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Non-monotonic systematic variation of the thermodynamic properties of lanthanide metals in liquid bismuth

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Abstract

In a system consisting of molten eutectic mixture of LiCl, KCl, and liquid bismuth, the excess enthalpy changes of Ce, Pr, Nd and Ho in liquid bismuth were evaluated in a temperature range from 850 K to 1100 K by electromotive force measurement. The newly determined values were compared with those previously determined for La, Gd, Tb, and Dy, and the systematic variation of these values along the lanthanide series was discussed. As a result, it was found that the excess enthalpy changes of lanthanides show non-monotonic variation as a function of 2/3 power of molar volumes, which does not agree with the linear trend of variation which is anticipated by the semi-empirical rule. Instead of the conventional definition of the excess enthalpy changes standardized to the metallic states, those standardized to the hypothetical metallic vapor states were adapted and their systematics were discussed.

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1. Introduction

The authors have studied the thermodynamic stabilities of lanthanide metals dissolved in liquid bismuth to improve the understanding of the thermodynamic basis for the pyrometallurgical liquid–liquid extraction of lanthanides between molten chloride and liquid metal. In our previous report [1], by electromotive force (EMF hereafter) measurement in a two-phase system consisting of molten eutectic mixture of LiCl and KCl and liquid Bi, the activity coefficients of La, Gd, Tb, and Dy in liquid Bi were determined. In that report, their excess enthalpy changes (ΔH^{ex}[M in B], where M and B denote lanthanide metal and liquid metal, respectively) in liquid Bi were determined. It was pointed out that ΔH^{ex}[M in B]'s of La, Gd, Tb, Dy, and Er approximately satisfy the Miedema's semi-empirical rule for mixing two liquid metals [2,3] whereas Ce, Pr, and Nd may deviate from this systematic relation. In the previous paper, the discussion about the singularity of Ce, Pr and Nd was based on the literature values [4]. However, this discussion should be extended using a thorough set of data obtained by ourselves so that now a comprehensive systematic assessment can be completed.

In this context, ΔH^{ex}[M in B] for Ce, Pr, Nd, and Ho were experimentally determined by the EMF measurement with the same experimental techniques and conditions adapted in the previous study [1]. In this present

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paper, by using these newly determined data, the systematic variation of ΔH^{ex}[M in B] along the lanthanide series is examined again.

2. Experimental

The experimental procedures adopted are the same as in our previous paper [1]. The EMF measurement technique was adapted to Ce, Pr, Nd, and Ho using the following galvanic cell consisting of eutectic melt of LiCl and KCl, where M(solid) and M(in B) represent pure lanthanide metals and M dissolved in liquid Bi, respectively.

M(solid) · molten LiCl–KCl · M(in B)

A rod (3 × 3 × 25 mm) of 99.9% pure lanthanide metals, one end of which was welded with a Ta wire, was used as a pure lanthanide electrode. The tested temperature ranges from 730 K to 1100 K, and the mole fraction of lanthanides in liquid Bi ($x_{\text{M(in B)}}$) ranged from about 10^{-2}–10^{-4}. After the achievement of the chemical equilibrium of the system, the EMF between pure lanthanide electrode and liquid Bi electrode was measured. The concentration of lanthanides in liquid Bi was determined by analyzing the samples of Bi phase by ICP-AES (ICPS-1000III, Shimadzu). All experiments were performed in a glove box filled with pure Ar, with oxygen and humidity content continuously kept less than about 1 ppm. All the reagents used are analytical grade of Wako Pure Chemicals. Anhydrous eutectic mixture of LiCl and KCl was purchased from APL. Co. Ltd., and used without any further treatment. The pure lanthanide metals of 99.9% purity were purchased from Rare Metallics Co. Ltd.

