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Reductive extraction behaviour of actinide and lanthanide elements in molten salt and liquid metal binary phase systems

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Abstract

In support of the development of a pyrochemical group-partitioning process of actinides and lanthanides, the equilibrium distributions of these elements were measured in some binary phase systems of molten salt and liquid metal. An LiF–BeF$_2$ mixture was selected as the salt phase and Bi, Sn, Cd and Zn were examined as the metal phase. In general, actinides were more easily reduced and extracted from the salt phase into the metal phase than were lanthanides. Group partitioning is thus feasible.

In different partitioning systems a systematic difference in the separation factor between actinides and lanthanides was observed. The difference is attributable to the difference in alloying energies in the metal phase. The thermodynamic quantities of solute elements in the metal phase were evaluated from the present analysis. Some regularities were inferred from the analysis which are theoretically interesting and helpful to estimate unknown distribution coefficients.

1. Introduction

Molten salt and liquid metal binary phase systems are expected to be very useful for future nuclear chemical processing because of their radiation resistance, compactness and rapid reaction kinetics. Extensive studies of these systems are thus seen, for example, for the development of molten salt breeder reactors [1] and metallic fuel fast breeder reactors [2]. Also, the application of some similar systems has been proposed for the recovery of such useful elements as platinum group ones from spent fuel [3, 4].

The experiment of Ferris *et al.* [5, 6] at ORNL is known for the reductive extraction of actinides and fission products in an LiF–BeF$_2$/Bi system. They measured the equilibrium distributions of several elements to show the technical feasibility of this pyrochemical method. We also measured the equilibrium distributions [7–13] and extraction kinetics [14] in the same and similar systems. The equilibrium distributions were determined as a function of salt phase composition, metal phase composition and temperature and the mechanism of the reductive extraction was discussed in some detail.

In these studies it has been shown that actinides are more easily reduced and extracted from the salt phase into the metal phase than are lanthanides and that the reductive extraction may be applied to the group partitioning of actinides and lanthanides. For a quantitative assessment of technical feasibility, however, it is especially needed to know the separation factors between actinides and lanthanides. Since some importance of the selection of the metal phase has been suggested in our previous study, the separation factors in various metal phase systems are compared in the present study. By selecting an LiF–BeF$_2$ mixture as the reference salt phase, Bi, Sn, Cd and Zn are examined as the metal phase.

2. Experimental details

All the reagents were of reagent grade and obtained from Nacalai Tesque, Co. An LiF–BeF$_2$ mixture with 66.7 mol% LiF was prepared by melting known amounts of LiF and BeF$_2$. The radioactive tracers of ^{239}Np and ^{233}Pa were produced by thermal neutron irradiation of U and Th metals and those of lanthanides were similarly produced by irradiation of the metals.

The experimental apparatus and procedures employed in the present study were much the same as in the previous ones [7–14]. In a typical experiment 2 mol of LiF–BeF$_2$ mixture, 2 mol of Bi, Sn, Cd or Zn and small amounts (less than 100 mg each) of radioactive

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solute metals were loaded in a graphite crucible. After drying at 450 K in vacuum, the system was heated to a given temperature under an inert gas atmosphere.

The distribution of solute elements was controlled by the incremental addition of a reductant Li to the system. The Li was added in the form of its alloy with each solvent metal in order to ensure the addition to the metal phase. After the equilibrium distributions had been attained with gas sparging, samples were removed from each phase with a stainless steel sampling tube under a reduced pressure. The concentrations of radioactive solutes were measured by direct γ spectrometry and those of the reductant Li in the metal phase were determined by atomic absorption spectrophotometry.

3. Results and discussion

3.1. *Mechanism of equilibrium distributions*

According to our previous studies [7–13], the equilibrium distribution of a solute element M is given by

$$\mathrm{Li}_{m-n}\mathrm{MF}_m + n\mathrm{Li} + x\mathrm{A} = \mathrm{MA}_x + m\mathrm{LiF} \qquad (1)$$

where $\mathrm{Li}_{m-n}\mathrm{MF}_m$ and MA_x represent complex compounds in the salt phase and intermetallic compounds in the metal phase respectively. The formation of these compounds has been inferred from the dependence of equilibrium distributions on the salt and metal phase compositions.

