

**Hydration change reaction of light REE<sup>3+</sup>(aq) series-II:  
Contrasting nephelauxetic effects between hydrated  
[REE(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup> and [REE(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup> series  
and the tetrad effects in their hydration enthalpies  
and REE-OH<sub>2</sub> distances**

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**ABSTRACT**

Light REE<sup>3+</sup>(aq) is a mixture of two distinguishable species of nonhydrate and octahydrate in equilibrium with respect the hydration change reaction that [REE(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup>(aq)+H<sub>2</sub>O(l)=[REE(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup>(aq), and the apparent hydration number of light REE<sup>3+</sup>(aq) is changing across the series. Here is discussed nephelauxetic effects of the two REE<sup>3+</sup>(aq) series from  $\Delta H_r^0$  data for the hydration change reaction and the tetrad effect variations of their hydration enthalpies ( $\Delta H_{hyd}$ ) and REE-OH<sub>2</sub> distances. The  $\Delta H_r^0$  data combined with those data for solution of REE(ES)<sub>3</sub>·9(H<sub>2</sub>O) with ES = C<sub>2</sub>H<sub>5</sub>SO<sub>4</sub><sup>-</sup> reported previously, suggest that Racah (E<sup>1</sup> and E<sup>3</sup>) parameters for light REE<sup>3+</sup> like Nd<sup>3+</sup> decrease in the following order: [REE(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup>(aq) > REE(ES)<sub>3</sub>·9(H<sub>2</sub>O) > [REE(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup>(aq). The average REE<sup>3+</sup>-OH<sub>2</sub> distance also decreases in this order. Hence this is a nephelauxetic series that Racah parameters are reduced with decreasing REE<sup>3+</sup>-OH<sub>2</sub> distance. The Racah parameters for [REE(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup>(aq) series are fairly large and comparable with those of gaseous free REE<sup>3+</sup>. No significant tetrad effect is expected in its series variation of ( $-\Delta H_{hyd}$ ). By contrast, [REE(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup>(aq) series has significantly smaller Racah parameters than gaseous free REE<sup>3+</sup>, and a convex tetrad effect is expected in the series variation of ( $-\Delta H_{hyd}$ ). Since ( $-\Delta H_{hyd}$ ) of [REE(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup>(aq) in heavy REE series is fitted to a linear function of the reciprocal of observed REE-OH<sub>2</sub> distance in REECl<sub>3</sub> solution, this relation has been extended to light REE series, and a similar relation for [REE(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup>(aq) in light REE series has also been determined from our thermodynamic mixture model and observed REE-OH<sub>2</sub> distances in REECl<sub>3</sub> (REE=La, Pr and Nd) solutions. The reciprocal of REE-OH<sub>2</sub> distance in [REE(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup>(aq), when plotted against the atomic number of REE, indicates a small convex tetrad effect whereas such an effect is absent in [REE(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup>(aq), in accordance with their nephelauxetic effects. Interestingly, ( $-\Delta H_{hyd}$ ) of [REE(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup>(aq) satisfies a linear function of 1/(REE

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–  $\text{OH}_2$ ), and at the same time, the series variations of both ( $-\Delta H_{\text{hyd}}$ ) and  $1/(\text{REE} - \text{OH}_2)$  exhibit small convex tetrad effects when plotted against the atomic number of REE. This is analogous to the relationship between the lattice enthalpy of  $\text{REEO}_{1.5}$  (cubic) and REE-O distance. The property of ( $-\Delta H_{\text{hyd}}$ ) and the lattice enthalpy of  $\text{REEO}_{1.5}$  can be understood from the viewpoints: i) the existence of REE(III) cluster with the equilibrium configuration having the minimum energy by itself, and ii) the classical limit in quantum-chemical energetics where Planck's constant ( $h$ ) equals zero. It is emphatically noted that the observed tetrad effects and RSPET can complement the classical ion model with a tactic by which internal structures of the real  $\text{REE}^{3+}$  ions are legitimately introduced into our thermodynamic discussion.

## INTRODUCTION

As described in the first part of this study (Kawabe *et al.*, 2006), the hydration state of light  $\text{REE}^{3+}(\text{aq})$  is changing across the series. Miyakawa *et al.* (1988) and Kawabe (1999a) independently presented the thermodynamic discussion of hydration change of  $\text{REE}^{3+}(\text{aq})$ . Miyakawa *et al.* (1988) discussed that  $\text{REE}^{3+}(\text{aq})$  is a mixture of two species of nonahydrate and octahydrate in equilibrium with respect to the hydration change reaction:



In fact, Miyakawa *et al.* (1988) used the reverse one of (1), but we will use (1) here in order to make the immediate comparison with the discussion by Kawabe (1999a). Miyakawa *et al.* (1988) estimated thermodynamic parameters for the hydration change reaction at 25°C and 1 atm from the calculated hydration enthalpies and free energies for  $[\text{REE}(\text{OH}_2)_9]^{3+}$  and  $[\text{REE}(\text{OH}_2)_8]^{3+}$  on the basis of an electrostatic bonding energy model for the complexes and Born's hydration model. At the same time, they presented the temperature variation of ultra-violet (4f→5d) absorption spectra of aqueous  $\text{Ce}(\text{III})(\text{ES})_3$  ( $\text{ES} = \text{C}_2\text{H}_5\text{SO}_4^-$ ) solution, and showed the absorption bands of octahydrate  $\text{Ce}^{3+}(\text{aq})$  and nonahydrate  $\text{Ce}^{3+}(\text{aq})$  in the aqueous  $\text{Ce}(\text{ES})_3$  solution. The thermodynamic parameters for the reverse reaction of (1) with  $\text{REE}=\text{Ce}$  were estimated from the temperature variation of ultra-violet absorption spectra of aqueous  $\text{Ce}(\text{III})(\text{ES})_3$  solution, and the parameters were moderately comparable with the calculated ones.

On the other hand, Kawabe (1999a) evaluated the thermodynamic parameters ( $\Delta H_{\text{hyd}}^*$  and  $\Delta G_{\text{hyd}}^* = \Delta H_{\text{hyd}}^* - T\Delta S_{\text{hyd}}^*$ ) for the following reaction for  $\text{REE} = \text{La}-\text{Gd}$  at 25°C and 1 atm:



The parameters represent the deviations of the thermodynamic quantities for real  $\text{REE}^{3+}(\text{aq})$  relative to those for hypothetical octahydrate  $\text{REE}^{3+}(\text{aq})$  in the light REE series. They were determined from the thermodynamic data for solution of the fully isomorphous series of  $\text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$  ( $\text{ES} = \text{C}_2\text{H}_5\text{SO}_4^-$ ) and the partly isomorphous series of  $\text{REECl}_3 \cdot n\text{H}_2\text{O}$  ( $n = 7$  for  $\text{La} - \text{Pr}$  and  $n = 6$  for  $\text{Nd} - \text{Lu}$ ) at 25°C and 1 atm, and their regressions to the improved RSPET (refined spin-pairing energy theory) equation by Kawabe (1992). The values of  $\Delta G_{\text{hyd}}^* = \Delta H_{\text{hyd}}^* - T\Delta S_{\text{hyd}}^*$  have been used to eliminate

the hydration change effect from  $\Delta G_r^0$  for geochemical reactions involving REE<sup>3+</sup>(aq) (Kawabe, 1999b; Kawabe *et al.*, 1999; Ohta and Kawabe, 2000a, b and 2001).

In the first part of our study (Kawabe *et al.*, 2006), we have demonstrated that the thermodynamic parameters for the reactions (2) are readily converted into those for the reaction (1) and *vice versa*, and that the standard-state  $\Delta G_r^0$  values for (1) from  $\Delta G_{hyd}^*$  in Kawabe (1999a) are more acceptable than those calculations by Miyakawa *et al.* (1988). The  $\Delta G_r^0$  values for (1) at hydrothermal conditions up to 250°C have been calculated using the standard-state  $\Delta H_r^0$  and  $\Delta S_r^0$  data for (1) and the equation by Helgeson (1967 and 1969). The theoretical estimates are compatible with our recent experimental results of REE(III) partition coefficients between Fe(III) oxyhydroxide and aqueous solution and stability constants of REE(III)-carbonate complexes in hydrothermal conditions (Takahashi and Kawabe, 2004).

This paper as the second part of our study of hydration change of REE<sup>3+</sup>(aq) series, deals with the nephelauxetic effects in  $[\text{REE}(\text{OH}_2)_9]^{3+}(\text{aq})$  and  $[\text{REE}(\text{OH}_2)_8]^{3+}(\text{aq})$  at 25°C and 1 atm pressure, together with the series variations of the hydration enthalpies and REE-OH<sub>2</sub> distances in the two REE<sup>3+</sup>(aq) complex series. The difference in nephelauxetic effect between the two hydrates can be seen as the tetrad effects of the series variations of the standard-state  $\Delta H_r^0$  data for the reaction (1), although the series variations are only for light REE. Individual nephelauxetic effects can be found in their series variations of negative of hydration enthalpies plotted against the atomic number of REE. The experimental hydration enthalpy of each light REE<sup>3+</sup>(aq) is an average of those for the two hydrates weighted by their abundances. Likewise, the observed REE-OH<sub>2</sub> distance in each light REE<sup>3+</sup>(aq) by X-ray diffraction (Habenschuss and Spedding, 1979a, b and 1980) must be an average of REE-OH<sub>2</sub> distances in the two hydrates with weighting factors given by their abundances. This is legitimate from the thermodynamic mixture model for light REE<sup>3+</sup>(aq) in the first paper (Kawabe *et al.*, 2006) as well as from the spectroscopic evidence in aqueous Ce(III) solutions by Jørgensen and Brinen (1963) and Miyakawa *et al.* (1988).

We will show that the negative of hydration energy of  $[\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq})$  not only satisfies a linear function of the reciprocal of observed REE-OH<sub>2</sub> distance approximately but also exhibits a convex tetrad effect when plotted against the atomic number of REE, in accordance with the nephelauxetic effect. This situation is quite analogous to the lattice energies of REEO<sub>1.5</sub>(cubic) and observed REE-O distances as discussed in Kawabe (1992). Previous studies in REE chemistry and geochemistry have paid little attention to the interesting facts, but how we understand the facts must be crucial in considering the relationships among structures, thermodynamics, and quantum-chemical energetics of 4f electrons of REE(III) complexes and compounds. The proper understanding may provide a new perspective of REE chemistry and geochemistry.

## RESULTS AND DISCUSSION

### 1) REE-OH<sub>2</sub> distance in REE<sup>3+</sup>(aq) affected by its hydration change

As shown in the first part (Kawabe *et al.*, 2006), each equilibrium constant for the hydration change reaction (1),

**Table 1** Summary of conventional hydration enthalpies for  $\text{REE}^{3+}(\text{aq})$  and octahydrate and nonahydrate  $\text{REE}^{3+}(\text{aq})$  series, experimental  $\text{REE-OH}_2$  distances in  $\text{REECl}_3$  solutions, and  $\text{REE-OH}_2$  distances for octahydrate and nonahydrate  $\text{REE}^{3+}(\text{aq})$  series calculated by the thermochemical model for hydration change of light  $\text{REE}^{3+}(\text{aq})$  series in this study.