3. Thermodynamic base of this experiment

All the notations of the substances and thermodynamic expressions are the same as in our previous paper [1]. The EMF between M(solid) and M(in B) can be related to the excess chemical potential of M in B, $\mu^{\text{ex}}_{\text{M(in B)}}$, by Eq. (1), where $x_{\text{M(in B)}}$ is mole fraction of M in B. $\Delta\mu^{\text{fusion}}_{\text{M}}$ is the difference between the chemical potentials of solid and liquid of M at a given temperature, and is calculated by the functions for their solid and liquid phases [5]. Thus, $\mu^{\text{ex}}_{\text{M(in B)}}$ in Eq. (1) is recognized as the excess function associated with mixing liquid of M with liquid metal B. Since the temperature is lower than the melting points of lanthanide metals in this experiment, $\mu^{\text{ex}}_{\text{M(in B)}}$ is understood as the excess function associated with the mixing of hypothetical super-cooled lanthanide metals.

$$\Delta E = \frac{1}{nF}\Delta\mu^{\text{fusion}}_{\text{M}} - \frac{RT}{nF}\ln x_{\text{M(in B)}} - \frac{1}{nF}\mu^{\text{ex}}_{\text{M(in B)}}. \qquad (1_{[\text{RJ1}]})$$

Since $\mu^{\text{ex}}_{\text{M(in B)}}$ equals the excess Gibbs energy change of M in B (ΔG^{ex}[M in B]), corresponding excess enthalpy change ΔH^{ex}[M in B] and the entropy change ΔS^{ex}[M in B] can be determined from the observed temperature dependence of $\mu^{\text{ex}}_{\text{M(in B)}}$. The activity coefficient of M in B, $\log f_{\text{M(in B)}}$, can be given by Eq. (2).

$$\mu^{\text{ex}}_{\text{M(in B)}} = RT\ln f_{\text{M(in B)}}. \qquad (2)$$

4. Experimental results and discussion

4.1. Determined ΔH^{ex}[M in B]

The observed EMF for the four elements showed approximately linear dependences on $\log x_{\text{M(in B)}}$, suggesting that Eq. (1) is approximately satisfied. Careful attention was taken with the result of Nd, because Nd metal may react with Nd^{3+} to form Nd^{2+} and this effect may disturb the EMF measurement. Fig. 1 shows the observed EMF of Nd as a function of $\log x_{\text{M(in B)}}$. In this figure, the EMF's of Nd at every temperature show good linearities and the observed slopes of the dependences approximately agree with the theoretical slopes for each temperature which are defined with $n = 3$ by Eq. (1). This shows that the above reaction of Nd did not significantly disturb the electrochemical equilibrium between two electrodes and Nd^{3+} in the salt phase. This is probably due to the very low Nd^{3+} concentration in the molten salt phase.

Determined $\log f_{\text{M(in B)}}$ showed slight dependences on the concentration, while the magnitude of the dependence is different for each element. The $\log f_{\text{M(in B)}}$ was

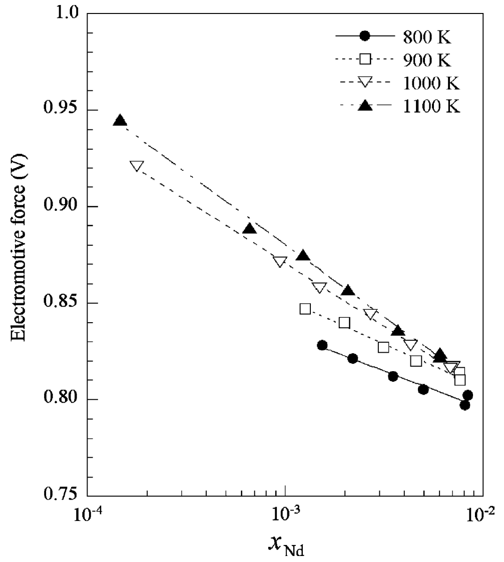

Fig. 1. Concentration dependence of the electromotive force of Nd.

formulated as a linear function by least square fitting method, and $\log f_{\mathrm{M(in\,B)}}$ at $x_{\mathrm{M(in\,B)}} = 5 \times 10^{-3}$ was calculated, as in the previous paper [1]. The $\log f_{\mathrm{M(in\,B)}}$ for every element was fitted to a linear function of the reciprocal of the temperature, which is defined by Eq. (3). The $\log f_{\mathrm{M(in\,B)}}$ showed a good linearity at higher temperatures. However, some points at lower temperatures tended to deviate from this line. As a result, points on the higher temperature side were selected for this fitting [1]. Table 1 summarizes the coefficients of Eq. (3) for all the tested elements in this study, together with those by previous study. The literature values are shown for comparison [4]. Using the data of Table 1 and Eq. (3), $\log f_{\mathrm{M(in\,B)}}$ can be calculated for any desired temperatures.