By taking reaction (1), the extractability $D_M/D_{Li}{}^n$ of each element is represented by

$$\begin{aligned}\log\left(\frac{D_M}{D_{Li}{}^n}\right) = &-(2.3RT)^{-1}[\Delta G_f{}^\circ(\mathrm{MA}_x)\\ &+m\Delta G_f{}^\circ(\mathrm{LiF}) - \Delta G_f{}^\circ(\mathrm{Li}_{m-n}\mathrm{MF}_m)]\\ &+x\log X_A-(m-n)\log X_{\mathrm{LiF}}\\ &-\log \gamma_{\mathrm{MA}_x} - m\log\gamma_{\mathrm{LiF}}\\ &+\log\gamma_{\mathrm{Li}_{m-n}\mathrm{MF}_m} + n\log\gamma_{\mathrm{Li}} + x\log\gamma_A \end{aligned} \qquad (2)$$

where the distribution coefficients D_M and D_{Li} are defined as

$$D_M = \frac{X_{M(\mathrm{metal})}}{X_{M(\mathrm{salt})}} \qquad (3)$$

$$D_{Li} = \frac{X_{Li(\mathrm{metal})}}{X_{Li(\mathrm{salt})}} \qquad (4)$$

The terms on the right-hand side of eqn. (2) are constant at a given temperature and composition and thus the logarithm of D_M is proportional to that of D_{Li} with a slope of n:

$$\log D_M = n \log D_{Li} + \log K_M' \qquad (5)$$

where K_M' is a constant. This relation has been observed to hold in the present study.

3.2. *Systematics of extractability*

Tables 1–4 summarize the equilibrium distributions measured in the LiF–BeF$_2$/Bi. LiF–BeF$_2$/Sn, LiF–BeF$_2$/Cd and LiF–BeF$_2$/Zn systems respectively. The extractability of La has been evaluated from the least-squares fitting of the measured D_{La} and D_{Li} values to eqn. (5). In the present measurement, however, the uncertainty of the La extractability is rather large, possibly owing to the difficulty in the measurement of very dilute Li concentrations. Because of the same difficulty, large uncertainties also accompany the extractability of the other elements. The extractability of these elements has thus been evaluated on a relative basis by comparing the measured D_M values with D_{La}.

Figure 1 shows the dependence of the evaluated extractability on atomic number. By comparing the extractability in the various systems, the following observations can be made.

(1) Actinides are more easily reduced and extracted from the salt phase into the metal phase than are

TABLE 1. Extractability values in $\log(D_M/D_{Li}{}^n)$ in LiF–BeF$_2$/Bi[a]

Element (n)	873 K	973 K	1073 K	Ref.
La (3)	7.33		5.62	8
	6.924	6.362		6
Ce (3)	7.67		5.98	8
Nd (3)	7.66 ± 0.30		5.75 ± 0.21	
	7.806			6
Sm (2)	4.65 ± 0.17		3.51 ± 0.01	
	4.740			6
Eu (2)	4.47 ± 0.21		3.33 ± 0.24	
	3.861			6
Gd (3)	6.40 ± 0.26		4.73 ± 0.11	
	6.217			6
Tb (3)	6.49 ± 0.34		4.91 ± 0.34	
Dy (3)	6.50 ± 0.01			
	5.663			6
Er (3)	5.85 ± 0.26		4.29 ± 0.10	
Tm (3)	6.68 ± 0.25		4.69 ± 0.17	
Yb (2)	4.08 ± 0.34		3.02 ± 0.06	
Lu (3)	4.15 ± 0.26		2.93 ± 0.35	
Th (4)	10.2			7
	9.731	8.702		6
Pa (4)	13.09		10.19	8
	13.304			6
U (3)	12.204			6
Np (3)	10.52		8.51	6
Pu (3)	11.265			6
Am (3)	11.44			6
Cm (3)	10.472			6
Cf (3)	11.472			6

[a] Uncertainties are the relative ones obtained from comparison of the D_M values with D_{La}. See text.