	$\Delta H_{\text{hyd}}(\text{REE}^{3+}, \text{aq})^{\text{a)}$ (kJ/mol)	$\text{REE-OH}_2$ in $\text{REECl}_3$ solutions <sup>b)</sup> (pm)	$\Delta H_{\text{hyd}}(\text{octa REE}^{3+}, \text{aq})^{\text{c)}$ (kJ/mol)	$\text{REE-OH}_2$ in octa $\text{REE}^{3+}(\text{aq})^{\text{d)}$ (pm)	$\Delta H_{\text{hyd}}(\text{nona REE}^{3+}, \text{aq})^{\text{e)}$ (kJ/mol)	$\text{REE-OH}_2$ in nona $\text{REE}^{3+}(\text{aq})^{\text{f)}$ (pm)
La	-12.0	258.0	-28.9	252.27	-11.01	258.59
Ce	-71.4		-83.8	249.74	-69.72	256.23
Pr	-111.1	253.9	-120.6	248.08	-108.90	254.68
Nd	-141.5	251.3	-149.1	246.80	-138.25	253.54
Sm	-196.8	247.4	-198.4	244.63	-192.20	251.45
Eu	-226.0	245.0	-226.3	243.42	-222.80	250.29
Gd	-253.5		-253.6	242.25	-251.00	249.22
Tb	-287.0	240.9	-287.0	240.82		
Dy	-317.4	239.6	-317.4	239.54		
Ho	-350.8		-350.8	238.15		
Er	-374.5	236.9	-374.5	237.18		
Tm	-408.3	235.8	-408.3	235.80		
Yb	-438.3		-438.3	234.58		
Lu	-461.4	233.8	-461.4	233.66		

- a) The conventional hydration enthalpies for  $\text{REE}^{3+}(\text{aq})$  given by eq. (8) in the text. Addition of three times the absolute hydration enthalpy for hydrogen ion [ $3 \times (-1114) = -3342$  kJ/mol, when Morss(1994) is accepted] to the conventional ones are the absolute hydration enthalpies for  $\text{REE}^{3+}(\text{aq})$ .
- b) X-ray diffraction data for  $\text{REECl}_3$  solutions ( $m = 3.2 - 3.8$  mol/kg) by Habenshuss and Spedding (1979a, b and 1980).
- c) The experimental values of conventional hydration enthalpies in the first column are corrected for the hydration change in light REE series from La to Gd by using the thermodynamic data listed in part-I:  $\Delta H_{\text{hyd}}(\text{octa REE}^{3+}, \text{aq}) = \Delta H_{\text{hyd}}(\text{REE}^{3+}, \text{aq}) - \Delta H^*(\text{REE}^{3+}, \text{aq})$ .
- d) The linear relation of eq. (9) between hydration enthalpy and the reciprocal of  $\text{REE-OH}_2$  distance in  $\text{REECl}_3$  solutions for heavy REE (Habenshuss and Spedding, 1979a, b and 1980) are extended into the entire series, and  $\text{REE-OH}_2$  distances for the other octahydrate  $\text{REE}^{3+}(\text{aq})$  have been evaluated. See Fig. 2.
- e) The experimental values of conventional hydration enthalpies in the first column are corrected for the hydration change in light REE series using the thermodynamic data listed in part-I:  $\Delta H_{\text{hyd}}(\text{nona REE}^{3+}, \text{aq}) = \Delta H_{\text{hyd}}(\text{octa REE}^{3+}, \text{aq}) + \Delta H^0(\text{REE}^{3+}, \text{aq})$ .
- f) The linear relation of eq. (9) between hydration enthalpy and the reciprocal of  $\text{REE-OH}_2$  distance for the nonahydrate series has been estimated by using eqs. (5), (7) and experimental  $\text{REE-OH}_2$  distances in  $\text{REECl}_3$  solutions for REE = La, Pr and Nd (Habenshuss and Spedding, 1979a, b and 1980). See Fig. 2.

$$K_{hyd} = \frac{a([\text{REE}(\text{H}_2\text{O})_9]^{3+}, aq)}{a([\text{REE}(\text{H}_2\text{O})_8]^{3+}, aq) \cdot a(\text{H}_2\text{O})} = a_{nona} / (a_{octa} \cdot a_w), \quad (3)$$

can be replaced by the molar fraction ratio between  $[\text{REE}(\text{OH}_2)_9]^{3+}(\text{aq})$  and  $[\text{REE}(\text{OH}_2)_8]^{3+}(\text{aq})$  approximately:

$$RT \ln[a_{nona} / (a_{octa} \cdot a_w)] \approx RT \ln[x_9 / x_8] \approx -\Delta G_{hc}^0(\text{REE}^{3+}, aq), \quad (4)$$

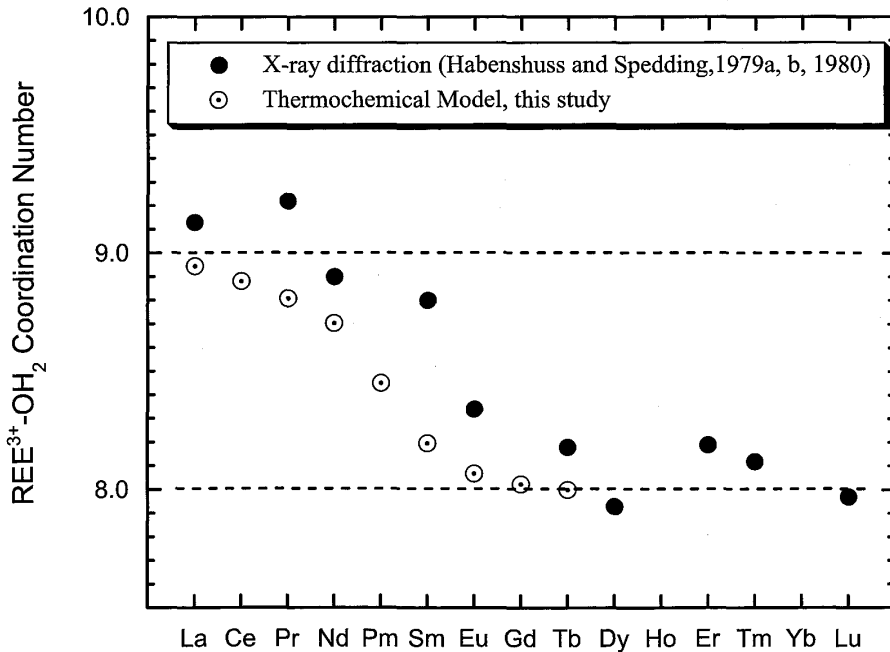
where  $x_9$  and  $x_8$  stand for the fractions of molal concentrations of  $[\text{REE}(\text{OH}_2)_9]^{3+}(\text{aq})$  and  $[\text{REE}(\text{OH}_2)_8]^{3+}(\text{aq})$ , respectively, to the total molal concentration of  $\text{REE}^{3+}(\text{aq})$ . This can be solved with respect to  $x_9$  ( $= 1 - x_8$ ):

$$x_9 = \exp[-\Delta G_{hc}^0 / (RT)] / \{1 + \exp[-\Delta G_{hc}^0 / (RT)]\} = 1 - x_8. \quad (5)$$

Using (5) and  $\Delta G_{hyd}^0(\text{REE}^{3+}, aq)$  at 25°C in Table 1 in the first part (Kawabe *et al.*, 2006), we can calculate the apparent hydration number of light  $\text{REE}^{3+}(\text{aq})$  as follows

$$N_{hyd}(\text{REE}^{3+}, calc) = 9 \cdot x_9 + 8 \cdot x_8. \quad (6)$$

Although  $N_{hyd}(\text{REE}^{3+}, calc)$  is limited within the range between 8 and 9 in our model, we have compared  $N_{hyd}(\text{REE}^{3+}, calc)$  with the hydration number of inner sphere water coordination of  $\text{REE}^{3+}$  determined in  $\text{REE}(\text{III})$  chloride solution by X-ray diffraction technique (Habenschuss and Spedding, 1979a, b and 1980) in Fig. 1. The other data



**Fig. 1** The hydration numbers of  $\text{REE}^{3+}(\text{aq})$  series determined in  $\text{REE}(\text{III})$  chloride solutions by X-ray diffraction technique by Habenschuss and Spedding (1979a, b and 1980), compared with the calculated ones of  $N_{hyd}(\text{REE}^{3+}, calc) = 9 \cdot x_9 + 8 \cdot x_8$  in this study. Here is assumed that  $N_{hyd}(\text{Tb}^{3+}, calc) = 8$ . Although highly concentrated  $\text{REE}(\text{III})$  chloride solutions with  $m > 3$  (mol/kg) have been used, the experimental hydration numbers for the light to middle  $\text{REE}^{3+}$  series by X-ray technique are fairly sub-parallel with  $N_{hyd}(\text{REE}^{3+}, calc) = 9 \cdot x_9 + 8 \cdot x_8$  in this study.

of hydration numbers of  $REE^{3+}(aq)$  in  $REE(III)$  chloride or other solutions determined by X-ray and neutron diffraction methods (Rizkalla and Choppin, 1991; Ohataki and Radnai, 1993) are not shown in Fig. 1, because they scatter considerably around the cited data. The hydration numbers by X-ray diffraction technique have been determined using concentrated  $REE(III)$  chloride solutions with  $m(REECl_3)=3.2-3.8$  mol/kg (Habenschuss and Spedding, 1979a,b and 1980), but it has been shown that the inner sphere water coordination of each  $REE^{3+}$  is made up exclusively of water molecules even in the concentrated chloride solution. In spite of the difference between such concentrated  $REE(III)$  chloride solutions and those of  $REE^{3+}(aq)$  in standard-state presumed here, the variation pattern of  $N_{hyd}(REE^{3+}, calc)$  across the light REE series in Fig. 1 is fairly parallel with that of the experimental hydration number of  $REE^{3+}$  reported by Habenschuss and Spedding (1979a, b and 1980).

