants of intermetallic compounds, rather one selects compounds for which the force constants vary smoothly [27,29]. For this reason, the examination of standard entropy data was firstly made for intermetallic compounds of the MX and M_2X stoichiometry (M is the metal forming a homologous series and X is another metal). We expected to obtain linear correlations by plotting $\ln S_{298}^0$ of the intermetallic compounds (here S_{298}^0 denotes standard molar entropy) versus reduced mass of M - X bond. In fact, the correlations presented for SnX in Figure 1 and for AlX and Al_2X in Figure 2 confirm this suggestion. The data from reference books [9-13] were used to perform the examination. It is seen that the points fit well on straight lines. The same relations were observed for Mg_2X , UX , antimonides (SbX) and silicides (SiX).

From these observations we propose the following equation for the entropy determination of the intermetallic compounds forming a homologous series:

$$\ln S_{298}^0 = c\mu + d \quad (10)$$

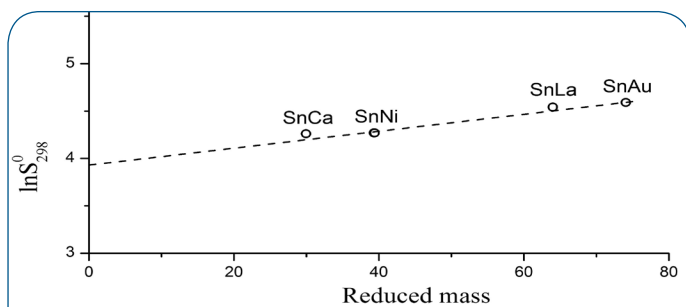


Figure 1: Dependence of the logarithm of standard entropy on the reduced mass of Sn-X bond for several tin intermetallic compounds

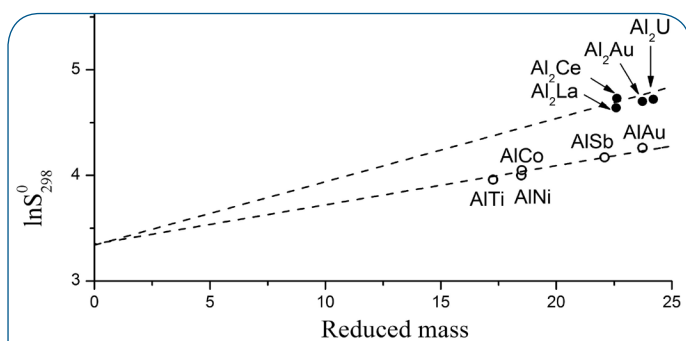


Figure 2: Dependence of the logarithm of standard entropy on the reduced mass of Al-M bond for several aluminum intermetallic compounds

where c (slope) and d (Y-intercept) are the specific constants for each homologous series. For several MX and M_2X groups of intermetallic compounds (including antimonides and silicides), the values of constants c and d were determined and are given in Table 1. We found that the values of constant d are close to $\ln S^0_{298}$ of the metal or p -metal forming the homologous series. It is clearly seen when comparing the values of $\ln S^0_{298}$ for Al (3.345), Mg (3.487), Sn (3.935), Si (2.934), Sb (3.818) and U (3.916) with the corresponding values of constant d (Table 1). Indeed, if these compounds are considered as the products of the metal atoms substitution by X in crystal lattices of “AlAl”, “MgMg”, “SnSn”, ... , the value of constant d has to match the logarithm entropy of pure metal or p -metal M when the reduced mass approaches zero. For homologous series of M_mX_n compounds formed by element M, Eq. (10) can be reformulated as follows:

$$\ln \frac{S^0_{298}(M_mX_n)}{S^0_{298}(M)} = c\mu \quad (11)$$

where $S^0_{298}(M_mX_n)$ and $S^0_{298}(M)$ are the standard entropy of solid M_mX_n and M, and m and n are the stoichiometric coefficients.

