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Enthalpies of formation of liquid binary lanthanide-metal alloys

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Pyrometallurgical liquid-liquid extraction of lanthanides and actinides between molten chloride and liquid metal (such as Bi, Cd, and Zn) is one of the alternative techniques for the future group separation of lanthanides and actinides in the irradiated fuel reprocessing industry [1, 2]. The extraction and separation performance of lanthanides and actinides by this pyrometallurgical system is significantly influenced by their activity coefficients in both phases of molten salt and liquid metal [3]. The extraction behavior of some trivalent lanthanides in a system of molten alkaline chloride and liquid metals (Bi, Cd, and Zn) was studied, and the thermodynamic properties were determined [3–5]. The enthalpies of formation of liquid Ln-B alloys (Ln = lanthanides; B = Bi, Cd, and Zn) ($\Delta H^{\mathrm{M}}_{\text{Ln-B}}$) at very low level Ln are still insufficiently established because of the complications and difficulty of high-temperature experiments. Therefore, to estimate the $\Delta H^{\mathrm{M}}_{\text{Ln-B}}$ according to a model is of great interest. Miedema and coworkers developed an extremely simple scheme for predicting the enthalpy of formation of binary metallic alloys, which is a very important achievement in recent years [6, 7]. The enthalpy of formation for most binary alloys can be calculated from the most basic properties such as molar volume V, electronegativity Φ, and electron density of elements in the systems. This method is 95% successful in predicting the sign of ΔH^{M} [8]. Miedema's model is a semi-empirical method. The purpose of this study is to investigate the possibility of applying Miedema's model in Ln-B systems based on obtained data, and hence to predict the unknown $\Delta H^{\mathrm{M}}_{\text{Ln-B}}$.

As a binary metallic alloy, the enthalpies of formation of Ln-B alloy can be reasonably calculated by a semi-empirical model which was developed by Miedema *et al.* [6–9]. In Miedema's model, the enthalpies of formation of liquid Ln-B alloys is represented by

$$\Delta H^{\mathrm{M}}_{\text{Ln-B}} = V_{\mathrm{Ln}}^{2/3} V_{\mathrm{B}}^{2/3} \frac{2P}{n_{\mathrm{b}}^{-1/3}(\mathrm{Ln}) + n_{\mathrm{b}}^{-1/3}(\mathrm{B})} \times \left[-(\Delta\Phi)^2 + \frac{Q}{P}\left(\Delta n_{\mathrm{b}}^{1/3}\right)^2 - \left(\frac{S}{P}\right) \right] \times \frac{x_{\mathrm{Ln}}[1 + u_{\mathrm{Ln}} x_{\mathrm{B}}(\Phi_{\mathrm{Ln}} - \Phi_{\mathrm{B}})] x_{\mathrm{B}}[1 + u_{\mathrm{B}} x_{\mathrm{Ln}}(\Phi_{\mathrm{B}} - \Phi_{\mathrm{Ln}})]}{x_{\mathrm{Ln}}[1 + u_{\mathrm{Ln}} x_{\mathrm{B}}(\Phi_{\mathrm{Ln}} - \Phi_{\mathrm{B}})] V_{\mathrm{Ln}}^{2/3} + x_{\mathrm{B}}[1 + u_{\mathrm{B}} x_{\mathrm{Ln}}(\Phi_{\mathrm{B}} - \Phi_{\mathrm{Ln}})] V_{\mathrm{B}}^{2/3}} \qquad (1)$$

where $V_{\mathrm{Ln}}^{2/3}$ and $V_{\mathrm{B}}^{2/3}$ are the molar volumes of metallic Ln and B, respectively (cm^3, at room temperature); $n_{\mathrm{b}}(\mathrm{Ln})$ and $n_{\mathrm{b}}(\mathrm{B})$ electron density of Ln and B at the boundary of Wigner-Seeitz atomicell as derived for the pure elements in the metallic state (electrons per (0.529Å)^3); $\Delta\Phi$ the difference of electronegativity between Ln and B; x_{Ln}, x_{B} the mole fractions of Ln and B in liquid metal phase; and P, Q, S, u specific constants. Here, $\Delta n_{\mathrm{b}}^{1/3} = n_{\mathrm{b}}^{1/3}(\mathrm{Ln}) - n_{\mathrm{b}}^{1/3}(\mathrm{B})$.