The following equation for  $REE-OH_2$  distances in  $REECl_3$  solutions analogous to (6),

$$[REE^{3+} - OH_2]_{obs} = x_9 \cdot [REE^{3+} - OH_2]_{nona} + x_8 \cdot [REE^{3+} - OH_2]_{octa}, \quad (7)$$

is to be considered more seriously than (6), since the experimental  $REE-OH_2$  distances in  $REECl_3$  solutions are much more precisely determined than the hydration numbers (Habenschuss and Spedding, 1979a, b and 1980). On the other hand, the conventional hydration enthalpies of  $REE^{3+}(aq)$  at the standard state are given by the following equation:

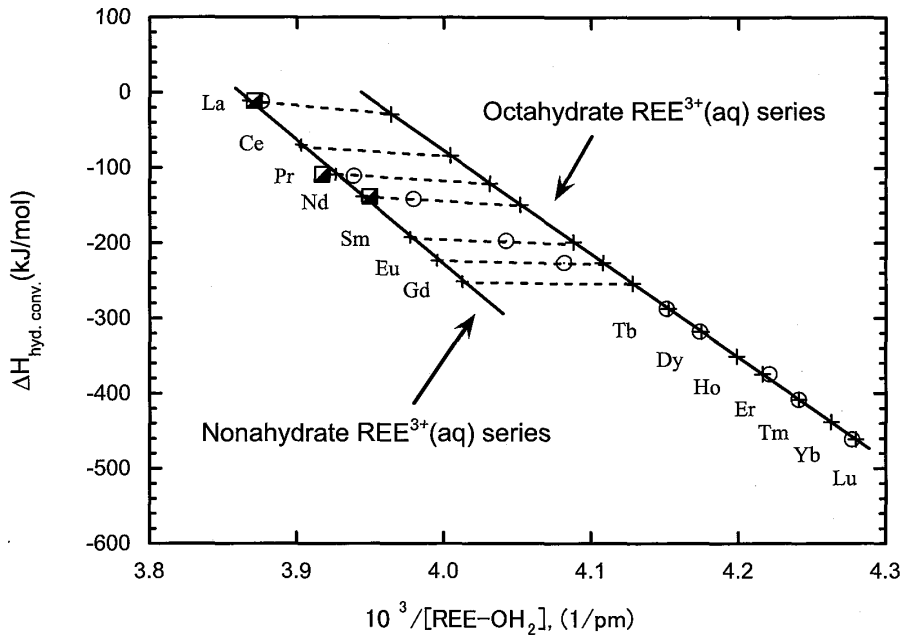
$$\begin{aligned} \Delta H_{hyd.comv} &\equiv \Delta H_{hyd.abs}^0 - 3\Delta H_{hyd.abs}^0(H^+) \\ &= \Delta H_f^0(REE^{3+}, aq) - \Delta H_v^0(REE, c) - \sum_{i=1}^3 I_i(REE) + 3[I_H + \Delta H_f^0(H, g)]. \end{aligned} \quad (8)$$

We will use  $\Delta H_{hyd.comv}$  instead of  $\Delta H_{hyd.abs}^0$ , because  $\Delta H_{hyd.abs}^0$  values depend on the choice of  $\Delta H_{hyd.abs}^0(H^+)$  values: Marcus (1977) recommended that  $\Delta H_{hyd.abs}^0(H^+) = -(1100 \pm 6)$ , but Rizkalla and Choppin (1991) used slightly different  $\Delta H_{hyd.abs}^0(H^+)$  values, and Morss (1994) argued that  $\Delta H_{hyd.abs}^0(H^+) = -1114$  kJ/mol. The values of  $\Delta H_{hyd.comv}$  for octahydrate  $REE^{3+}(aq)$  series can be approximated by a linear function of the reciprocal of  $[REE^{3+} - OH_2]$  distance reported by Habenschuss and Spedding (1979a, b and 1980):

$$\Delta H_{hyd.comv} = \frac{A}{[REE^{3+} - OH_2]} + B. \quad (9)$$

The plots of eq. (9) for the heavy  $REE^{3+}(aq)$  are shown in Fig. 2. The values of  $\Delta H_{hyd.comv}$  of (8) have been calculated using the vaporization enthalpies for REE metals and the sum of first three ionization energies of REE in Kawabe (1992), the experimental data of  $\Delta H_f^0(REE^{3+}, aq)$  in Morss (1994), and  $3[I_H + \Delta H_f^0(H, g)] = 4584.0$  (kJ/mol). Hereafter we will write  $\Delta H_{hyd.comv}$  in (8) and (9) as  $\Delta H_{hyd}$  in short.

In Fig. 2, the linear relation for octahydrate  $REE^{3+}(aq)$  series has been determined using  $\Delta H_{hyd}$  in this study and the observed  $REE - OH_2$  distances in the inner sphere water coordination in  $REECl_3$  solutions for  $REE = Tb, Dy, Er, Tm$  and  $Lu$  (Habenschuss and Spedding, 1979a, b and 1980), and then it has been extended into light REE one. The linear relation in (kJ/mol) and *pm* for  $(REE - OH_2)$  is given by



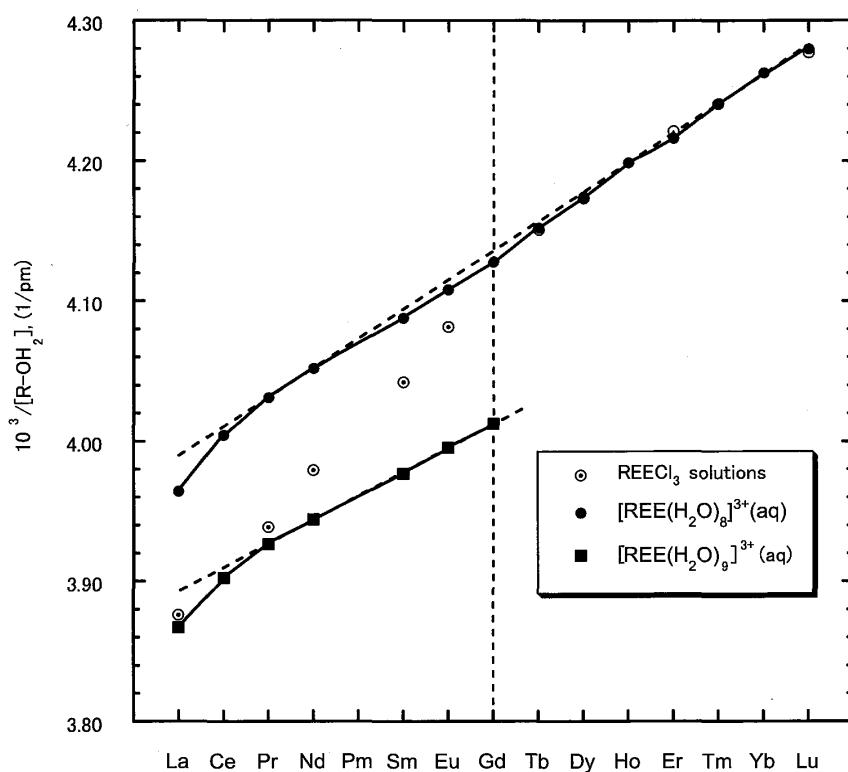
**Fig. 2** The conventional hydration enthalpies,  $N_{hyd}(REE^{3+},aq)$ , in this study are plotted against the reciprocal of REE-OH<sub>2</sub> distance in REECl<sub>3</sub> solution by X-ray diffraction (Habenschuss and Spedding, 1979a, b and 1980) with open circles. The linear relationship (solid line) for the octahydrate series is determined using the  $\Delta H_{hyd}(REE^{3+},octa)$  values in this study and  $[REE^{3+} - OH_2]_{obs}$  data in REECl<sub>3</sub> solutions with REE=Tb, Dy, Er, Tm, and Lu. The  $1/[REE^{3+} - OH_2]$  values for the others (crosses) are calculated by the linear relation and  $\Delta H_{hyd}(REE^{3+},octa)$  values in this study. The three half-filled squares for nonahydrate REE<sup>3+</sup>(aq) (La, Pr and Nd) have been calculated from our mixture model and the REE-OH<sub>2</sub> distances in REECl<sub>3</sub> solutions for REE=La, Pr and Nd (see text), and they have been regressed by the solid line. The  $1/[REE^{3+} - OH_2]_{nona}$  values for La ~ Gd (crosses) have been re-calculated by the linear relation and the  $\Delta H_{hyd}(REE^{3+},nona)$  values in this study.

$$\Delta H_{hyd}(REE^{3+},aq)_{octa} = -1370.22 \times [10^3/(REE - OH_2)] + 5402.74.$$

The light REE-OH<sub>2</sub> distances in octahydrate series can be evaluated from the extended linear relation and  $\Delta H_{hyd}$  for octahydrate REE<sup>3+</sup>(aq) in this study. The data of  $\Delta H_{hyd}$  and  $[REE^{3+} - OH_2]$  plotted in Fig. 2 are summarized in Table 1. With going from Gd to La in Fig. 2, the reciprocal of observed  $[REE^{3+} - OH_2]$  distances in REECl<sub>3</sub> solutions (Habenschuss and Spedding, 1979a, b and 1980) obviously deviate from the linear relationship for the octahydrate series and approaches that for nonahydrates. This is the hydration change effect in the relationship between  $\Delta H_{hyd}$  and the reciprocal of  $[REE^{3+} - OH_2]$  distance in REE<sup>3+</sup>(aq) series. How the linear relation for the nonahydrate REE<sup>3+</sup>(aq) series shown in Fig. 2 was derived will be explained in the next subsection.

## 2) Linear relationships between $\Delta H_{hyd}$ and $1/[REE^{3+} - OH_2]$ in the two series

Using the linear function of (9) and  $\Delta H_{hyd}$  for the octahydrates of heavy REE in this study (Fig. 2), we have estimated the  $[REE^{3+} - OH_2]_{(octa)}$  distances in the octahydrates of light REE. We also assume a similar linear function for the nonahydrate series in light REE, and we have evaluated  $[REE^{3+} - OH_2]_{(nona)}$  in the light REE series by