The accuracy of the estimations depends on the magnitude of similarity between the reference compound and the compound of interest. To illustrate it, let us consider the results of the standard entropy estimation for $NbCo_2$, $CaSn$ and $CaPb$ taking $NbCr_2$ and $CaZn$ as reference compounds. Thus, using $S^0_{298}(NbCr_2) = 83.6 \pm 0.6 \text{ JK}^{-1}\text{mol}^{-1}$ [12], $S^0_{298}(Nb) = 36.48 \text{ JK}^{-1}\text{mol}^{-1}$ [12] and $\mu(Nb-Cr) = 33.34$ we calculated (Eq. (11)) that $c = 2.49 \cdot 10^{-2}$. Then, substituting $\mu(Nb-Co) = 36.06$ and c into Eq. (11) gives $S^0_{298}(NbCo_2) = 89.5 \text{ JK}^{-1}\text{mol}^{-1}$. The reported value is $90.3 \text{ JK}^{-1}\text{mol}^{-1}$ [31]. The error is -0.9% , compared to the standard error in the determined $NbCr_2$ entropy of $\pm 0.7\%$. The similar calculations for $CaSn$ and $CaPb$ give $S^0_{298}(CaSn) = 73.3$ (tabulated value is $70.7 \text{ JK}^{-1}\text{mol}^{-1}$ [10]) and $S^0_{298}(CaPb) = 78.5 \text{ JK}^{-1}\text{mol}^{-1}$ (tabulated value is $80.7 \text{ JK}^{-1}\text{mol}^{-1}$ [10]). The errors are $+3.7\%$ and -2.7% , respectively. Since the magnitude of the similarity between $CaZn$ (Zn is d -metal) and $CaSn$ and $CaPb$ (Sn and Pb are p -metals) is lower than between $NbCo_2$ and $NbCr_2$, the errors are higher. To increase the reliability of the estimations, two or more reference compounds should be used.

Laves phases

Further, analyzing the relations between natural logarithm of the entropy and reduced mass for Laves phases in the graphical form, we have obtained that the points fit well on two series of correlation equations permitting validation of Eq. (10) for description of these relations. To draw the graphs we have used the tabulated entropy data [10-13] and data from original papers [31-36]. It was found that the value of constant d is specific for a group of similar intermetallic compounds while the value of constant c holds constant for each of two series of the parallel lines, of $5.85 \cdot 10^{-2}$ and $-1.71 \cdot 10^{-2}$, respectively (Table 2). Different values of constant d indicate that the invariance of the interatomic forces is fulfilled only within the group.

Considering the values of constant d for the linear correlations with a slope of $-1.71 \cdot 10^{-2}$, it was found that they obey the following sequence:

$$d = 4.66 + 0.25n \quad (n = 0, 1, 2, \dots, 9) \quad (12)$$

In turn, the values of constant d for correlations with the opposite slope ($c = 5.85 \cdot 10^{-2}$), forming the analogous sequence, are:

$$d = 3.84 - 0.28n \quad (n = 0, 1, 2, \dots, 6) \quad (13)$$

Although it is impossible to define a group to which a Laves phase of interest belongs *a priori*, the problem becomes solvable if we take into account that the entropy of the same compound was taken, as it can be seen from Table 2, as a point in the construction of the linear correlation equations with the opposite slopes.

Table 1: Values of c and d constants for homologous series of several intermetallic compounds

Homologous series	Fitting values of the constants	
	c	d
AlX intermetallics, X = Sb, Ti, Fe, Co, Ni, Au	$3.52 \cdot 10^{-2}$	3.34
UX intermetallics, X = Si, Ge, Pb, Bi	$6.45 \cdot 10^{-3}$	4.06
SnX intermetallics, X = Ca, Fe, Co, Ni, La, Au	$9.00 \cdot 10^{-3}$	3.93
SiX (silicides) X = Fe, Cr, Mn, Co, Ni, Zr, Th	$4.80 \cdot 10^{-2}$	2.93
SbX (antimonides), X = Ni, Co, Zn, Cd, Al, Ga, In	$1.22 \cdot 10^{-2}$	3.82
Al ₂ X intermetallics, X = Fe, La, Ce, Pr, Au, U	$5.70 \cdot 10^{-2}$	3.34
Mg ₂ X intermetallics, X = Si, Ge, Ni, Pb, Sn, Cu	$5.60 \cdot 10^{-2}$	3.49