TABLE 2. Extractability values in $\log(D_M/D_{Li}{}^n)$ in LiF–BeF$_2$/Sn[a]

Element (n)	873 K	1073 K
La (3)	9.94±0.56	7.82±1.06
Ce (3)	10.3±0.15	8.29±0.12
Nd (3)	10.8	8.31±0.10
Sm (2)	7.55±0.45	5.20±0.12
Eu (2)	5.24±0.55	3.78±0.10
Gd (3)	10.0±0.15	7.20±0.11
Dy (3)	10.4±0.30	7.06±0.18
Er (3)	9.78±0.36	6.26±0.12
Tm (3)	9.95±0.45	6.12±0.16
Yb (2)	6.43±0.20	3.98±0.11
Pa (4)	16.0±0.83	14.8±0.17
Np (3)	12.4±0.68	9.88±1.09

[a] Uncertainties for La are obtained from the least-squares fitting of the D_{La} and D_{Li} values to eqn. (5). Uncertainties for other elements are the relative ones obtained from comparison of the D_M values with D_{La}. See text.

TABLE 3. Extractability values in $\log(D_M/D_{Li}{}^n)$ in LiF–BeF$_2$/Cd[a]

Element (n)	773 K	873 K
La (3)	9.45±0.49	8.58±0.12
Ce (3)	9.93±0.14	8.88±0.01
Nd (3)	9.78±0.08	8.70±0.06
Sm (2)	5.37±0.25	4.96±0.08
Eu (2)	<5.05	4.94±0.06
Gd (3)	8.59±0.18	8.05±0.04
Dy (3)	<8.15	7.41±0.06
Er (3)	7.75±0.12	7.44±0.09
Tm (3)	<8.03	<7.09
Yb (2)	4.75±0.16	4.86±0.04
Pa (4)	12.4±0.09	12.1±0.28
Np (3)	8.27±0.13	8.23±0.10

[a] Uncertainties for La are obtained from the least-squares fitting of the D_{La} and D_{Li} values to eqn. (5). Uncertainties for other elements are the relative ones obtained from comparison of the D_M values with D_{La}. See text.

TABLE 4. Extractability values in $\log(D_M/D_{Li}{}^n)$ in LiF–BeF$_2$/Zn[a]

Element (n)	873 K	1073 K
La (3)	9.75±0.47	7.60±0.62
Ce (3)	10.0±0.17	8.00±0.18
Nd (3)	10.4±0.23	8.23±0.22
Sm (2)	6.38±0.12	5.65±0.27
Eu (2)	3.98±0.43	3.63±0.41
Gd (3)	10.0±0.25	8.03±0.04
Dy (3)	10.3±0.43	8.86±0.06
Er (3)	10.0±0.61	7.78±0.04
Tm (3)	10.2±0.64	8.78±0.61
Yb (2)	5.56±0.29	3.63±0.43
Pa (4)	15.2±1.09	12.9±0.10
Np (3)	10.5±0.59	9.36±0.11

[a] Uncertainties for La are obtained from the least-squares fitting of the D_{La} and D_{Li} values to eqn. (5). Uncertainties for other elements are the relative ones obtained from comparison of the D_M values with D_{La}. See text.

lanthanides. Thus actinides and lanthanides behave as different groups.

(2) The separation factor between actinides and lanthanides depends on the selection of the metal phase. The highest separation factor is achieved in the Bi system.

These observations are important for the application of these systems to group partitioning.