Table 1
Temperature dependence of $\log f_{\mathrm{M(in\,B)}}$ for $x_{\mathrm{M(in\,B)}} = 5 \times 10^{-3}$

	$\log f_{\mathrm{M(in\,B)}} = a1/T + b$			
	This study[a]		Lebedev et al.[b]	
	a	b	a	b
La	−11572	1.47	−10957	0.78
Ce	−11586	1.54	−11400	2.03
Pr	−11711	1.94	−11940	2.91
Nd	−12119	1.85	−11074	1.90
Gd	−10564	1.92	−9856	1.23
Tb	−10438	2.01	–	–
Dy	−10123	1.44	–	–
Ho	−9901	1.64	–	–
Er	–	–	−8593	1.23

[a] Values of La, Gd, Tb, and Dy are from previous study.
[b] Ref. [4].

$$\log f_{\mathrm{M(in\,B)}} = a \cdot 1/T + b. \tag{3}$$

ΔH^{ex}[M in B] and ΔS^{ex}[M in B] were calculated from the determined coefficients a and b. Table 2 summarizes the results of ΔH^{ex}[M in B] and ΔS^{ex}[M in B] in comparison with the literature values. The literature values of ΔH^{ex}[M in B] and ΔS^{ex}[M in B] were those calculated from the temperature dependence coefficients of $\log f_{\mathrm{M(in\,B)}}$ as reported by Lebedev [4].

4.2. Variation of ΔH^{ex}[M in B] along the lanthanide series

From the Miedema's semi-empirical model [2,3], the enthalpy change of solution of metal A into metal B which is denominated as ΔH_{sol}[A in B] is given by

$$\Delta H_{\mathrm{sol}}[\text{A in B}] = V^{2/3}\frac{2P}{n_{\mathrm{b}}(\mathrm{A})^{-1/3}+n_{\mathrm{b}}(\mathrm{B})^{-1/3}}\left[-(\Delta\Phi)^2+\frac{Q}{P}\left(\Delta n_{\mathrm{b}}^{1/3}\right)^2-\frac{R}{P}\right], \tag{4}$$

where V is the molar volume of metal A, n_{b}(A) and n_{b}(B) are electron density at the boundary of Wigner–Seitz cell, $\Delta\Phi$ is the difference of electronegativities between A and B, and P, Q, R are specific constants [2,3]. As long as lanthanide series can be treated by this semi-empirical method and lanthanides have common constants, ΔH_{sol}[M in B] for lanthanides should show an approximately linear dependency on $V^{2/3}$.

Determined ΔH^{ex}[M in B] and reported values are plotted in Fig. 2 as functions of $V^{2/3}$. The solid thin line drawn in Fig. 1 is calculated by Eq. (4) with $R/P = 0.99$ [1], and the dotted line is obtained with $R/P = 1.175$,

Table 2
ΔH^{ex}[M in B] and ΔS^{ex}[M in B] determined and reported

	$V^{2/3}$ (cm^2/mol$^{2/3}$)	ΔH^{ex}[M in B] (kJ/mol)		ΔS^{ex}[M in B] (J/mol)	
		Lebedev et al.[a]	This study	Lebedev et al.[a]	This study
La	7.98	−219.15	−221.54 ± 2.31[b]	−22.93	−28.11 ± 2.71[b]
Ce	7.76	−225.77	−221.81 ± 4.41	−45.96	−29.51 ± 5.17
Pr	7.56	−237.45	−224.21 ± 0.05	−63.31	−37.23 ± 0.05
Nd	7.51	−220.07	−232.02 ± 0.18	−42.68	−35.36 ± 0.19
Pm	7.43				
Sm	7.37				
Eu	7.36				
Gd	7.34	−200.89	−202.25 ± 1.80[b]	−30.95	−36.84 ± 1.88[b]
Tb	7.2		−199.83 ± 0.55[b]		−38.49 ± 0.56[b]
Dy	7.12		−193.80 ± 0.99[b]		−27.65 ± 1.00[b]
Ho	7.06		−189.55 ± 9.07		−31.44 ± 9.29
Er	6.98	−182.46		−32.75	
Tm	6.9				
Yb	6.86				
Lu	6.81				

[a] Derived from Ref. [4].
[b] Previous study [1].