In our previous studies and literature [3–5], the activity coefficients of some trivalent Ln in liquid metal phase (γ_{Ln}) have been obtained by electromotive force (EMF) measurement. The EMF measurement could be performed at very low-level Ln content as $x_{\mathrm{Ln}} \leq 10^{-5}$. The Ln-B melt was treated as a regular solution at very low-level Ln concentration, thus, the $\Delta H^{\mathrm{M}}_{\text{Ln-B}}$ values were obtained using the following equation [9, 10]

$$\Delta H^{\mathrm{M}}_{\text{Ln-B}} = x_{\mathrm{Ln}} RT \ln \gamma_{\mathrm{Ln}}. \qquad (2)$$

The activity coefficient of Ln was found to be effected by the x_{Ln} [4]. In order to compare the enthalpies of formation, $x_{\mathrm{Ln}} = 0.005$ was chosen as the representative concentration in this study. The experimental data of $\Delta H^{\mathrm{M}}_{\text{Ln-B}}$ are summarized in Table I [3–5].

The parameters of lanthanides needed for Miedema's model are listed in Table II [3, 6, 7]. Calculated and measured values of $\Delta H^{\mathrm{M}}_{\text{Ln-B}}$ at 873 K and $x_{\mathrm{Ln}} = 0.005$ are plotted in Figs 1–3 as functions of $V_{\mathrm{Ln}}^{2/3}$. A linear dependency of $\Delta H^{\mathrm{M}}_{\text{Ln-B}}$ on $V_{\mathrm{Ln}}^{2/3}$ was clearly observed for both calculated and measured values. It is interesting that the calculated values are more negative than the experimental values. This fact was also observed in the La-Cu and Zr-Cu systems [11].

The term of $\frac{S}{P}$ in Equation 2 is introduced when one of the two components is a non-transition metal [9]. It is ascribed as the *p–d* hydridization or as a result of pressure relation of different types of valence electrons in the alloy [11]. The term of $\frac{S}{P}$ represents the degree of an additional metallic bonding that is not accounted for only by the difference of electronegativities and electron densities of Ln and B. The actual values of $\frac{S}{P}$ in liquid Ln-B alloys are based on experimental $\Delta H^{\mathrm{M}}_{\text{Ln-B}}$. In our study, the commonly quoted value of $\frac{S}{P} = 1.175$, which is recommended by Alonso *et al.* [12], is used for calculation. It is necessary to introduce a lower value

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TABLE I Measured values of $\Delta H^{M}_{\text{Ln-B}}$ (873 K, $x_{\text{Ln}} = 0.005$)

Ln	$\Delta H^{M}_{\text{Ln-Bi}}$ (kJ/mol)	$\Delta H^{M}_{\text{Ln-Cd}}$ (kJ/mol)	$\Delta H^{M}_{\text{Ln-Zn}}$ (kJ/mol)
La	−0.984	−0.585	−0.772
Ce	−0.969	−0.553	−0.746
Pr	−0.927	−0.529	−0.691
Nd	−0.900	–	−0.705
Gd	−0.849	–	–
Tb	−0.830	–	–
Dy	−0.848	–	–
Ho	−0.810	–	–
Er	–	–	−0.620

TABLE II Parameters for Miedema's semi-empirical model[a]

Ln	$V^{2/3}_{\text{Ln}}$ (cm^2/mol$^{2/3}$)[b]	Φ (V)$^{(b)}$	$n_b^{1/3} (du^{1/3})$[c]
La	7.98	3.17	1.18
Ce	7.76	3.18	1.19
Pr	7.56	3.19	1.2
Nd	7.51	3.19	1.2
Pm	7.43	3.19	1.21
Sm	7.37	3.20	1.21
Eu	7.36	3.20	1.21
Gd	7.34	3.20	1.21
Tb	7.20	3.21	1.22
Dy	7.12	3.21	1.22
Ho	7.06	3.22	1.22
Er	6.98	3.22	1.23
Tm	6.90	3.22	1.23
Yb	6.86	3.22	1.23
Bi	7.20	4.15	1.16
Cd	5.53	4.05	1.24
Zn	4.38	4.10	1.32