3.3. *Thermodynamic quantities of intermetallic compounds*

The group behaviour of actinides and lanthanides can be discussed by evaluating the thermodynamic quantities of intermetallic compounds in the metal phase. Because of the variety of the studied elements, especially actinides, the Bi system is discussed here. Equation (2) is used to calculate the Gibbs free energy of formation of intermetallic compounds, $\Delta G_f{}^\circ(\mathrm{MA}_x)$. Also, we can calculate the $\Delta H_f{}^\circ(\mathrm{MA}_x)$ and $\Delta S_f{}^\circ(\mathrm{MA}_x)$ values from the temperature dependence of the $\Delta G_f{}^\circ(\mathrm{MA}_x)$ values:

$$\Delta G_f{}^\circ(\mathrm{MA}_x) = \Delta H_f{}^\circ(\mathrm{MA}_x) - T\Delta S_f{}^\circ(\mathrm{MA}_x) \tag{6}$$

In the systems investigated, each solute is present in low concentration (less than 1 mol%). Assuming that $\mathrm{Li}_{m-n}\mathrm{MF}_m$ and MA_x do not interact with the solvent, the values of γ_{MA_x} and $\gamma_{\mathrm{Li}_{m-n}\mathrm{MF}_m}$ are approximately estimated to be unity. The γ_{LiF} value is taken from Ref. 15 and γ_{Li} in Bi is given by [5]

$$\log \gamma_{\mathrm{Li(Bi)}} = 0.196 - \frac{3780}{T} \tag{7}$$

The other thermodynamic data of $\Delta G_f{}^\circ(\mathrm{MF}_n)$ are taken from refs. 16–19 and, referring to the case of Th [9], those of $\Delta G_f{}^\circ(\mathrm{Li_2MF_6})$ are estimated by

$$\Delta G_f{}^\circ(\mathrm{Li_2MF_6}) = \Delta G_f{}^\circ(\mathrm{MF_4}) + 2\Delta G_f{}^\circ(\mathrm{LiF}) - 10\ \mathrm{kcal\ mol^{-1}} \tag{8}$$

Figure 2 shows the evaluated enthalpy of formation of intermetallic compounds. As mentioned above, the error bars for La include the uncertainty in the determination of Li concentration in the metal phase but the others do not. For comparison, the values from refs. 20–22 are also plotted in the figure.

As pointed out by Brewer [23], the change in electron configurations should be taken into account to explain the systematic change in thermodynamic quantities of actinide and lanthanide compounds. The enthalpy of solution of gaseous atoms in the metal phase has been calculated in this way. The heat of sublimation [16, 17, 24] and the energy data of electron configurations [17, 23] have been taken from the literature. As a