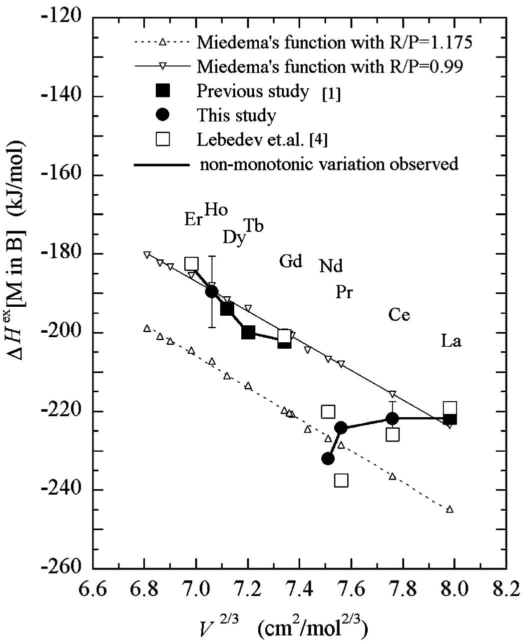

Fig. 2. Excess enthalpy changes of lanthanides in liquid bismuth as a function of $V^{2/3}$.

which was a value recommended by Alonso and March [3]. As was pointed out in the previous report [1], the line calculated with $R/P = 0.99$ appears to be rather suitable for the data points of La, Gd, Tb, Dy, Ho, and Er. On the other hand, the observed values of Ce, Pr, and Nd obviously deviate from this line. This was predicted in the previous report, and we can again recognize this non-monotonic trend of the variation of lanthanides. In the sense of the explanation by Miedema's rule, Ce, Pr, and Nd seem to be unique elements that do not obey its monotonic trend. However, apart from Miedema's rule, Fig. 2 can be understood to show the presence of two separate groups of elements, one consisting of La through Nd and another of Gd through Er. The former group, which are of lighter lanthanides having larger molar volumes, shows a slight increasing trend along with $V^{2/3}$, and the latter group, which are of heavier lanthanides having smaller molar volumes, shows a decreasing trend. These different trends of two separate groups are indicated by thick solid lines in Fig. 2.

In general, lanthanides should show a smooth and monotonic variation of chemical characteristics along the series, because the increasing 4f electrons do not significantly participate in the chemical interaction with the neighbor elements. Miedema's rule is a model based on this general principle, and it expects a smooth variation of the degree of metallic interaction along the series. The observed non-monotonic trend of variation of ΔH^{ex}[M in B] may be attributable to the presence of an element-specific intermetallic interaction of lanthanide with Bi, which Miedema's rule does not cover.

4.3. Consideration on the non-monotonic trend

It should be noted that ΔH^{ex}[M in B] is defined as the enthalpy difference from the liquid pure metals as the standard, and hence the intrinsic different physical properties of the liquid lanthanide metals may influence it. To avoid the possible non-uniformity of the thermodynamic standard for the discussion, instead of the liquid lanthanide metal as the standard, a hypothetical metal vapor was introduced as the new standard. Newly introduced $\Delta H^{\mathrm{ex}}[\mathrm{M\ in\ B}]_{\mathrm{vap}}$ is the enthalpy change associated with dissolving a hypothetical elemental vapor of lanthanide into liquid Bi. Here in this paper, metal vapor having three outer shell electrons, $4f^{n-1}5d^{1}6s^{2}$, is used because lanthanides in Bi alloy are also considered to be in trivalent state. This is the thermodynamic correction in terms of Born–Haber Cycle, which was successfully introduced as 'Promotion Energy' by Nugent et al. [7] and David et al. [8] for explaining systematic chemical characteristics of lanthanides and actinides, and is adoptable and suitable for this discussion also. This treatment for enthalpy changes is based on an assumption that entropy changes associated with both sublimation and mixing of metals are approximately constant over the series. The latter assumption is validated by the results of ΔS^{ex}[M in B] within an acceptable approximation.