Table 2: Values of c and d constants for different groups of Laves phases

Group	Constant		Average deviation, %
	c	d	
ThMg ₂ , NiTi ₂ , NbCr ₂ , CaMg ₂ , MgCu ₂ , ZrMo ₂ , ...	-1.71·10 ⁻²	4.90	±1.4
Mg ₂ Pb, Ca ₂ Sn, NbFe ₂ , NbCo ₂ , TaCr ₂ , YFe ₂ , PtSn ₂ , ...	-1.71·10 ⁻²	5.15	±2.6
Ca ₂ Pb, LaNi ₂ , TaFe ₂ , UFe ₂ , PuFe ₂ , ThRu ₂ , ...	-1.71·10 ⁻²	5.42	±2.2
Ba ₂ Sn, ThOs ₂ , PuPt ₂ , ...	-1.71·10 ⁻²	5.89	±5.2
AuSn ₂ , AuSb ₂ , PuRu ₂ , ...	-1.71·10 ⁻²	6.10	±4.5
ThRe ₂ , PuOs ₂ , ...	-1.71·10 ⁻²	6.55	±2.7
AuPb ₂ , UBi ₂ , ...	-1.71·10 ⁻²	6.92	±1.7
FeAl ₂ , ThMg ₂ , UAl ₂ , ...	5.85·10 ⁻²	3.28	±3.8
MnSn ₂ , Ca ₂ Sn, Ca ₂ Pb, TiCo ₂ , ...	5.85·10 ⁻²	2.76	±5.5
NbCr ₂ , NbFe ₂ , NbCo ₂ , ...	5.85·10 ⁻²	2.45	±6.6
TaCr ₂ , TaFe ₂ , ...	5.85·10 ⁻²	2.20	±5.1

Thus, the solution (described by Glibin *et al.* [30]) consists in the substitution of all values of d constant (Eqs. 12, 13) and c constant into Eq. (10) to calculate the possible values of the compound's entropy. Further, by comparing the obtained two series of values one can choose the closest ones and take the average, which represents the most reliable value. To increase the reliability, it is desirable to choose a couple which correlates well with the additive value (calculated as the sum of the constituent metals entropy). To illustrate, let us calculate the entropy of CoTi₂ ($\mu = 26.42$). The values of entropy closest to each other and to the additive value (95.3 JK⁻¹ mol⁻¹) are equal to 85.5 ($c = -1.71 \cdot 10^{-2}$; $d = 4.91$) and 94.2 JK⁻¹ mol⁻¹ ($c = 5.85 \cdot 10^{-2}$; $d = 3.0$), respectively. The mean value is 89.9 JK⁻¹ mol⁻¹, compared to the reported value of $S_{298}^0(\text{CoTi}_2) = 90.6 \text{ JK}^{-1} \text{ mol}^{-1}$ [32]. The error is -0.8%.

Complex intermetallic compounds (M_mX_n stoichiometry, n ≥ 2)

For the entropy determination of complex intermetallic compounds such as Co₂Al₅, Mo₂Fe₃, U₃Sn₅ and others we suggest that the rule of additivity can be applicable. In the literature an additivity rule is presented by two different techniques: the "zero entropy of formation" method [37] and the constituent additivity method [38,39]. The "zero entropy of formation" method assumes that the entropy of an intermetallic compound can be calculated as the sum of the constituent metals entropy. The constituent additivity method is based on the assumption that the forces acting between atoms in the complex intermetallic compound are approximately equal to those in intermetallic compounds having simple stoichiometry and composed of the same atoms. Table 3 shows some results of the methods application. As seen from Table 3, the constituent additivity method coupled with the proposed techniques for an estimation of missing values of the "constituents" entropy allows us to predict more correct values as compared with the widely used "zero entropy of formation" method. Its application noticeably reduces the average deviation from the experimental and/or tabulated data. The "zero entropy of formation" method yields the reasonable results in several cases only.

Heusler phases

Heusler phases are an interesting class of intermetallic compounds with general formulas XYZ (often called Half-Heusler) and

X₂YZ comprising more than 1500 members [4]. Half-Heusler compounds can be considered as compounds consisting of a covalent and an ionic parts. The X and Y atoms have a distinct covalent character, whereas more electronegative Z atoms can be considered as anions [4]. The X₂YZ Heusler compounds consist of X and Y atoms of transition metals and Z atoms which are the main group elements [4].