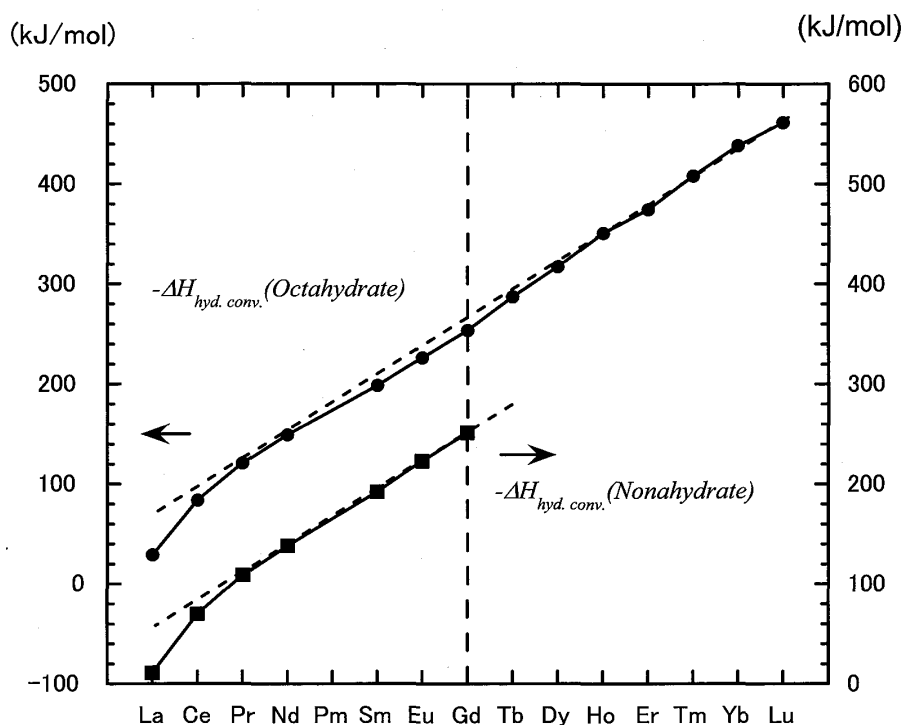
**Fig. 3-1** Plots of  $1/[REE^{3+} - OH_2]_{nona}$  and  $1/[REE^{3+} - OH_2]_{octa}$  for light  $REE^{3+}(aq)$  against the atomic number of REE. The experimental REE- $OH_2$  distances in  $REECl_3$  solutions (Habenschuss and Spedding, 1979a, b and 1980) are also plotted. The plotted data (filled circles and squares) are the same as the crosses in Fig. 2. They are satisfying the linear relations with their hydration enthalpies. A small concave tetrad effect is suggested in the series variation of  $1/[REE^{3+} - OH_2]_{octa}$ , but such an effect cannot be suggested in that of  $1/[REE^{3+} - OH_2]_{nona}$ .

using eq. (7),  $x_8$  and  $x_9$  from (5), and  $[REE^{3+} - OH_2]_{(octa)}$ . The REE- $OH_2$  distances in  $REECl_3$  solutions are not perfectly consistent with our model as is seen in Fig. 1, but the REE- $OH_2$  distance data in La, Pr and Nd chloride solutions could be used as approximate values of  $[REE^{3+} - OH_2]_{(obs)}$  for eq. (7). In this way, we have calculated  $[REE^{3+} - OH_2]_{(nona)}$  for La, Pr and Nd (three half-filled squares in Fig. 2), and then the linear function of (9) for  $[REE^{3+} - OH_2]_{(nona)}$  has been determined from the three data points. After that,  $[REE^{3+} - OH_2]_{(nona)}$  for all light  $REE^{3+}$  have been re-calculated using the linear relation and  $\Delta H_{hyd}$  for nonhydrate  $REE^{3+}(aq)$  in this study. The results have already been shown in Fig. 2 are listed in Table 1. The linear relation for nonhydrate  $REE^{3+}(aq)$  series in (kJ/mol) for  $\Delta H_{hyd}$  and  $pm$  for  $(REE - OH_2)$  is written as

$$\Delta H_{hyd}(REE^{3+}, aq)_{nona} = -1650.18 \times [10^3/(REE - OH_2)] + 6370.40.$$

The regressed values of  $1/[REE^{3+} - OH_2]_{(octa)}$  for all REE and  $1/[REE^{3+} - OH_2]_{(nona)}$  for light REE are plotted against the atomic number of REE, together with those data in  $REECl_3$  solutions (Habenschuss and Spedding, 1979a, b and 1980) in Fig. 3-1. A small convex tetrad effect is suggested in the series variation of  $1/[REE^{3+} - OH_2]_{(octa)}$ , but no such an effect is in the variation of  $1/[REE^{3+} - OH_2]_{(nona)}$ . Figure 3-2 shows





**Fig. 3-2** Plots of  $-\Delta H_{hyd}(\text{octahydrate } REE^{3+}, aq)$  and  $-\Delta H_{hyd}(\text{nonahydrate } REE^{3+}, aq)$  against the atomic number of REE. The sets of  $(-\Delta H_{hyd})$  values for the two  $REE^{3+}(aq)$  series are satisfying the respective linear relations with the reciprocals of  $[REE^{3+} - OH_2]$  distances shown in Fig. 2 (cross symbols). The plot of  $(-\Delta H_{hyd})$  for octahydrate series suggest a small convex tetrad effect, but that for nonahydrate series does not.

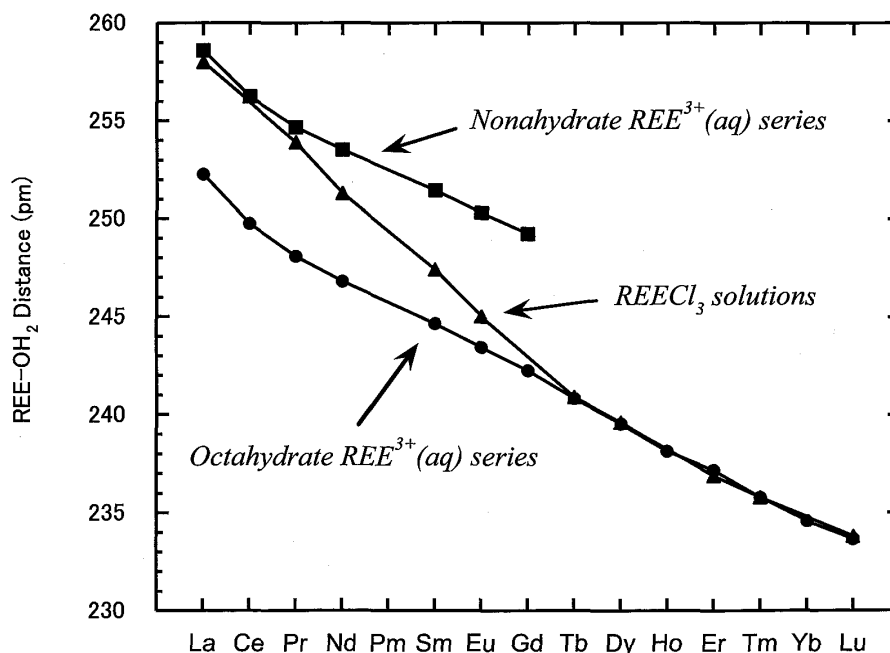
the negatives of  $\Delta H_{hyd}$  plotted against the atomic number of REE. Because the constant coefficient  $A$  of the linear function of eq. (9) is negative, so that  $(-\Delta H_{hyd})$  for octahydrate  $REE^{3+}(aq)$  shows a small convex tetrad effect in the same manner as in Fig. 3-1. The interesting and important point is that the linear relations in Fig. 2 are totally compatible with the plots of Fig. 3-1 and 3-2. The set of  $(-\Delta H_{hyd})$  data for octahydrate  $REE^{3+}(aq)$  shows a small convex tetrad effect when plotted against the atomic number of REE (Fig. 3-2), but  $(-\Delta H_{hyd})$  for the octahydrate series exhibits a linear relation when plotted against  $1/[REE^{3+} - OH_2]_{(octa)}$  (Fig. 2).

Kawabe (1992) showed that the lattice energy of  $REEO_{1.5}(\text{cub})$ , which is approximately the same as the enthalpy change for the reaction  $REEO_{1.5}(\text{cub}) = REE^{3+}(g) + (3/2)O_2(g)$ , is regressed by a linear function of  $1/[REE-O]$  like (9), and at the same time the lattice enthalpy of  $REEO_{1.5}(\text{cub})$  shows a convex tetrad effect when plotted against the atomic number of REE. The latter means that  $REEO_{1.5}(\text{cub})$  has smaller Racah parameters than  $REE^{3+}(g)$ . This is quite analogous to the situation indicated by Figs. 2, 3-1 and 3-2. Notice that  $(-\Delta H_{hyd})$  is the enthalpy change for the reaction that  $REE^{3+}(aq) = REE^{3+}(g)$ . The convex series variation of  $(-\Delta H_{hyd})$  for octahydrate  $REE^{3+}(aq)$  means that octahydrate  $REE^{3+}(aq)$  has smaller Racah parameters than  $REE^{3+}(g)$ .  $\Delta H_{hyd}$  itself corresponds to the reaction that  $REE^{3+}(g) = REE^{3+}(aq)$ , and then  $\Delta H_{hyd}$  for octahydrate  $REE^{3+}(aq)$  indicates a small concave tetrad effect when plotted against the atomic number of REE.

### 3) $REE^{3+}$ ionic radii, $REE^{3+} - OH_2$ distances in $REE^{3+}(aq)$ and their reciprocals

When  $[REE^{3+} - OH_2]_{(nona)}$  and  $[REE^{3+} - OH_2]_{(octa)}$  are plotted against the atomic number of REE as in Fig. 4, the series variation of  $[REE^{3+} - OH_2]_{(octa)}$  indicates a smooth variation with a small concave tetrad effect, but that of  $[REE^{3+} - OH_2]_{(nona)}$  appears to be a smooth one without such a tetrad effect. In our view, however, the linear relationship between  $\Delta H_{hyd}$  and  $1/[REE^{3+} - OH_2]$  (Fig. 2) and the plots of  $1/[REE^{3+} - OH_2]$  or  $\Delta H_{hyd}$  against the atomic number of REE (Figs. 3-1 and 3-2) are more significant than the plot of  $[REE^{3+} - OH_2]$  against the atomic number of REE (Fig. 4), because the reciprocal of  $[REE^{3+} - OH_2]$  is a "good" energy parameter relating directly to the hydration enthalpy of  $REE^{3+}(aq)$  (Fig. 2), but  $[REE^{3+} - OH_2]$  cannot be such an energy parameter. The linear relationships between  $\Delta H_{hyd}$  and  $1/[REE^{3+} - OH_2]$  (Fig. 2) can illustrate the hydration change in light  $REE^{3+}(aq)$ , and the plots of  $1/[REE^{3+} - OH_2]$  and  $(-\Delta H_{hyd})$  against the atomic number of REE (Fig. 3-1 and -2) reveal convex tetrad effects in  $1/[REE^{3+} - OH_2]$  and  $(-\Delta H_{hyd})$ . The interaction energy between a pair of classical charged ions is proportional to  $r^{-1}$  (the reciprocal of their distance), but the interaction energies for the pair of ion-dipole, dipole-dipole, ion-induced dipole, and dipole-induced dipole are all proportional to higher orders of power than  $r^{-1}$  (Marcus, 1982). Water molecule ( $H_2O$ ) is not charged ion, but it is frequently approximated as a dipole (Ohtaki *et al.*, 1976). Nevertheless a linear function of  $r^{-1}$  is clearly seen in the relationship between  $\Delta H_{hyd}$  and  $1/[REE^{3+} - OH_2]$  (Fig. 2).

Habenschuss and Spedding (1980) used the plot of  $[REE^{3+} - OH_2]$  against the ionic radius of  $REE^{3+}$  in order to show the coordination change in light  $REE^{3+}(aq)$  series.



**Fig. 4** Plots of  $[REE^{3+} - OH_2]_{(nona)}$  and  $[REE^{3+} - OH_2]_{(octa)}$  against the atomic number of REE. The series variation of  $[REE^{3+} - OH_2]_{(octa)}$  indicate a small concave tetrad effect. The experimental REE- $OH_2$  distances in  $REECl_3$  solutions (Habenschuss and Spedding, 1979a, b and 1980) are also plotted.