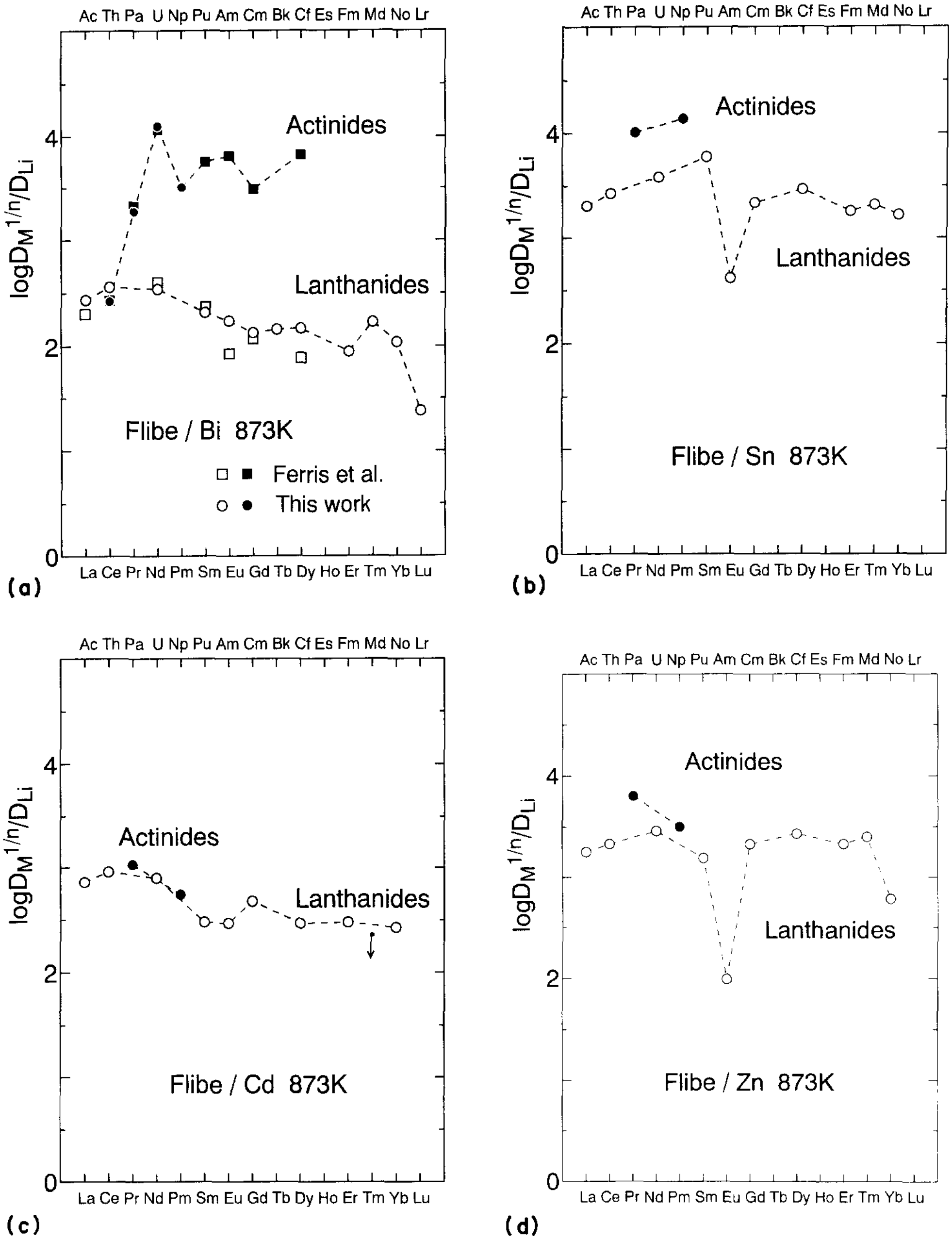

Fig. 1. Atomic number dependence of measured extractability in (a) LiF–BeF$_2$/Bi, (b) LiF–BeF$_2$/Sn, (c) LiF–BeF$_2$/Cd and (d) LiF–BeF$_2$/Zn systems at 873 K: circles, present study; squares, ref. 6.

result, Fig. 3 shows the enthalpy of solution of gaseous atoms in the Bi phase. Brewer has suggested that the ground state configuration $f^n s^2$ of gaseous lanthanide atoms is changed to $f^{n-1}dsp$ or $f^{n-1}ds^2$ in the metal phase [22] and the same situation seems to hold in the present case. As shown in Fig. 3, the enthalpy of solution which is corrected to the electron configuration dsp or ds^2 is nearly constant for all the lanthanide elements. This is well consistent with the homologous behaviour of lanthanide elements in the present extraction system. In the case of actinide elements from Th to Np the configuration d^2s^2 may be suggested as well.

Some regularities of actinides and lanthanides have been inferred from the present analysis. These are expected to be helpful for predicting unknown extractability data. However, the fine structures of the regularities are still unclear and should be studied further. For example, it may be noted that an interesting regularity, the so-called tetrad effect or double–double effect [25, 26], of the extractability of actinides and lanthanides is found in Fig. 1.

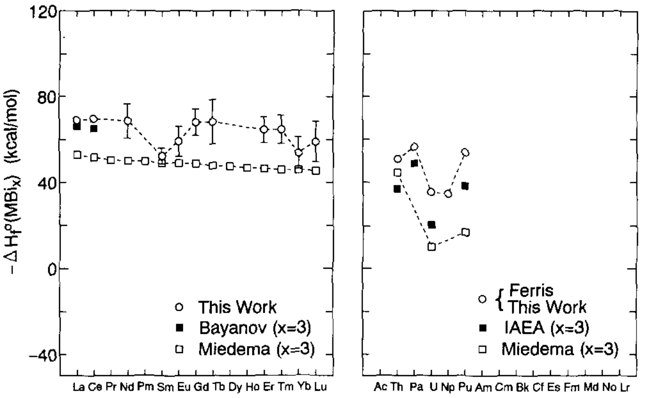

Fig. 2. Enthalpy of formation of intermetallic compounds in the Bi phase.