In this work, due to the lack of the information on standard entropy of Heusler phases, which are important for different applications, we have made the assessments of this thermodynamic quantity for a number of compounds applying the constituent additivity method (Table 4). To make a judgment on the reliability of the estimations, we have compared the obtained results with the calculations using Guillermet and Grimvall modification of the Debye model for entropy [40]. The Debye theory gives the entropy as a function of (T/θ_D), where T is the temperature and θ_D is the Debye temperature. The Debye temperature of a compound is usually determined from the elastic constants of a compound, but Guillermet and Grimvall [40] proposed to use so-called "entropy related Debye temperature", θ_D^s . It is defined as the θ_D value that reproduces the experimental entropy per mole of atoms when inserted in the Debye model expression for entropy, S_D :

$$S(T) = S_D \left[\frac{\theta_D^s}{T} \right] \quad (14)$$

Here, the θ_D^s temperatures of Heusler compounds are calculated from the "entropy related Debye temperatures" of their components by the following equation [41]:

$$\theta_D^s(\text{compound}) = \sqrt{\sum x_i (\theta_D^s)_i^2} \quad (15)$$

where x_i is the molar fraction of the i -th component in the formula unit of a compound. The θ_D^s values of the transition metals were taken from [42] and for elements of the p -block were calculated from the values of the standard entropy according to [42]. On the base of the θ_D^s values of Heusler phases, their standard entropies were determined using the tabulated Debye entropy function from [27, Table A2-4]. The obtained results are presented in Table 4. It should be noted, that the entropies of the binary intermetallics ("constituents") are the results of

Table 3: Assessment of the standard entropy of several intermetallic compounds

Compound	Scheme of the constituents entropy [9-13] summation	S_{298}^0 (JK ⁻¹ mol ⁻¹)			Deviation (%)	
		method (1) ^c	method (2) ^d	Ref. or reported data	method (1) ^c	method (2) ^d
Ni ₃ Sn ₄	3NiSn ^a + Sn	266.3	294.3	257.7 [10]	3.3	14.2
	NiSn ₂ ^b + 2NiSn	257.0	-	-	-0.3	-
Mo ₂ Fe ₃	MoFe ₂ ^b +Fe +Mo	150.9	139.2	146.4 [10]	3.1	-4.9
U ₃ Sn ₅	USn ₃ + 2USn ^b	394.9	406.5	397.9 [9]	-0.7	2.2
Ni ₂ Al ₃	NiAl ₂ ^b + NiAl	135.0	144.8	136.4 [10]	-1.0	6.2
U ₃ Bi ₄	UBi ₂ + 2UBi	346.0	377.6	342.7 [10]	1.0	10.2
Co ₂ Al ₅	2CoAl ₂ ^b + Al	190.4	201.8	193.7 [10]	-1.7	4.2
	CoAl ₂ +CoAl+2Al	192.1	-	-	-0.8	-
U ₅ Ge ₃	3UGe + 2U	371.6	344.3	374.9 [10]	-0.9	-8.2
	UGe ₃ + 4U	371.5	-	-	-0.9	-
NiSi ₂	NiSi ^b + Si	63.2	67.5	61.5 [43]	2.8	9.8
La ₃ Sn ₅	2LaSn ₂ ^b + LaSn	407.6	426.6	413.5 [44]	-1.4	3.2
AlNi ₃	AlNi + 2Ni	113.8	118.0	113.8 [10]	0	3.7
Co ₃ Nb	Co ₂ Nb + Nb	126.7	126.6	121.7 [9]	4.1	4.0
NiTi ₂	NiTi + Ti	85.7	95.1	83.7 [12]	2.4	13.6
Ni ₅ Si ₂	2NiSi ^b +3Ni	178.4	187.0	182.0 [43]	-2.0	2.7
Average deviation:					±1.7%	±6.7%

^aNiSn = 71.7 JK⁻¹mol⁻¹ [23]

^b present estimate using the above techniques

^c (1) denotes the constituent additivity method

^d (2) denotes the “zero entropy of formation” method.