[a] $P = 12.35$, $\frac{Q}{P} = 0.944$, $\frac{S}{P} = 1.175$, $u_{\text{Ln}} = 0.07$, $u_{\text{B}} = 0.04$.
[b] Ref. [7].
[c] $du = 6 \times 10^{22}$ electrons/cm^3.

of $\frac{S}{P}$ to fit the experimental values. Since the *d* band of Ln is filled, there is no transfer of *d* electrons from the *d* band of Ln metal to the *d* band of Bi, Cd, and Zn. This can explain why the $\frac{S}{P}$ value has to be reduced to fit the experimental values.

In Fig. 1, the line calculated with $\frac{S}{P} = 0.86$ for Ln-Bi alloys appears to be suitable for a good fit to the experimental data of $\Delta H^{M}_{\text{Ln-Bi}}$. This value of $\frac{S}{P} = 0.86$ also was obtained by using the least squares fitting of experimental data. The same treatment is available for Ln-Cd alloys and Ln-Zn alloys. As shown in Figs 2 and 3, the calculated results using $\frac{S}{P} = 0.05$ for Ln-Cd alloys and $\frac{S}{P} = 0.50$ for Ln-Zn alloys are in good agreement with the experimental data. The linear relations of experimental $\Delta H^{M}_{\text{Ln-B}}$ with $V^{2/3}_{\text{Ln}}$ drawn in Figs 1–3 are expressed by

$$\Delta H^{M}_{\text{Ln-Bi}} = 0.208 - 0.147 V^{2/3}_{\text{Ln}} \pm 0.04 \text{ (kJ/mol)} \quad (3)$$

$$\Delta H^{M}_{\text{Ln-Cd}} = 0.482 - 0.134 V^{2/3}_{\text{Ln}} \pm 0.01 \text{ (kJ/mol)} \quad (4)$$

$$\Delta H^{M}_{\text{Ln-Zn}} = 0.459 - 0.154 V^{2/3}_{\text{Ln}} \pm 0.03 \text{ (kJ/mol)}. \quad (5)$$

Regardless of its physical meanings, this linearity provides a useful tool for accurate predicting $\Delta H^{M}_{\text{Ln-B}}$ of liquid Ln-B alloys when experimentally based values are currently unavailable.

In summary, the present work attempts to devise an approach to determine the heat of formation of Ln-B alloys. Miedema's model has provided quantitative predictions of Ln-B alloys. A linear dependency of $\Delta H^{M}_{\text{Ln-B}}$ on $V^{2/3}_{\text{Ln}}$ was observed, which would be useful for predicting the unknown thermodynamic properties from a