The ionic radius of REE<sup>3+</sup> with CN (coordination number) = 6, however, is derived from the REE-O distance in REEO<sub>1.5</sub>(cub), and it inevitably reflects the characteristics of REE-O bonding in REEO<sub>1.5</sub>(cub) (Kawabe,1992). Therefore, the plot of  $1/[REE^{3+} - OH_2]$  against the atomic number of REE (Fig. 3-1) is much better than the plot of  $[REE^{3+} - OH_2]$  against the ionic radius of REE<sup>3+</sup> by Habenschuss and Spedding (1980). Our plot of  $\Delta H_{hyd}$  vs.  $1/[REE^{3+} - OH_2]$  (Fig. 2) can illustrate the importance of experimental  $[REE^{3+} - OH_2]$  distances from the viewpoint of the hydration change in light REE<sup>3+</sup>(aq) series,

Bratsch and Silber (1982) discussed the hydration enthalpy of REE<sup>3+</sup>(aq) using a similar linear equation to eq. (9). They argued that the hydration enthalpy of REE<sup>3+</sup>(aq) is given as a linear function of the reciprocal of the ionic radii, and that the straight line means the absence of “crystal field effect”. However, their arguments are unacceptable from the following reasons: the first is the total neglect of the hydration change in light REE<sup>3+</sup>(aq) series, the second is the use of the ionic radii determined from REE-O distances in REEO<sub>1.5</sub>(cub) in the discussion of REE-OH<sub>2</sub> distance, and the third is misunderstanding of lanthanide tetrad or double-deouble effect as the “crystal field effect”. In their later publications (Bratsch and Lagowski, 1985a, b) the tetrad or double-double effect and the crystal (or ligand) field effect were distinguished, but they wrote still that such small effects are comparable with the fitting errors of hydration enthalpy of REE<sup>3+</sup>(aq) by the linear function of the reciprocal of ionic radius or the sum of ionic radius and some constant for the ligand. Indeed the convex tetrad effect of  $(-\Delta H_{hyd})$  we suggested in Figs. 3-2 is small: The maximum deviation at Gd from the linear trend is at best about -20 kJ/mol. The small tetrad effect in  $(-\Delta H_{hyd})$ , however, appears as a significant one in the series variation of  $\Delta H_{hc}^0(REE^{3+},aq)$  for the hydration change reaction between the octa- and nonahydrate REE<sup>3+</sup>(aq) series. Bratsch and Lagowski (1985a, b) were too hasty to conclude the absence of “crystal field effect” and the negligibly small tetrad effect and crystal (or ligand) field effect. This point will be clarified in the next subsection.

#### 4) Nephelauxetic effects in octahydrate and nonahydrate series of REE<sup>3+</sup>(aq)

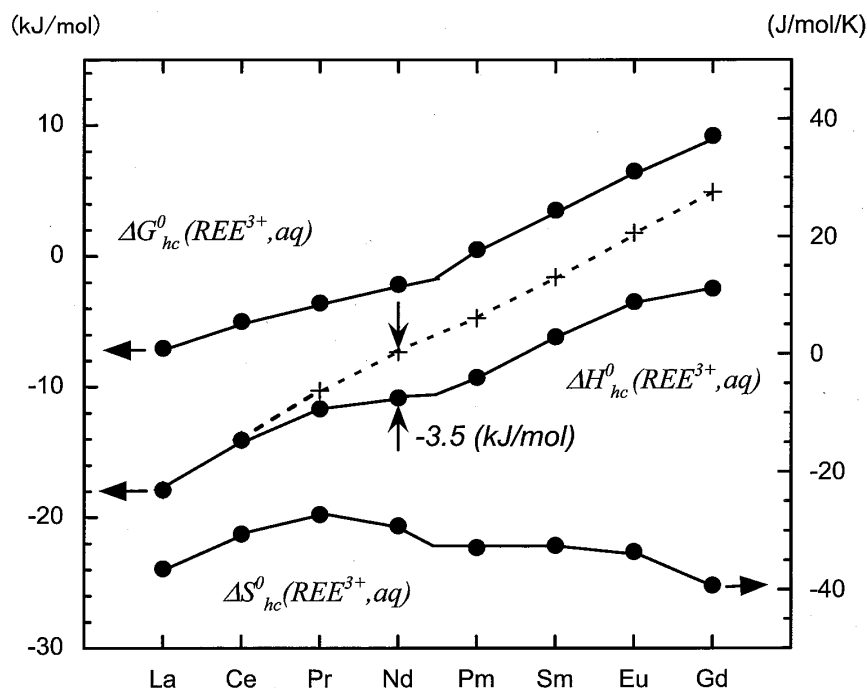
Figure 5 shows the series variations of  $\Delta G_{hc}^0(REE^{3+},aq)$ ,  $\Delta H_{hc}^0(REE^{3+},aq)$  and  $\Delta S_{hc}^0(REE^{3+},aq)$  for the hydration change reaction between the octa- and nonahydrate REE<sup>3+</sup>(aq) series at 25°C and 1 atm pressure listed in Table 1 of the first part (Kawabe *et al.*, 2006). The thermodynamic parameters appear to show convex tetrad-like variations across light REE series. They are neither smooth variations nor linear ones. The tetrad effects are sometimes understood as the “crystal field effect” in an analogy of (3d)<sup>q</sup> metal complex series, but this is a miss-understanding. In REE(III) compounds or complexes, the LS term-energy splitting ( $\sim 10,000$  cm<sup>-1</sup>) of REE<sup>3+</sup> due to inter-electron repulsion of 4f electrons is much greater than the J-level splitting ( $\sim 1,000$  cm<sup>-1</sup>) by spin-orbit interaction, and then the J-level splitting is still much greater than the crystal (or ligand) field splitting ( $\sim 100$  cm<sup>-1</sup>) by the non-spherical crystal (or ligand) field (Reisfeld and Jørgensen, 1977). Hence, the differences in the LS term-energy splitting given by Racah parameters among REE(III) complexes are primarily important in the (4f)<sup>q</sup> series. They are called nephelauxetic effects evaluated by the differences in Racah parameters among REE(III) complexes in an order of %

or less, but they are not the crystal field effects at all (Reisfeld and Jørgensen, 1977; Jørgensen, 1979). The nephelauxetic effects produce tetrad-like series variations of thermodynamic data for the reactions for pair of REE(III) complexes or compounds. They can be quantitatively treated by Jørgensen's (1962) refined spin-pairing energy theory (RSPET) derived from the Slater-Condon-Racah theory for atomic spectra.

In view of the improved RSPET equation (Kawabe, 1992), the convex tetrad effect of  $\Delta H_{hc}^0(REE^{3+},aq)$  is indicating that Racah ( $E^1$  and  $E^3$ ) parameters of nonahydrate  $REE^{3+}(aq)$  series are systematically greater than those of octahydrate  $REE^{3+}(aq)$  series. In Fig. 5, we can roughly estimated that the tetrad effect contribution of  $\{(9/13)n(S)\Delta E^1 + m(L)\Delta E^3\}$  to  $\Delta H_{hc}^0(Nd^{3+},aq)$  is  $-(3.5 \pm 0.5)$  kJ/mol. Hence the differences in Racah ( $E^1$  and  $E^3$ ) parameters between nonahydrate and octahydrate of  $Nd^{3+}(aq)$  are evaluated in the following way:

$$\begin{aligned} & (9/13)n(S)\Delta E^1 + m(L)\Delta E^3 \\ &= [(9/13)n(S) + (\Delta E^3/\Delta E^1)m(L)]\Delta E^1 \\ &= [(9/13)(-3) + (0.23)(-21)]\Delta E^1 \approx -(3.5 \pm 0.5) \text{ (kJ/mol)}, \end{aligned} \quad (10)$$

where it is assumed that  $(\Delta E^3/\Delta E^1) \approx 0.23$  from the nephelauxetic effects known spectroscopically for various Nd(III) compounds (Kawabe and Masuda, 2001). From



**Fig. 5** The series variations of  $\Delta G_{hc}^0(REE^{3+},aq)$ ,  $\Delta H_{hc}^0(REE^{3+},aq)$  and  $\Delta S_{hc}^0(REE^{3+},aq)$  at 25°C and 1 atm pressure listed in Table 1 of part-I (Kawabe *et al.*, 2006). The thermodynamic parameters appear to show convex tetrad effects across light REE series. The convex tetrad effect of  $\Delta H_{hc}^0(REE^{3+},aq)$  means that Racah ( $E^1$  and  $E^3$ ) parameters of nonahydrate  $REE^{3+}(aq)$  series are systematically greater than those of octahydrate  $REE^{3+}(aq)$  series (Kawabe, 1992; Kawabe and Masuda, 2001). The tetrad effect contribution to  $\Delta H_{hc}^0(Nd^{3+},aq)$  is estimated to be  $-(3.5 \pm 0.5)$  kJ/mol. The cross symbols with a dashed smooth curve show  $\Delta H_{hc}^0(REE^{3+},aq)$  corrected for the tetrad effect contributions.

the third equation of (10) and  $1 \text{ kJ/mol} = 83.593 \text{ cm}^{-1}$ ,  $\Delta E^1$  and  $\Delta E^3$  for Nd<sup>3+</sup> have been estimated that

$$E^1(\text{Nd}^{3+}, \text{nonahydrate}) - E^1(\text{Nd}^{3+}, \text{octahydrate}) \approx (42 \pm 6) \text{ cm}^{-1} \quad (11)$$

and

$$E^3(\text{Nd}^{3+}, \text{nonahydrate}) - E^3(\text{Nd}^{3+}, \text{octahydrate}) \approx (10 \pm 1) \text{ cm}^{-1}. \quad (12)$$

The cross symbols with a dashed smooth curve in Fig. 5 indicate the values of  $\Delta H_{hc}^0(\text{REE}^{3+}, \text{aq})$  corrected for the respective contributions by the tetrad effects in the same way as the case of Nd<sup>3+</sup>.