Table 4: Results of the assessment of standard entropy for several Heusler compounds

Compound	Θ° , K	Scheme of the constituents entropy summation	S_{298}^0 (JK ⁻¹ mol ⁻¹)	
			Constituent additivity method	Debye model
CoVSb	324	VSb + Co	100.5	101.1
TiCoSb	311	TiSb + Co	99.2	98.6
MnNiSb	319	MnSb + Ni	102.1	96.9
MnPtSb	267	PtSb ^a + Mn	108.4	109.5
LuPtSb	189	PtSb ^a + Lu	127.4	134.6
MnAuSn	244	MnSn + Au	118.1	116.0
ZrNiSn	273	ZrSn + Ni	109.7	107.9
Fe ₂ VAl	397	FeAl + Fe +V	107.4	108.7
Co ₂ MnAl	366	CoAl + Co + Mn	116.4	116.1
Co ₂ MnSn	323	MnSn + 2Co	130.8	128.1
Co ₂ TiSi	427	TiSi + 2Co	104.0	102.1
Co ₂ FeSi	440	CoSi + Co +Fe	100.7	99.4
Co ₂ MnSi	428	CoSi +Co + Mn	105.4	101.9
Ru ₂ MnSi	436	RuSi + Ru + Mn	101.4	100.2
Ru ₂ MnSn	333	MnSn + 2Ru	127.8	124.9
Co ₂ HfAl	335	HfAl + 2Co	124.8	124.4

^a Latimer’s method [22]

the calculations by Eq. (10) using the values of constants *c* and *d* from Table 1. The agreement between the results of two methods is very good, and, consequently, this approach can be also applied to the determination of the entropy of more complex

intermetallic compounds. This observation opens also a route to the prediction of the temperature dependences of the entropy of intermetallic compounds and Heusler phases. It consists, provided that the standard entropy of a compound is known, in

the determination of “the entropy related Debye temperature”, θ_D , of this compound, and then in the calculation of the entropy at different temperatures using the tabulated Debye functions [27].

Conclusions

This work was performed based on the Grimvall and co-workers assumption that the influence of interatomic forces on the entropy in the groups of chemically similar compounds at high temperatures ($T \geq 298\text{K}$) can be separated from the “mass effect”.

The available reference data and the data from original works on the standard entropy of intermetallic compounds have been treated in an approach through the correlations between natural logarithm of the entropy and the reduced mass for the pair of interacting atoms in the compound. On the base of the obtained correlations, simple and well-defined predictive schemes were proposed. Regularities that connect the fitting constants in the groups of similar compounds have been revealed.

The validity of the additivity principle (in the form of the constituent additivity method) for predicting the entropy of complex ($M_m X_n$ stoichiometry, $n \geq 2$) intermetallic compounds and Heusler phases was shown. The application of this method in comparison with the widely used “zero entropy of formation method” noticeably reduces the average deviation from the experimental and/or tabulated data.

We propose also a route to the prediction of nano-sized intermetallic compounds and Heusler phases’ entropy which consists in the combination of Jiang and Yang’s equation for entropy of nano-particles and developed techniques in this work for the assessment of missing values of crystal phases’ entropy.

The mean deviations of the standard entropy estimations from experimental and/or tabulated data using new techniques are in the range of $\pm 1-5\%$ that is comparable with errors in experimental determinations of the entropy.