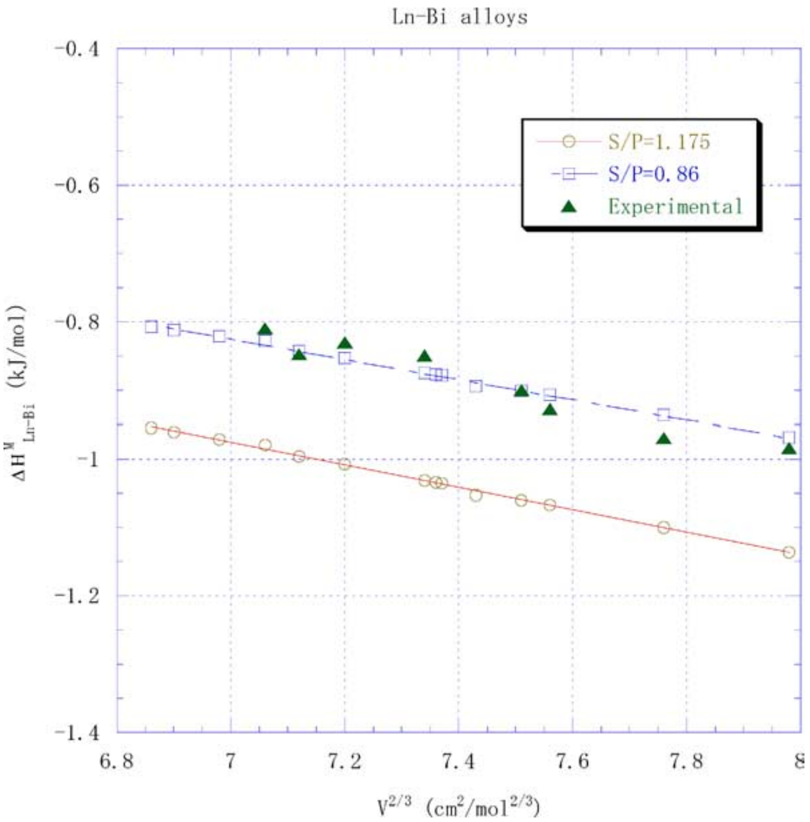

Figure 1 $\Delta H^{M}_{\text{Ln-Bi}}$ as a function of $V^{2/3}_{\text{Ln}}$ (873 K, $x_{\text{Ln}} = 0.005$).

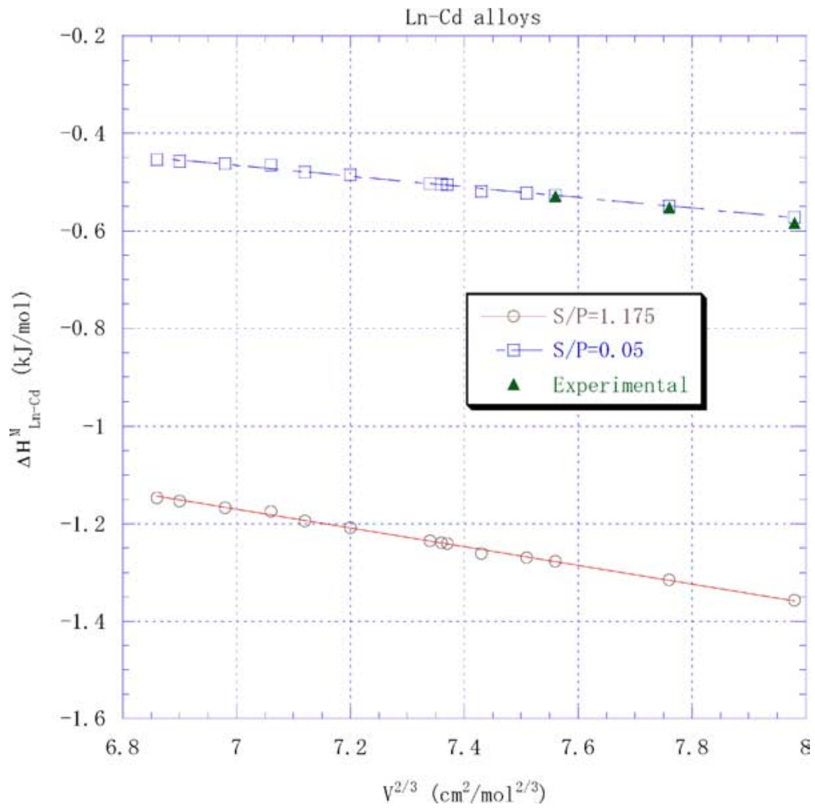

Figure 2 $\Delta H^{\mathrm{M}}_{\text{Ln-Cd}}$ as a function of $V^{2/3}_{\mathrm{Ln}}$ (873 K, $x_{\mathrm{Ln}} = 0.005$).