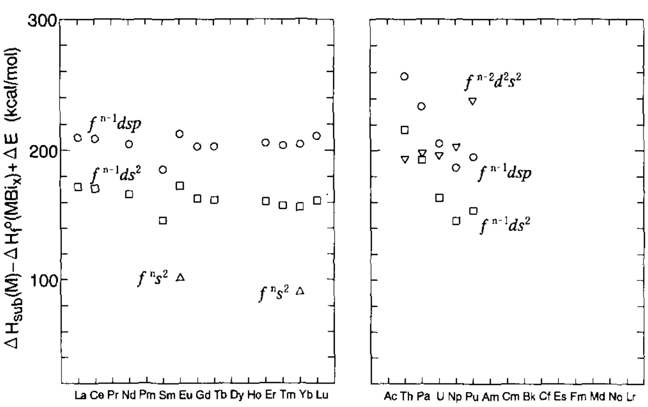

Fig. 3. Enthalpy of solution of gaseous atoms in the Bi phase.

3.4. Separation factors

The separation factors between actinide and lanthanide groups have been found to depend markedly on the nature of the metal phase, as shown in Fig. 1. The separation factor is highest in the Bi system and becomes progressively smaller in the Sn, Zn and Cd systems. The observed tendency is discussed here on the basis of the atomistic model of Miedema [22]. Such an analysis is important for searching the extraction systems for the highest performance.

Miedema has proposed the following equation for the enthalpy of formation of alloys [22]:

$$\frac{\Delta H}{N_0} = f(c)[-P(\Delta\phi^*)^2 + Q(\Delta n_{ws}{}^{1/3})^2 - R] \qquad (9)$$

where $\Delta H/N_0$ is the enthalpy of formation per atom, $f(c)$ includes factors such as the concentration dependence, $\Delta\phi^*$ is the difference in electronegativity between atoms, Δn_{ws} is the difference in electron density and P, Q and R are constants. The electronegativity ϕ^* has been determined from the work functions of metals and the electron density n_{ws} from the compressibilities and molar volumes of metals. The concentration dependence factor $f(c)$ has been given by simple equations and the parameters P, Q and R have been determined empirically.

Examining the parameters of Miedema, one may find that the correction factor R, which is attributed to additional energy contributions such as hybridization between d- and p-elements, is important for actinides and lanthanides. According to him, the R value is 2.3, 2.1, 1.4 and 1.4 for Bi, Sn, Cd and Zn respectively. A higher R value suggests a higher contribution of hybridization energies, which may give a higher separation factor between actinides and lanthanides. In fact, the order is found to be consistent with the observed tendency of the separation factors. Consequently, it can be said that a metal phase of higher R value is preferred for the group partitioning of actinides and lanthanides. From this point of view, Sb ($R = 2.3$) and Pb ($R = 2.1$) are also promising as the metal phase.

4. Conclusions

The reductive extraction behaviour of actinides and lanthanides in molten salt and liquid metal systems was studied and some conclusions were obtained as follows.

(1) By selecting LiF–BeF$_2$ as the reference salt phase, Bi, Sn, Cd and Zn have been examined as the metal phase. Actinides and lanthanides behaved as different groups and the separation factor between the two groups depended markedly on the selection of the metal phase.

(2) The thermodynamic quantities of actinides and lanthanides in the metal phase were evaluated and some regularities were found. The regularities might be useful for predicting unknown extractability values. Their fine structures should be studied further.

(3) With the help of Miedema's model, the separation factor between actinides and lanthanides was attributed to hydridization energies such as those of d- and p-elements. A metal phase of higher hybridization energy may be suggested for a higher separation factor.