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References

1. Matar SF. Intermetallic hydrides: A review with *ab initio* aspects. *Progress Solid State Chem.* 2010; 38(1-4):1-37. doi:10.1016/j.progsolidstchem.2010.08.003.
2. Benedek B, Thackeray MM. Lithium reactions with intermetallic-compound electrodes. *J. Power Sources.* 2002; 110(2):1-37. doi:10.1016/S0378-7753(02)00204-5.
3. Jakšić MM. Brewer intermetallic phases as synergetic electrocatalysts for hydrogen evolution. *Mater. Chem. Phys.* 1989; 22(1-2):1-26. doi:10.1016/0254-0584(89)90029-1.
4. Graf T, Felser C, Parkin SSP. Simple rules for the understanding of Heusler compounds. *Progress Solid State Chem.* 2011; 39(1):1-50. doi:10.1016/j.progsolidstchem.2011.02.001.
5. Lucia U. A link between nano- and classical thermodynamics: Dissipation analysis (The entropy generation approach in nano-thermodynamics). *Entropy.* 2015; 17(3):1309-1328. doi:10.3390/e17031309.
6. Avramov I, Michailov M. Specific heat of nanocrystals. *J. Phys.: Condens. Matter.* 2008; 295224:1-4. doi:10.1088/0953-8984/20/29/295224.
7. Zhang H, Banfield JF. A model for exploring particle size and temperature dependence of excess heat capacities of nano-crystalline substances. *NanoStructured Materials.* 1998; 10(2):185-194. doi:10.1016/S0965-9773(98)00059-2.
8. Jiang Q, Yang CC. Size effect on the phase stability of nano-structures. *Current Nanoscience.* 2008; 4(2):179-200. doi:10.2174/157341308784340949.
9. Karapet’yants MK, Karapet’yants ML, *Thermodynamic Constants of Inorganic and Organic Compounds.*, London: Ann Arbor-Humphrey Science Publications; 1970.
10. Barin I (in collab. with Gregor Platzki). *Thermochemical Data of Pure Substances.* 3rd ed. Vol (1 and 2). VCH, Weinheim, New York, Basel, Cambridge, Tokyo; 1995.
11. Binnewies M, Milke E. *Thermochemical Data of Elements and Compounds.* 2nd ed. Wiley-VCH; 2002.
12. *Thermal Constants of Substances.* Glushko VP, Medvedev VA, Gurvich LV, Yungman VS, editors. 8 volumes; New York: Wiley; 1999. 6592 p.
13. Knake O, Kubaschewski O, Hesselmann K, editors. *Thermochemical Properties of Inorganic Substances.* 2nd ed. Berlin: Springer; 1971.
14. Li Zi-Kui. First-principles calculations and CALPHAD modeling of thermodynamics. *J. Phase Equilibria and Diffusion.* 2009; 30(5):517-534. doi: 10.1007/s11669-009-9570-6.
15. Hafner J. Atomic-scale computational materials science. *Acta mater.* 2000; 48(1):71-92. doi:10.1016/S1359-6454(99)00288-8.
16. Stoffel RP, Wessel C, Lumey MW, Dronkowski R. *Ab initio thermochemistry of solid-state materials.* *Angew Chem Int Ed.* 2010; 49(31):5242-5266. doi: 10.1002/anie.200906780.
17. Fultz B. *Vibrational thermodynamics of materials.* *Progress Mater. Sci.* 2010; 55(4):247-352. doi:10.1016/j.pmatsci.2009.05.002.
18. Glasser L, Jenkins HDB. Volume-based thermodynamics: A prescription for its application and usage in approximation and prediction of thermodynamic data. *J. Chem. Eng. Data.* 2011; 56(4):874-880. doi: 10.1021/je100683u.
19. Vassiliev VP, Legendre B, Zlomanov VP. The critical analysis and mutual coherence of the thermodynamic data of the $A^m B^v$ phases. *Intermetallics.* 2011;19(12):1891-1901. doi:10.1016/j.intermet.2011.07.023.
20. Treadwell WD, Mauderli B. Zur Kenntnis der Entropie Werte in homologen Reichen salzartiger fester Körper. *Helv. Chim. Acta.* 1944; 27:567-572 (in German).
21. Moiseev GK, Seštak J. Some calculation’s methods for estimation of thermodynamic and thermochemical properties of inorganic compounds. *Prog. Crystal Growth and Charact.* 1995; 30:23-81.
22. Spencer PJ. Estimation of thermodynamic data for metallurgical applications. *Thermochim. Acta.* 1998; 314(1-2):1-21. doi:10.1016/S0040-6031(97)00469-3.