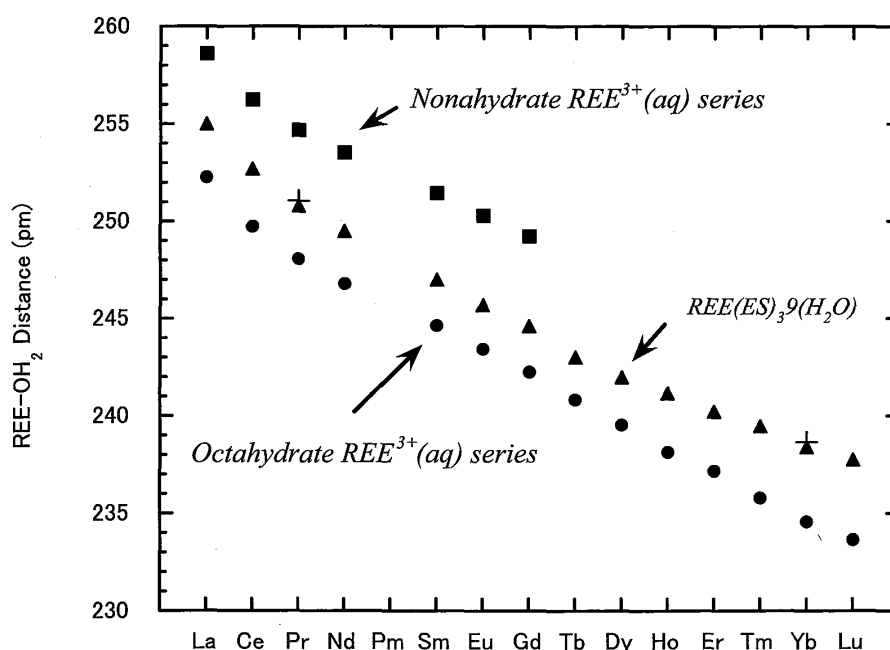
On the other hand, from the tetrad effect variation of the enthalpy data for solution of the fully isomorphous crystalline hydrate series of  $\text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$ , Kawabe (1999a) estimated that

$$E^1(\text{Nd}(\text{ES})_3 \cdot 9\text{H}_2\text{O}) - E^1(\text{Nd}^{3+}, \text{octahydrate}) \approx (23 \pm 6) \text{ cm}^{-1} \quad (13)$$

and

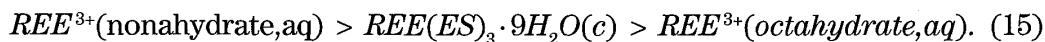
$$E^3(\text{Nd}^{3+}(\text{ES})_3 \cdot 9\text{H}_2\text{O}) - E^3(\text{Nd}^{3+}, \text{octahydrate}) \approx (4.9 \pm 1.8) \text{ cm}^{-1}. \quad (14)$$

Our estimates of (11) – (14) signify that Racah ( $E^1$  and  $E^3$ ) parameters for light REE<sup>3+</sup>



**Fig. 6** REE<sup>3+</sup>-OH<sub>2</sub> distances in  $[\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq})$  and  $[\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq})$  compared with that of the weighted means of REE<sup>3+</sup>-OH<sub>2</sub> distances in the tricapped trigonal prisms of  $\text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}(\text{c})$  series. Each weighted mean of REE<sup>3+</sup>-OH<sub>2</sub> distance in the tricapped trigonal prism has been calculated as  $(\text{REE} - \text{OH}_2)_{\text{mean}} = (3/9) \cdot [\text{REE} - \text{OH}_2(\text{vertex})]$  from the X-ray structural studies at 295 K (crosses: Albertsson and Elding, 1977) and at 171K (filled triangles: Gerkin and Reppart, 1984). The REE-OH<sub>2</sub> distance at the normal condition decreases in the following order that  $[\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq}) > \text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}(\text{c}) > [\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq})$ . This is the same order as that for the Racah parameters of (15).

like  $\text{Nd}^{3+}$  decrease in the following order:



The first coordination sphere of each  $\text{REE}^{3+}$  in  $\text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$  series is a slightly distorted tricapped trigonal prism composed of nine water molecules (Albertsson and Elding, 1977; Gerkin and Reppart, 1984).  $\text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$  has been a model hydrate for  $[\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq})$ . We have compared our estimates of  $\text{REE}^{3+}\text{-OH}_2$  in  $[\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq})$  and  $[\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq})$  (Figs. 2, 3-1, and 4) with the weighted means of  $\text{REE}^{3+}\text{-OH}_2$  distances in the tricapped trigonal prisms of  $\text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$  series (Fig. 6). Each weighted mean of  $\text{REE}^{3+}\text{-OH}_2$  distances in  $\text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$  has been calculated as

$$\begin{aligned} (\text{REE} - \text{OH}_2)_{\text{mean}} &= (3/9) \cdot [\text{REE} - \text{OH}_2(\text{equatorial})] \\ &+ (6/9) \cdot [\text{REE} - \text{OH}_2(\text{vertex})], \end{aligned} \quad (16)$$

where we have used the two types of  $\text{REE}^{3+}\text{-OH}_2$  distances reported in the X-ray structural studies of  $\text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$  at 22°C (Albertsson and Elding, 1977) and at 171K (Gerkin and Reppart, 1984). The mean  $\text{REE}\text{-OH}_2$  distances in  $\text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$  series are little different between 295 K (Albertsson and Elding, 1977) and 171K (Gerkin and Reppart, 1984):  $(\text{Pr} - \text{OH}_2)_{\text{mean}} = 251.1$  pm at 295K and 250.8 pm at 171 K, and  $(\text{Yb} - \text{OH}_2)_{\text{mean}} = 238.7$  pm at 296 K and 238.4 pm at 171 K. The mean  $\text{REE}\text{-OH}_2$  distances at 295 K are only 0.3 pm greater than those at 171 K. Figure 6 demonstrates that  $[\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq})$  have about 4 pm greater  $\text{REE}^{3+}\text{-OH}_2$  distances than  $\text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$ , and that  $[\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq})$  have about 4 pm smaller  $\text{REE}^{3+}\text{-OH}_2$  distances than  $\text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$ . The  $\text{REE}^{3+}\text{-OH}_2$  distances in the three hydrated  $\text{REE}(\text{III})$  complexes decrease in the same order as in (15). Hence the nephelauxetic series of (15) is an important example that the reduction of Racah parameters is correlating with decreasing distance between  $\text{REE}^{3+}$  and the same ligand (Jørgensen, 1971; Tröster, 2003). It is also worthy to note that the tricapped trigonal prism of  $\text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$  is not a very good model for  $[\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq})$  as it has been expected for a long time.

The Racah parameters of nonahydrate  $\text{REE}^{3+}(\text{aq})$  are fairly larger than those of  $\text{REE}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$ , and probably comparable even with those of  $\text{REE}^{3+}$  in fluoride and gaseous free  $\text{REE}^{3+}$  (Kawabe and Masuda, 2001). This means that no significant tetrad effect is expected in the series variation of hydration enthalpy of nonahydrate  $\text{REE}^{3+}(\text{aq})$  or in the plot of  $1/[\text{REE}^{3+}\text{-OH}_2]$  for nonahydrate  $\text{REE}^{3+}(\text{aq})$  against the atomic number of REE. This has been already seen in Figs. 3-1 and 3-2. On the other hand, it is evident from (15) that the Racah parameters of octahydrate  $\text{REE}^{3+}(\text{aq})$  are significantly smaller than those of gaseous free  $\text{REE}^{3+}$ . Hence a convex tetrad effect is expected in the series variation of the negative of hydration enthalpy for octahydrate  $\text{REE}^{3+}(\text{aq})$ . At the same time, we can expect a convex tetrad effect in the series variation of  $1/[\text{REE}^{3+}\text{-OH}_2]$  of octahydrate  $\text{REE}^{3+}(\text{aq})$ , because the negative of hydration enthalpy of octahydrate  $\text{REE}^{3+}(\text{aq})$  is positively correlated with the reciprocal of  $[\text{REE}^{3+}\text{-OH}_2]$  distance. We have already found this situation in the plots of Figs. 2, 3-1 and 3-2. The nephelauxetic effects of  $\text{REE}^{3+}\text{-OH}_2$  bonding in (15) are reflected not only in the thermodynamic data for the hydration change reaction but also in  $\text{REE}\text{-OH}_2$  distances of the two hydrates of  $[\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq})$  and  $[\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq})$ .

### 5) Apparent success of "electrostatic" equation for quantum-chemical entities

The 4f-electronic energy due to the partly-filled (4f)<sup>n</sup> electronic configuration is undoubtedly contributing to REE<sup>3+</sup>-OH<sub>2</sub> bonding energy and REE-OH<sub>2</sub> distance (Figs. 2, 3-1 and 3-2). The bonding energy calculations for [REE(H<sub>2</sub>O)<sub>n</sub>]<sup>3+</sup> by Miyakawa *et al.* (1988) are based on the electrostatic model including the ion-dipole and dipole-dipole interactions, polarization of dipole due to induced dipoles, and the van der Waals repulsion. This is the same as the electrostatic model for hydrated divalent (3d)<sup>n</sup> metal ions by Ohtaki *et al.* (1976). The electrostatic model, however, does not include the 4f electronic energy term, and they treated REE<sup>3+</sup> ions as if they were the spin-less ions with closed electronic configurations. This means the neglect of the first order Jahn-Teller effect, but this must be a representative constraint among the degenerated 4f electronic energy states of REE<sup>3+</sup>, REE-ligand distance, and the symmetry of REE(III) cluster when the equilibrium configuration with the minimum energy is realized. Hence, even if the equilibrium configuration constraint is imposed on such a model cluster of the classical theory, the situation does not correspond to that of the real REE<sup>3+</sup> clusters. This is an obvious dilemma when the quantum-chemical entity of REE<sup>3+</sup> is treated by the classical electrostatic theory, although no discussion on this point has been given in Ohtaki *et al.* (1976) and Miyakawa *et al.* (1988).

As a matter of fact, however, the simple "electrostatic" model represented by eq. (9) appears to work well empirically. Equation (9) is indeed compatible with the lanthanide tetrad effects recognized in hydration enthalpy of REE<sup>3+</sup>(aq) and ΔH<sub>r</sub> for the hydration change reaction (1). Why does the simple equation work so well notwithstanding it does not care the symmetry properties, the Jahn-Teller effect, and the 4f electronic energy of REE<sup>3+</sup>-H<sub>2</sub>O clusters at all? The previous reports emphasizing the hydration enthalpy of REE<sup>3+</sup>(aq) as a linear function of the reciprocal of ionic radius or ionic radius plus some constant for the ligand (Bratsch and Silber, 1982; Bratsch and Lagowski, 1985a,b), also did not give any explanation for this situation.

### 6) Equilibrium configuration and classical limit of quantum mechanics

In our view, the reason can be found in eq. (9) itself: we accept (-ΔH<sub>hyd</sub>) on the left-hand side of (9) confidently, because they are the experimental results for [REE(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup> of heavy REE series. The acceptance is independent of our knowledge about the symmetry properties of [REE(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup> cluster, the Jahn-Teller effect and the 4f electronic energy. Likewise, on the right-hand side of eq. (9), we are accepting the observed REE-OH<sub>2</sub> distances in the sense that each observed REE-OH<sub>2</sub> distance is the structural and energy parameter for the real equilibrium configuration with the minimum energy. In other words, we acknowledge the real [REE(H<sub>2</sub>O)<sub>8</sub>]<sup>3+</sup> cluster as such an entity that has already established the equilibrium configuration with the minimum energy using "the variation principle" by itself.