For the case of La, Ce, and Gd, $\Delta H^{\mathrm{ex}}[\mathrm{M\ in\ B}]_{\mathrm{vap}}$ is simply obtained by correcting ΔH^{ex}[M in B] with $\Delta H_{\mathrm{fusion}}$ and ΔH_{sub}, sublimation enthalpy change, because they have electron configuration, $4f^{n-1}5d^{1}6s^{2}$, either in metal or vapor. In contrast, other lanthanides need to add ΔE, which is an energy difference between electron configuration $4f^{n-1}5d^{1}6s^{2}$, and $4f^{n}6s^{2}$, because their lowest energy state of metal vapor is divalent state, $4f^{n}6s^{2}$. $\Delta H^{\mathrm{ex}}[\mathrm{M\ in\ B}]_{\mathrm{vap}}$ is given by the next equations, the parameters of which are listed in Table 3.

$$\Delta H^{\mathrm{ex}}[\mathrm{M\ in\ B}]_{\mathrm{vap}} = \Delta H^{\mathrm{ex}}[\mathrm{M\ in\ B}] + \Delta H_{\mathrm{fusion}} - \Delta H_{\mathrm{sub}} \quad (\mathrm{La,\ Ce,\ Gd}), \tag{5}$$

$$\Delta H^{\mathrm{ex}}[\mathrm{M\ in\ B}]_{\mathrm{vap}} = \Delta H^{\mathrm{ex}}[\mathrm{M\ in\ B}] + \Delta H_{\mathrm{fusion}} - \Delta H_{\mathrm{sub}} - \Delta E \quad (\mathrm{Pr,\ Nd,\ Tb,\ Ho,\ Dy,\ Er}). \tag{6}$$

The sum of the first two terms of Eqs. (5) and (6), ΔH^{ex}[M in B] + $\Delta H_{\mathrm{fusion}}$, is given as $\Delta H^{\mathrm{ex}}[\mathrm{M\ in\ B}]_{\mathrm{solid}}$ in Table 3.

Obtained $\Delta H^{\mathrm{ex}}[\mathrm{M\ in\ B}]_{\mathrm{vap}}$ is plotted in Fig. 3 as a function of $V^{2/3}$, which gives a different profile from Fig. 2. The term $(-\Delta H_{\mathrm{sub}} - \Delta E)$ in Eqs. (5) and (6), working as a correction term for $\Delta H^{\mathrm{ex}}[\mathrm{M\ in\ B}]_{\mathrm{solid}}$,

Table 3
ΔH^{ex}[M in B]$_{vap}$ and related thermodynamic quantities

	$V^{2/3}$ (cm^2/mol$^{2/3}$)	ΔH^{ex}[M in B]$_{solid}$ (kJ/mol)	ΔH_{sub}[M in B][b] (kJ/mol)	ΔE (kJ/mol)	ΔH^{ex}[M in B]$_{vap}$ (kJ/mol)
La	7.98	−212.7 ± 1.9	431.2	−180.0	−643.9 ± 1.9
Ce	7.76	−215.5 ± 5.4	422.9	−57.0	−638.4 ± 5.4
Pr	7.56	−215.0 ± 0.1	355.9	46.0	−616.9 ± 0.1
Nd	7.51	−223.1 ± 0.6	327.8	81.0	−631.9 ± 0.6
Pm	7.43		330.8	96.0	
Sm	7.37		206.8	185.0	
Eu	7.36		177.5	300.0	
Gd	7.34	−189.6 ± 1.3	395.0	−131.0	−584.6 ± 1.3
Tb	7.2	−188.3 ± 0.9	389.0	3.0	−580.3 ± 0.9
Dy	7.12	−186.3 ± 0.1	290.6	90.0	−566.9 ± 0.1
Ho	7.06	−176.2 ± 8.7	301.0	92.0	−569.2 ± 8.7
Er	6.98	−164.5[a]	317.4	86.0	−567.9
Tm	6.9		230.3	157.0	
Yb	6.86		152.4	277.0	
Lu	6.81		427.9		

[a] Derived from Ref. [4].

[b] Ref. [6]

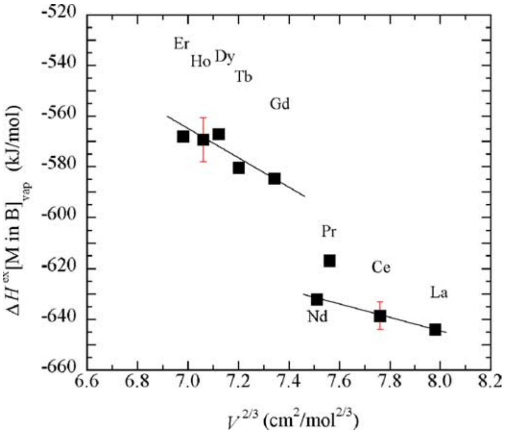

Fig. 3. Variation of excess enthalpy changes of lanthanides in liquid bismuth standardized to vapor state.