23. Glibin VP, Vorobyova TN, Kuznetsov BV. New thermodynamic assessment of nickel-tin solid and liquid alloys. *Thermochim. Acta.* 2010; 507-508:35-44. doi:10.1016/j.tca.2010.04.026.
24. Latimer VM. Methods of estimating the entropy of solid compounds. *J. Amer. Chem. Soc.* 1951; 73(4):1480-1485. doi: 10.1021/ja01148a021.
25. Guosheng H, Hongjie L, Leshan W, Fhihong X. Estimation of entropies for intermetallic compounds and applications to phase diagram calculations. *Thermochim. Acta.* 1990; 173:47-52.
26. Girifalco LA. *Statistical Mechanics of Solids.* Oxford: Oxford University Press; 2000.
27. Pitzer KS. *Thermodynamics.* 3rd ed. New York: McGraw-Hill; 1995.
28. Weckhuysen BM, Wachs IE. Raman spectroscopy of supported chromium oxide catalyst. Determination of chromium-oxygen bond distances and bond orders. *J. Chem. Soc. Faraday Trans.* 1996; 92:1969-1973. doi: 10.1039/FT9969201969.
29. Grimvall G, Rosen J. Vibrational entropy of polyatomic solids: metal carbides, metal borides, and alkali halides. *Int. J. Thermophys.* 1983; 4(2):139-148. doi: 10.1007/BF00500137.
30. Glibin VP, Vorobyova TN, Kuznetsov BV. An empirical approach to the estimation of standard entropy of binary, ternary and higher component sulfides. In: *A Collection of Papers "Sviridov Readings"*. Ivashkevich O.A. et al, editors. 2015; 11:186-198. <http://elib.bsu.by/handle/123456789/125593>.
31. Zhu JH, Liu CT, Pike LM, Liaw PK. Enthalpies of formation of binary Laves phases. *Intermetallics.* 2002; 10(6):579-595. doi:10.1016/S0966-9795(02)00030-4.
32. Davidov AV, Kattner UR, Jossel D, Blendell JE, Waterstrat RM, Shapiro AJ, et al. Determination of the CoTi₂ congruent melting point and thermodynamic reassessment of the Co-Ti system. *Metall. Materials Trans. A.* 2001; 32A:2175-2186.
33. Grolier V, Schmid-Fetzer R. Thermodynamic analysis of the Pt-Sn system. *J. Alloys Compd.* 2008; 450(1-2):265-271. doi:10.1016/j.jallcom.2006.11.027.
34. Jacobs MHG, Spencer PJ. A critical thermodynamic evaluation of the system Mg-Ni. *CALPHAD.* 1998; 22(4):513-525. doi:10.1016/S0364-5916(99)00008-5.
35. Ghosh P, Mezbahul-Islam M, Medraj M. Critical assessment and thermodynamic modeling of Mg-Zn, Mg-Sn, Sn-Zn and Mg-Sn-Zn system. *CALPHAD.* 2012; 36:28-43. doi:10.1016/j.calphad.2011.10.007
36. Morishita M, Koyama K. Standard entropy of formation of SnMg₂ at 298 K. *J. Alloys Compd.* 2005; 398(1-2):12-15. doi:10.1016/j.jallcom.2005.02.016.
37. Guillermet AF. Bonding properties and vibrational entropy metal MeB₂(AlB₂) diborides. *J. Less-Common Metals.* 1991; 169:257-281.
38. Grimvall G, Oberschmidt D. Correlation and prediction of thermodynamic data for oxide and silicate minerals. *Int. J. Thermophys.* 1999; 20(1):353-361. doi: 10.1023/A:1021427608329.
39. Qiu L and White MA. The constituent additivity method to estimate heat capacities of complex inorganic solids. *J. Chem. Educ.* 2001; 78(8):1076-1079. doi: 10.1021/ed078p1076.
40. Guillermet AF, Grimvall G. Cohesive properties and vibrational entropy of 3d-transition metal carbides. *J. Phys. Chem. Solids.* 1992; 53(1):105-125. doi:10.1016/0022-3697-(92)90019-A.
41. Hu R, Nash P, Chen Q, Zhang L, Du Y. Heat capacities of several Al-Ni-Ti compounds. *Thermochim. Acta.* 2009; 486:57-65.
42. Guillermet AF, Grimvall G. Homology of interatomic forces and Debye temperatures in transition metals. *Phys Rev B Condens Matter.* 1989; 40(3):1521-1527.
43. Acker J, Bohmhammel K. Optimization of thermodynamic data of the Ni-Si system. *Thermochim. Acta.* 1999; 337(1-2):187-193.
44. Witusiewicz VT, Sidorko VR, Bulanova MV. Assessment of thermodynamic functions of formation for rare-earth silicides, germanides, stannides and plumbides. *J. Alloys Compd.* 1997; 248(1-2):233-245. doi:10.1016/S0925-8388-(96)02659-X.