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References

1 A.M. Weinberg *et al.*, *Nucl. Appl. Technol.*, *8* (1970) 105.
2 D.C. Wade and Y.I. Chang, *Nucl. Sci. Eng.*, *100* (1988) 507.

3 G.A. Jensen, A.M. Platt, G.B. Mellinger and W.J. Bjorklund, *Nucl. Technol., 65* (1984) 305.

4 K. Naito, T. Matsui and Y. Tanaka, *J. Nucl. Sci. Technol., 23* (1986) 540.

5 L.M. Ferris, J.C. Mailen and F.J. Smith, *J. Inorg. Nucl. Chem., 32* (1970) 2019.

6 L.M. Ferris, J.C. Mailen and F.J. Smith, *J. Inorg. Nucl. Chem., 33* (1971) 1325.

7 H. Moriyama, K. Yajima, Y. Tominaga, K. Moritani and J. Oishi, *Nucl. Technol., 62* (1983) 133.

8 H. Moriyama, K. Yajima, N. Nunogane, T. Ohmura, K. Moritani and J. Oishi, *J. Nucl. Sci. Technol., 21* (1984) 949.

9 H. Moriyama, N. Nunogane and J. Oishi, *J. Nucl. Sci. Technol., 24* (1987) 120.

10 J. Oishi, H. Moriyama, K. Moritani, S. Maeda, M. Miyazaki and Y. Asaoka, *J. Nucl. Mater., 154* (1988) 163.

11 H. Moriyama, K. Kinoshita and Y. Ito, *J. Nucl. Sci. Technol., 27* (1990) 827.

12 H. Moriyama, K. Kinoshita, Y. Asaoka, K. Moritani and Y. Ito, *J. Nucl. Sci. Technol., 27* (1990) 937.

13 H. Moriyama, K. Kinoshita, T. Seshimo, Y. Asaoka, K. Moritani and Y. Ito, *Proc. 3rd Int. Conf. on Nuclear Fuel Reprocessing and Waste Mamagement, Sendai, 1991*, The Atomic Energy Society of Japan, 1991, Vol. 2, p. 639.

14 H. Moriyama, M. Miyazaki, Y. Asaoka, K. Moritani and J. Oishi, *J. Nucl. Mater., 182* (1991) 113.

15 A.L. Mathews and C.F. Baes Jr., *Inorg. Chem., 7* (1963) 373.

16 Y.-C. Kim, Thermochemical study of lanthanide elements and their halides, *Thesis*, Kyoto University, 1979.

17 J.J. Katz, G.T. Seaborg and L.R. Morss, *The Chemistry of the Actinide Elements*, Vol. 2, Chapman and Hall, London, 1986.

18 W.J. Hamer, M.S. Malmberg and B. Rubin, *J. Electrochem. Soc., 112* (1965) 750.

19 N.P. Galkina, *Basic Properties of Inorganic Fluorides*, Atom, Moscow, 1976.

20 P. Chiotti, V.V. Akhachinskij, I. Ansara and M.H. Rand, *The Chemical Thermodynamics of Actinide Elements and Compounds*, Part 5, *The Actinide Binary Alloys*, IAEA, Vienna, 1981.

21 A.P. Bayanov, *Russ. Chem. Rev., 44* (1975) 122.

22 F.R. de Boer, R. Boom, W.C.M. Mattens, A.R. Miedema and A.K. Niessen, *Cohesion in Metals, Transition Metal Alloys*, North-Holland, Amsterdam, 1988.

23 L. Brewer, *J. Opt. Soc. Am., 61* (1971) 1101.

24 R.C. Weast, M.J. Astle and W.H. Beyer, *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 1984.

25 D.F. Peppard, C.A.A. Bloomquist, E.P. Horwitz, S. Lewey and G.W. Mason, *J. Inorg. Nucl. Chem., 33* (1971) 1325.

26 V.I. Spitsyn, V.G. Vokhmin and G.V. Ionova, *Int. Rev. Phys. Chem., 4* (1985) 57.