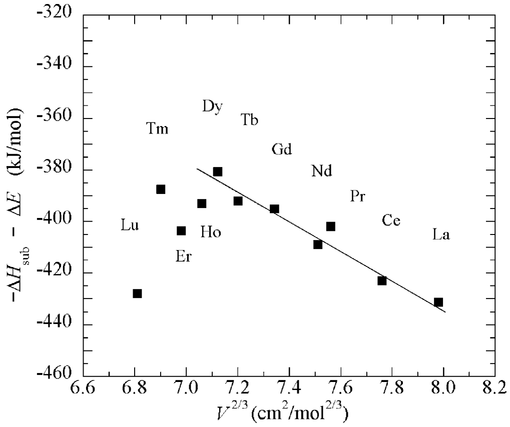

Fig. 4. Enthalpy changes associated with the aggregation of lanthanide metals as a function of $V^{2/3}$.

equals the enthalpy change associated with the aggregation of trivalent lanthanide elements into their pure metallic states. Fig. 4 shows the trend of $(-\Delta H_{sub} - \Delta E)$ along the series. In Fig. 4, elements from La through Dy show a rough linear trend with a slight deviation of Pr, but Ho, Er, and heavier ones deviate from this linear trend. The monotonic increase of $(-\Delta H_{sub} - \Delta E)$ in the order from La to Dy indicates the monotonic decreasing trend of the aggregation energy of pure metals along with their volume decrease. The singularity of the elements beyond Ho means their intrinsic stronger metallic bonding than lighter elements.

The comparison of Figs. 4 and 3 gives some characteristic differences. In contrast to the roughly linear increasing trend from La up to Dy in Fig. 4, Fig. 3 seems to have a gap between Nd and Gd. This suggests that lighter and heavier lanthanides seem to show two separate groups showing two different increasing trends in the order of the elements. The former group consists of elements from La through Nd, and the latter consists of elements heavier than Gd. The gap between them is about 40 kJ/mol, and each group shows a roughly increasing trend in the order of the elements with different slopes. The pure metals show a smooth trend up to Dy. The valence band with the participation of two 6s and one 5d electrons, should result in a smooth variation, approximately of the nature shown along the series. The obviously different appearances of the two groups in Fig. 3 suggest that the nature of the bonding, which results from the participation of two 6s and one

5d electrons of lanthanide to the valence band consisting of p orbital of Bi, have a drastic change at the transition from Nd to Gd. The lighter lanthanide group has f-electrons less than seven, half-filling, but the heavier group has more f-electrons than half-filling. The drastic change of the nature of the metallic bonding effected by the localized f-electrons is quite interesting, and should be examined carefully.

The rough increasing trends in the order of the elements in the two groups are not simple. For the group of lighter lanthanides, if we consider that La, Ce and Nd satisfy a good linear trend, Pr looks to have a singularity with about 20 kJ/mol deviation. This singularity of Pr from other three is also seen in Fig. 4, but it is more intensified in Fig. 3. The singularity of the valence electron band of Pr can be seen in its anomalous higher electronic specific heat constant than other trivalent lanthanides. In the second group, a roughly linear increasing trend can be seen. This shows that, within this group, it remains a monotonic variation as a function of the molar volume, and other factors such as electronegativity and electron density.

5. Conclusion

The ΔH^{ex}[M in B]'s of eight lanthanides in liquid Bi were comprehensively determined by electromotive force measurements. The results shows that light lanthanides have different properties compared to other heavier lanthanides, and that Miedema's semi-empirical rule does not successfully represent this non-monotonic trend. Different expression of the excess enthalpy changes based on a hypothetical vapor state of lanthanide as the standard explains more explicitly the characteristic trend of ΔH^{ex}[M in B]. Further re-examination of the related thermodynamic parameters is necessary and desired for more explicit modeling of the non-monotonic systematic trend of ΔH^{ex}[M in B] of lanthanide metals in liquid bismuth.

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