The 4f electronic energy is contributing to the minimized total energy, but the equilibrium configuration condition imposes the internal relations among different energy terms and structural parameters including the 4f electronic energy and REE<sup>3+</sup>-H<sub>2</sub>O distance. The first order Jahn-Teller effect is a typical result of compromising the interplay among the different electronic energy terms and structural parameters. For the established equilibrium configuration, the partial derivative of total energy

(U) with respect each structural parameter ( $R_i$ ) equals zero:

$$\left(\frac{\partial U}{\partial R_i}\right)_{(R_i=(R_i)_0; i=1,2,\dots,m)} = 0 \quad (17)$$

The collection of such constraints like (17) includes the interrelation between the 4f electronic energy and REE<sup>3+</sup>-H<sub>2</sub>O distance. It does not matter at all whether we can describe explicitly all the constraints for the energy minimization or not.

In addition to the specific constraint of the equilibrium condition, there exists an important general constraint given by the classical limit of quantum mechanics where Planck's constant ( $h$ ) approaches zero, namely, the correspondence principle (Messiah, 1964; Feynman and Hibbs, 1965). The de Broglie wavelength ( $\lambda_{DB}$ ) and the thermal wavelength ( $\lambda_T$ ) given by (18) are important in the discussion of the classical limit (Chandler, 1987):

$$\lambda_{DB} = h/\sqrt{(8/\pi)mk_B T} \quad \text{and} \quad \lambda_T = h/\sqrt{2\pi mk_B T}, \quad (18)$$

where  $m$ ,  $k_B$  and  $T$  are the mass of particle, Boltzmann's constant and absolute temperature, respectively. Either the condition that  $\lambda_{DB} \ll [REE^{3+} - OH_2]$ , or the condition that the average of interacting force between REE<sup>3+</sup> and water molecule,  $\langle |F| \rangle$ , times  $\lambda_T$  ( $\approx \lambda_{DB}$ ) is much smaller than the thermal energy of  $k_B T$ , namely,  $\langle |F| \rangle \lambda_T \ll k_B T$ , means the classical limit where Planck's constant ( $h$ ) can be regarded as zero practically. The discussion in terms of the de Broglie wavelength and the thermal wavelength may justify the model of classical mechanics for heavy rare gases like Ar and the classical electrostatic model for heavy ions, especially for those ions with closed electronic configurations.

For example, the Debye-Hückel theory for dilute electrolyte solutions assumes that the energy ( $z_j e \psi$ ) of an ion with charge  $z_j e$  at the potential  $\psi$  is much smaller than  $k_B T$ , and then the Boltzmann factor is expanded into a linear function of  $(z_j e \psi)/(k_B T)$  (Pitzer and Brewer, 1961; Marcus, 1977). This is equivalent to the condition that  $\langle |F| \rangle \lambda_T \ll k_B T$ , and then the Debye-Hückel theory is an acceptable approximation in the classical limit. This is the reason why the classical Debye-Hückel theory is applicable to the quantum-chemical entities of various ions in dilute solutions. However, it does not appear to justify immediately the electrostatic model for the hydrated (3d)<sup>9</sup> and (4f)<sup>9</sup> metal ions with partly-filled subshells and parallel electron spins, because they cannot correspond to the charged classical particles without any internal structure.

In this context, the apparent success of electrostatic model calculations for hydrated divalent (3d)<sup>9</sup> metal ions (Mn, Fe, Ni, Co, Cu and Zn) using experimental structure data (Ohtaki *et al.*, 1976) seems to an instructive example for us: The distorted octahedral hydrate structure of Cu<sup>2+</sup> with (3d)<sup>9</sup> due to the first order Jahn-Teller effect was used in the calculations. The calculated values of  $(-\Delta H_{hyd})$  for M<sup>2+</sup>, when plotted against the number of 3d electrons, reproduce the characteristic series variation with the well-known cusp at Mn<sup>2+</sup> with [Ar](3d<sup>5</sup>) in the plot of experimental  $(-\Delta H_{hyd})$  values *vs.* the number of 3d electrons. The dilemma of classical electrostatic model treating the quantum-chemical entities of the hydrated (3d)<sup>9</sup> and (4f)<sup>9</sup> metal ions may not be so serious eventually as long as the observed structure of hydrated REE<sup>3+</sup> cluster and REE<sup>3+</sup>-OH<sub>2</sub> distances are used.



### 7) Charged classical particle model and internal properties of real REE<sup>3+</sup> ions

In the discussion of series variation of  $(-\Delta H_{hyd})$  for REE<sup>3+</sup>(aq) or the lattice enthalpy of REEO<sub>1.5</sub>(cub), we are acknowledging the internal structures of real REE<sup>3+</sup> ions. The following understanding of the lanthanide contraction by Cotton and Wilkinson (1980) and Cotton *et al.* (1995) is widely accepted: The lanthanide contraction of ionic radius of REE<sup>3+</sup> is realized because the increasing nuclear charge of REE<sup>3+</sup> across the series cannot be shielded perfectly by the increasing number of 4f electrons. Nevertheless we must be very careful about this kind of notions referring to both the classical particles of ions and their internal structures like nuclear charges and 4f electrons simultaneously, because no internal structures can be allowed in the charged classical particles model for ions as cautioned by Landau and Lifshitz (1980) in §45 of their textbook of statistical mechanics.

In the charged classical particles theory, each ion is described by its mass, charge and size parameter. When real ions like REE<sup>3+</sup> are dealt with by this classical concept, all the properties originating from the internal structures of real ions are inevitably absorbed only by their size parameters, which are actually evaluated from ion-ligand distances in the respective real materials. Hence, as long as the charged classical particle model is accepted, the plot of  $(-\Delta H_{hyd})$  against  $1/[REE^{3+}-OH_2]$  of (9) shown in Fig. 2 can be put forward, but the plot of  $1/[REE^{3+} - OH_2]$  or  $(-\Delta H_{hyd})$  against the atomic number of REE or the 4f electron number of  $q$  for [Xe](4f<sup>q</sup>) of REE<sup>3+</sup> (Figs. 3-1 and 3-2) cannot be allowed at all. Therefore the charged classical particles model for ions cannot discuss the tetrad effects of  $(-\Delta H_{hyd})$  and  $1/[REE^{3+} - OH_2]$ . This is a logical statement because the charged classical particle model itself cannot allow the internal structures and states of real REE<sup>3+</sup> ions at all.

On the other hand, the Schrödinger equation for the REE<sup>3+</sup> cluster involves the coordinates for electrons and nuclear masses, but it does not involve the operator of the spin coordinates. Hence, it could be approximated by the equation with respect to the coordinates of nuclear masses in the classical limit. Implicitly this leads to almost the same consequence as the case of the charged classical particle model, but here can be discussed both the plot of  $1/[REE^{3+} - OH_2]$  against the atomic number of REE and the plot of  $(-\Delta H_{hyd})$  against  $1/[REE^{3+}-OH_2]$ , because we understand that the observed results correspond to those of the classical limit of quantum-chemical energetics in real material systems. When we accept RSPET (Refined spin-pairing energy theory) by Jørgensen (1979) and Kawabe (1992), we can treat the data set of  $(-\Delta H_{hyd})$  or the lattice enthalpy of REEO<sub>1.5</sub>(cub) as the function the 4f electron number of  $q$  for [Xe](4f<sup>q</sup>) of REE<sup>3+</sup> more explicitly. Actually the observed tetrad effects and RSPET never contradict the charged classical particle model, but they can complement the classical model with the tactic by which internal structures of the real REE<sup>3+</sup> ions are legitimately introduced into our thermodynamic discussion. Only in this context, the notion by Cotton and Wilkinson (1980) and Cotton *et al.* (1995) is acceptable.

The apparent success of the simple equation of (9) which is compatible with the tetrad effects of  $(-\Delta H_{hyd})$  and  $1/[REE^{3+}-OH_2]$ , is the rationale to acknowledge the existence of hydrated REE<sup>3+</sup> cluster having already realized the equilibrium configuration with the minimum energy by itself, and the classical limit approximation of the quantum-chemical energetics. Whether we can describe explicitly all the constraints

in the energy minimization from the first principles or not is a separate problem. The pressure-induced nephelauxetic effects in REE(III) compounds (Tröster, 2003), for example, are quite analogous to the nephelauxetic series of (15), and they may be providing a clue to understanding of the internal relation between the Racah parameters and  $\text{REE}^{3+}$ -ligand distance *via* the wave functions for relevant electrons. Unfortunately, however, it is not yet successfully achieved at present to derive explicitly the interrelation between Racah parameters of  $\text{REE}^{3+}$  and REE-ligand distance starting from the first principles.

## CONCLUSIONS

(1) The difference in nephelauxetic effect between  $[\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq})$  and  $[\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq})$  can be estimated from thermodynamic data for the hydration change reaction that  $[\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) = [\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq})$ . The thermodynamic data combined with those data for solution of  $\text{REE}(\text{ES})_3 \cdot (\text{H}_2\text{O})_9$  ( $\text{ES} = \text{C}_2\text{H}_3\text{SO}_4^-$ ) previously reported by one of us, strongly suggest that Racah ( $E^1$  and  $E^3$ ) parameters for light  $\text{REE}^{3+}$  like  $\text{Nd}^{3+}$  decrease in the order:  $[\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq}) > \text{REE}(\text{ES})_3 \cdot (\text{H}_2\text{O})_9 > [\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq})$ . All the first coordination spheres in the three hydrated REE(III) complexes are composed of water molecules alone, but the averaged  $\text{REE}^{3+}$ - $\text{OH}_2$  distance decreases in the same order as do the Racah parameters. Hence this is the nephelauxetic series that the reduction of Racah parameters is correlating with decreasing  $\text{REE}^{3+}$ - $\text{OH}_2$  distance. The hydration polyhedrons of  $\text{REE}^{3+}$  in  $\text{REE}(\text{ES})_3 \cdot (\text{H}_2\text{O})_9$  series are not so good models for  $[\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq})$  as they have been expected.

(2) Racah parameters of  $[\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq})$  are larger than those of  $\text{REE}(\text{ES})_3 \cdot (\text{H}_2\text{O})_9$  but comparable with gaseous free  $\text{REE}^{3+}$ , and then no significant tetrad effect is expected in the series variation of the negative of its hydration enthalpy. In contrast,  $[\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq})$  series has significantly smaller Racah parameters than gaseous free  $\text{REE}^{3+}$ , suggesting a significant convex tetrad effect in the negative of its hydration enthalpy.