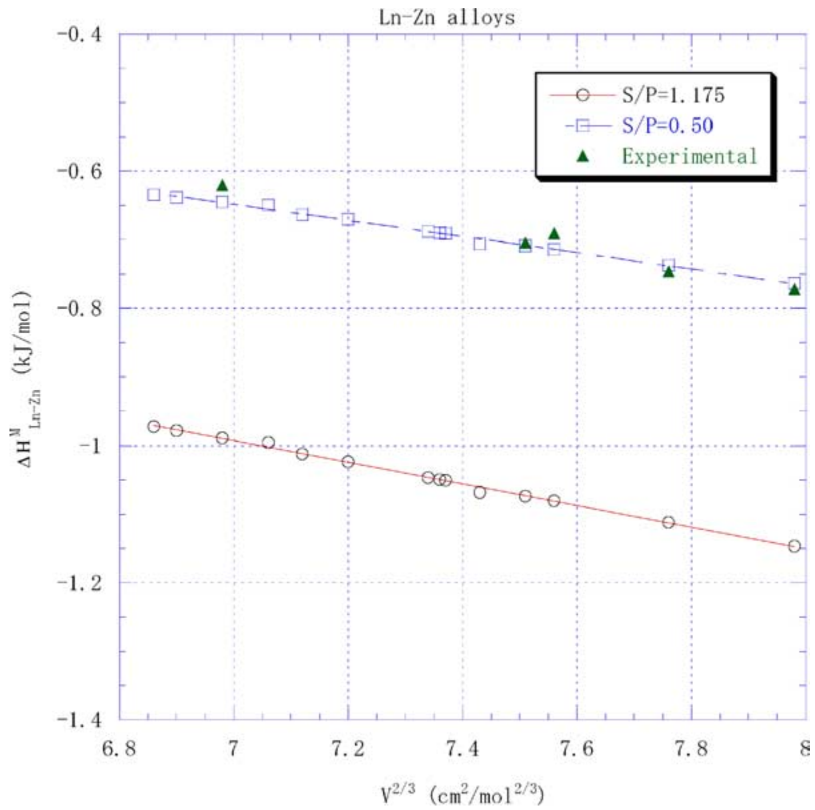

Figure 3 $\Delta H^{\mathrm{M}}_{\text{Ln-Zn}}$ as a function of $V^{2/3}_{\mathrm{Ln}}$ (873 K, $x_{\mathrm{Ln}} = 0.005$).

limited number of currently available thermodynamic data. Because there is no transfer of *d* electrons from the *d* band of Ln metal to the *d* band of Bi, Cd, and Zn, the $\frac{S}{P}$ constant in Miedema's model has to be modified to fit the experimental data. Values of $\frac{S}{P} = 0.86$ for Ln-Bi alloys, $\frac{S}{P} = 0.05$ for Ln-Cd alloys and $\frac{S}{P} = 0.50$ for Ln-Zn alloys in Miedema's model yield calculated results that are in good agreement with experimental data.

References

1. H. MORIYAMA, H. YAMANA, S. NISHIKAWA, Y. MIYASHITA, K. MORITANI and T. MITSUGASHIRA, *J. Nucl. Mater.* **247** (1997) 197.
2. H. MORIYAMA, H. YAMANA and S. NISHIKAWA, *J. Alloys Compd.* **271–273** (1998) 587.
3. H. YAMANA, N. SOUDA and H. MORIYAMA, *J. Nucl. Mater.* **278** (2000) 37.
4. H. YAMANA, J. SHENG, N. SOUDA and H. MORIYAMA, *ibid.* **294** (2001) 232.
5. V. A. LEBEDEV, Selectivity of Liquid Metal Electrons in Molten Halides, Metallurgiya, Chelyabinsk, 1993 (in Russian).
6. A. R. MIEDEMA, P. F. DE CHATEL and F. R. DE BOER *Physica* **100B** (1980) 1.
7. F. R. DE BOER, R. BOOM, W. C. MATTENS, A. R. MIEDEMA and A. K. NIESSEN, "Cohesion in Metals-transition Metal Alloys" (North-Holland Physics Publishing, Amsterdam, 1988).
8. C. COLINET, *J. Alloys Compd.* **225** (1995) 409.
9. W. PAN, R. LI, J. CHEN, R. SUN and J. LIAN, *Mater. Sci. Eng.* **A 287** (2000) 72.
10. X. DING, P. FAN and W. WANG, *Metall. Mater. Trans.* **30B** (1999) 271.
11. F. MEYER-LIAUTAUD, A. PASTUREL, C. H. ALLIBERT and C. COLINET, *J. Less-Comm. Met.* **110** (1985) 75.
12. J. A. ALONSO and N. H. MARCH, "Electrons in Metals and Alloys" (Academic Press, London 1989).

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