(3) The negative of hydration enthalpies of  $[\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq})$  in heavy REE series fit a linear function of the reciprocals of observed  $\text{REE}^{3+}$ - $\text{OH}_2$  distances in  $\text{REECl}_3$  solutions. This relation can be extended to light REE series, and a similar relation has been determined for  $[\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq})$  in light REE series on the basis of our thermodynamic mixture model and the REE- $\text{OH}_2$  data for the inner sphere water coordination in  $\text{REECl}_3$  ( $\text{REE}=\text{La}, \text{Pr}$  and  $\text{Nd}$ ) solutions. The reciprocals of REE- $\text{OH}_2$  in all the members of  $[\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq})$ , when plotted against the atomic number of REE, indicate a small convex tetrad effect, but such an effect is not suggested in  $[\text{REE}(\text{H}_2\text{O})_9]^{3+}(\text{aq})$ . This is in agreement with the nephelauxetic series of  $\text{REE}^{3+}$ - $\text{OH}_2$  bonding.

(4) The negative of hydration energy of  $[\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq})$  satisfies a linear function of the reciprocal of observed  $\text{REE}^{3+}$ - $\text{OH}_2$  distance, and at the same time, its series variation exhibits a convex tetrad effect in accordance with the nephelauxetic effect. This is quite analogous to the situation as to the lattice enthalpies of  $\text{REEO}_{1.5}$  (cubic) and observed  $\text{REE}^{3+}$ -O distances. The reason why such situations come out has been discussed from the viewpoints of the existence of  $[\text{REE}(\text{H}_2\text{O})_8]^{3+}(\text{aq})$  with the

equilibrium configuration having the minimum energy by itself and of the classical limit of quantum-chemical energetics. It is emphatically pointed out that the observed tetrad effects and RSPET can complement the classical ion model with the tactic by which internal structures of the real REE<sup>3+</sup> ions are legitimately introduced into our thermodynamic discussion.

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### REFERENCES

- Albertsson, J. and Elding, I. (1977) The geometry of the nona-aqualanthanoid(3+) complex in the solid bromates and ethyl sulphates. *Acta Cryst.*, **B33**, 1460–1469.
- Bratsch, S. and Silber, H.B. (1982) Lanthanide thermodynamic predictions. *Polyhedron*, **1**, 219–223.
- Bratsch, S. and Lagowski, J.J. (1985a) Lanthanide thermodynamic predictions. 6. Thermodynamics of gas-phase ions and revised enthalpy equation for solids at 298.15 K. *J. Phys. Chem.*, **89**, 3310–3316.
- Bratsch, S. and Lagowski, J.J. (1985b) Lanthanide thermodynamic predictions. 7. Thermodynamics of 2+, 3+, and 4+ aquo ions and standard electrode potentials at 298.15 K. *J. Phys. Chem.*, **89**, 3317–3319.
- Chandler, D. (1987) *Introduction to Modern Statistical Mechanics*, Chap. 7, Oxford Univ. Press, 274 pp.
- Cotton, F.A. and Wilkinson, G. (1980) *Advanced Inorganic Chemistry, A Comprehensive Text*, Chap. 23, John Wiley & Sons, New York, 1,396 pp.
- Cotton, F.A., Wilkinson, G., and Gaus, P.L. (1995) *Basic Inorganic Chemistry (3rd ed.)* John Wiley & sons, Inc., 838 pp.
- Feynman, R.P. and Hibbs, A.R. (1965) *Quantum Mechanics and Path Integrals*, McGraw-Hill, Inc., New York.: Japanese Transl. (1995) by Kitahara, K, Misuzu Publ. Comp., Tokyo, 344 pp.
- Gerkin, R. and Reppart, W. J. (1984) The structure of the lanthanide ethyl sulfate enneahydrate, M(C<sub>2</sub>H<sub>5</sub>SO<sub>4</sub>)·9H<sub>2</sub>O [M=La-Lu (except Pm)], at 171 K. *Acta Cryst.*, **C40**, 781–786.
- Habenschuss, A. and Spedding, F.H. (1979a) The coordination (hydration) of rare earth ions in aqueous chloride solutions from x-ray diffraction. I. TbCl<sub>3</sub>, DyCl<sub>3</sub>, ErCl<sub>3</sub>, TmCl<sub>3</sub>, and LuCl<sub>3</sub>. *J. Chem. Phys.*, **70**, 2797–2806.
- Habenschuss, A. and Spedding, F.H. (1979b) The coordination (hydration) of rare earth ions in aqueous chloride solutions from x-ray diffraction. II. LaCl<sub>3</sub>, PrCl<sub>3</sub> and NdCl<sub>3</sub>. *J. Chem. Phys.*, **70**, 3758–3763.
- Habenschuss, A. and Spedding, F.H. (1980) The coordination (hydration) of rare earth ions in aqueous chloride solutions from x-ray diffraction. III. SmCl<sub>3</sub>, EuCl<sub>3</sub> and series behavior. *J. Chem. Phys.*, **73**, 442–450.
- Helgeson, H.C. (1967) Thermodynamics of complex dissociation in aqueous solution at elevated temperatures. *J. Phys. Chem.*, **71**, 3121–3136.
- Helgeson, H.C. (1969) Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *Am. J. Sci.*, **267**, 729–3804.
- Jørgensen, C.K. and Brinen, J.S. (1963) Far-ultra-violet absorption spectra of cerium(III) and europium (III) aqua ions. *Mol. Phys.*, **6**, 629–631.
- Jørgensen, C.K. (1971) *Modern Aspects of Ligand Field Theory*, North-Holland Publ. Comp., Amsterdam, 538 pp.

- Jørgensen, C.K. (1979) Theoretical chemistry of rare earths. In: *Handbook on the Physics and Chemistry of Rare Earths* (Editors, Gschneider, K. A. Jr. and Eyring, L.), **3**, 111–169, North-Holland, Amsterdam.
- Kawabe, I. (1992) Lanthanide tetrad effect in the Ln<sup>3+</sup> ionic radii and refined spin-pairing energy theory. *Geochem. J.* **26**, 309–335.
- Kawabe, I. (1999a) Thermochemical parameters for solution of lanthanide(III) ethylsulphate and trichloride hydrate series: Evidence for tetrad effect and hydration change in aqua Ln<sup>3+</sup> ion series. *Geochem. J.* **33**, 249–265.
- Kawabe, I. (1999b) Hydration change of aqueous lanthanide ions and tetrad effects in lanthanide (III)-carbonate complexation. *Geochem. J.* **33**, 267–275.
- Kawabe, I., Ohta, A., Ishii, S., Tokumura, M., and Miyauchi, K. (1999) REE partitioning between Fe-Mn oxyhydroxide precipitates and weakly acid NaCl solutions: Convex tetrad effect and fractionation of Y and Sc from heavy lanthanides. *Geochem. J.*, **33**, 167–179.
- Kawabe, I. and Masuda, A. (2001) The original examples of lanthanide tetrad effect in solvent extraction: A new interpretation compatible with recent progress in REE geochemistry. *Geochem. J.*, **35**, 215–224.
- Kawabe, I., Takahashi, T., Tanaka, K. and Ohta, A. (2006) Hydration change reaction of light REE<sup>3+</sup>(aq) series-(I): An important constraint on REE(III) partitioning and complex formation reactions in low-temperature to hydrothermal condition. *J. Earth Planet. Sci. Nagoya Univ.*, **53**, 33–50.
- Landau, L.D. and Lifshitz, E.M. (1980) *Statistical Physics (3rd), Part 1, (English ed. Transl. by Sykes J. B. and Kearsley, M. J.)*, Butterworth Heinemann, 544 pp.
- Marcus, Y. (1977) *Introduction of Liquid State Chemistry*, Chap. 6, John Wiley & Sons Ltd. (Japanese ed. translated by Seki, S., Ikeda, S., Ozeki, T., Ogawa, N. and Yokoi, K., 1982, pp. 406, Kagaku-Dojin Publ. Comp., Kyoto)
- Messiah, A. (1964) *Quantum Mechanics (English ed. translated by Temmer, G.M.)*, Chap. 6, vol. I, North-Holland Publ. Comp., Amsterdam.
- Miyakawa, K., Kaizu, Y. and Kobayashi, H. (1988) An electrostatic approach to the structure of hydrated lanthanoid ions [REE(OH<sub>2</sub>)<sub>9</sub>]<sup>3+</sup> versus [REE(OH<sub>2</sub>)<sub>8</sub>]<sup>3+</sup>. *J. Chem. Soc., Faraday Trans. 1*, **85**, 1517–1529.
- Morss, L.R. (1994) Comparative thermochemical and oxidation-reduction properties of lanthanides and actinides. In: *Handbook on the Physics and Chemistry of Rare Earths* (eds. Gschneider, K.A. Jr., G.R. Choppin and G.H. Lander), **18**, 239–291, Elsevier Scienc B. V.
- Ohta, A. and Kawabe, I. (2000a) Rare earth element partitioning between Fe oxyhydroxide precipitate and aqueous NaCl solutions doped with NaHCO<sub>3</sub>: Determinations of rare earth element complexation constant with carbonate ions. *Geochem. J.*, **34**, 439–454.
- Ohta, A. and Kawabe, I. (2000b) Theoretical study of tetrad effects observed in REE distribution coefficients between marine Fe-Mn deposit and deep seawater, and in REE(III)-carbonate complexation constants. *Geochem. J.*, **34**, 455–473.
- Ohta, A. and Kawabe, I. (2001) REE(III) adsorption onto Mn dioxide ( $\delta$ -MnO<sub>2</sub>) and Fe oxyhydroxide: Ce(III) oxidation by  $\delta$ -MnO<sub>2</sub>. *Geochim. Cosmochim. Acta*, **65**, 695–703.
- Ohtaki, H., Yamaguchi, T., and Maeda, M. (1976) X-ray diffraction studies of the structures of hydrated divalent transition-metal ions in aqueous solution. *Bull. Chem. Soc. Japan.*, **49**, 701–708.
- Ohtaki, H. and Radnai, T. (1993) Structure and dynamics of hydrated ions, *Chem. Rev.*, **93**, 1157–1204.
- Pitzer, K.S. and Brewer, L. (1961) *Thermodynamics (2nd ed.)*, McGraw-Hill Book Company, New York, 723 pp.
- Reisfeld, R. and Jørgensen, C.K. (1977) *Lasers and Excited States of Rare Earths*, Springer, Berlin, 226 pp.
- Rizkalla, E.N. and Choppin, G.R. (1991) Hydration and hydrolysis of lanthanides, In: *Handbook on the physics and Chemistry of Rare earths* (Gschneider, K.A., Jr. and Eyring, L., eds.), **15**, 393–442, Elsevier Science Publ. B. V.
- Takahashi, T. and Kawabe, I. (2004) REE partitioning bwtween Fe oxyhydroxide and NaCl solu-

- tions under hydrothermal conditions. *Geochim. Cosmochim. A., Special Suppl. Abst. 13<sup>th</sup> Ann. V. G. Goldschmidt Conf. Copenhagen, Denmark*, A288.
- Tröster, T. (2003) Optical studies of non-metallic compound under pressure. In: *Handbook on the Physics and Chemistry of Rare Earths* (eds. Gschneidner, K.A. Jr., J-G.G. Bunzli and V.K. Pecharsky), **33**, 515–589, Elsevier Scienc B. V.