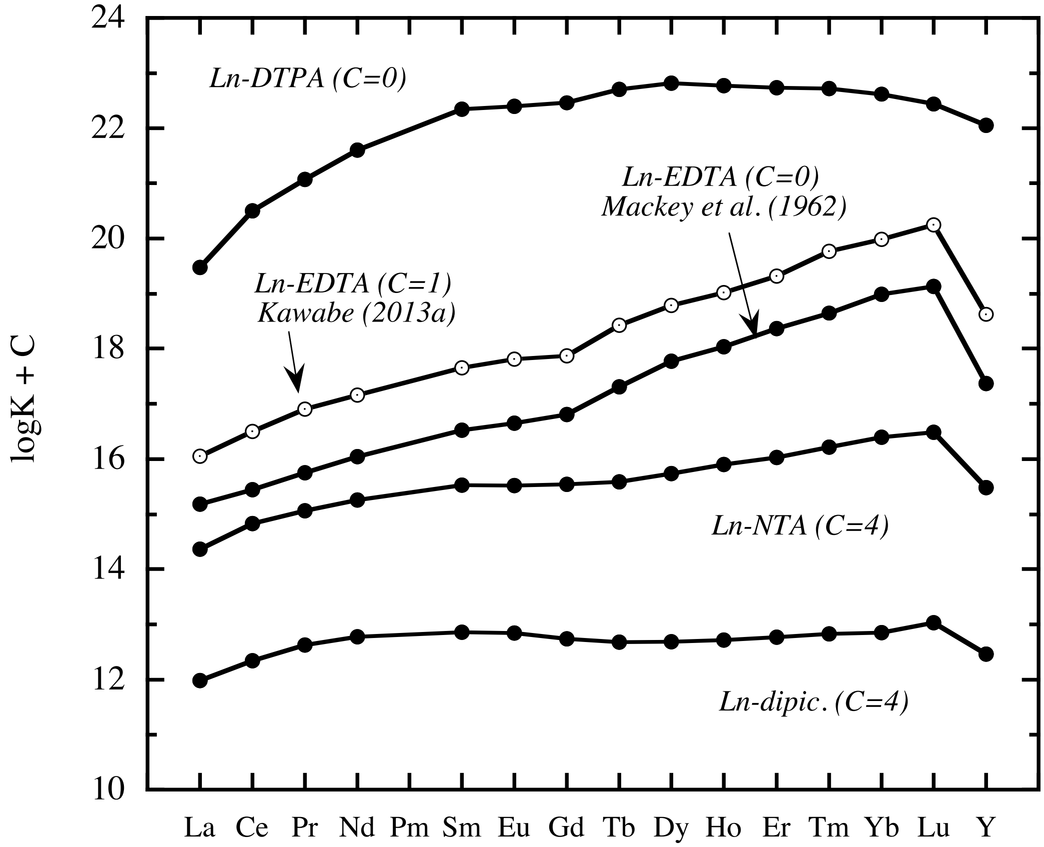

Fig. 1. Series variations of logK for selected (1:1) Ln(III) complexes including those of Y(III). DTPA=diethylenetriaminepentaacete, EDTA=ethylenediaminetetraacetate, NTA=nitrilotriacetate, dipic.=dipicolinate. Plotted data are from Moeller (1973) except those for Ln-EDTA. T= 25°C and μ=0.1 M, but T= 20°C for Ln-NTA. The numbers of electron donor groups of DTPA, EDTA, NTA, and dipic. are 8, 6, 4, and 3, respectively. The respective constants of C for the plots are given as the parenthesized figures. The two plots for Ln-EDTA are displaced by one in log unit in order to avoid overlapping plots.

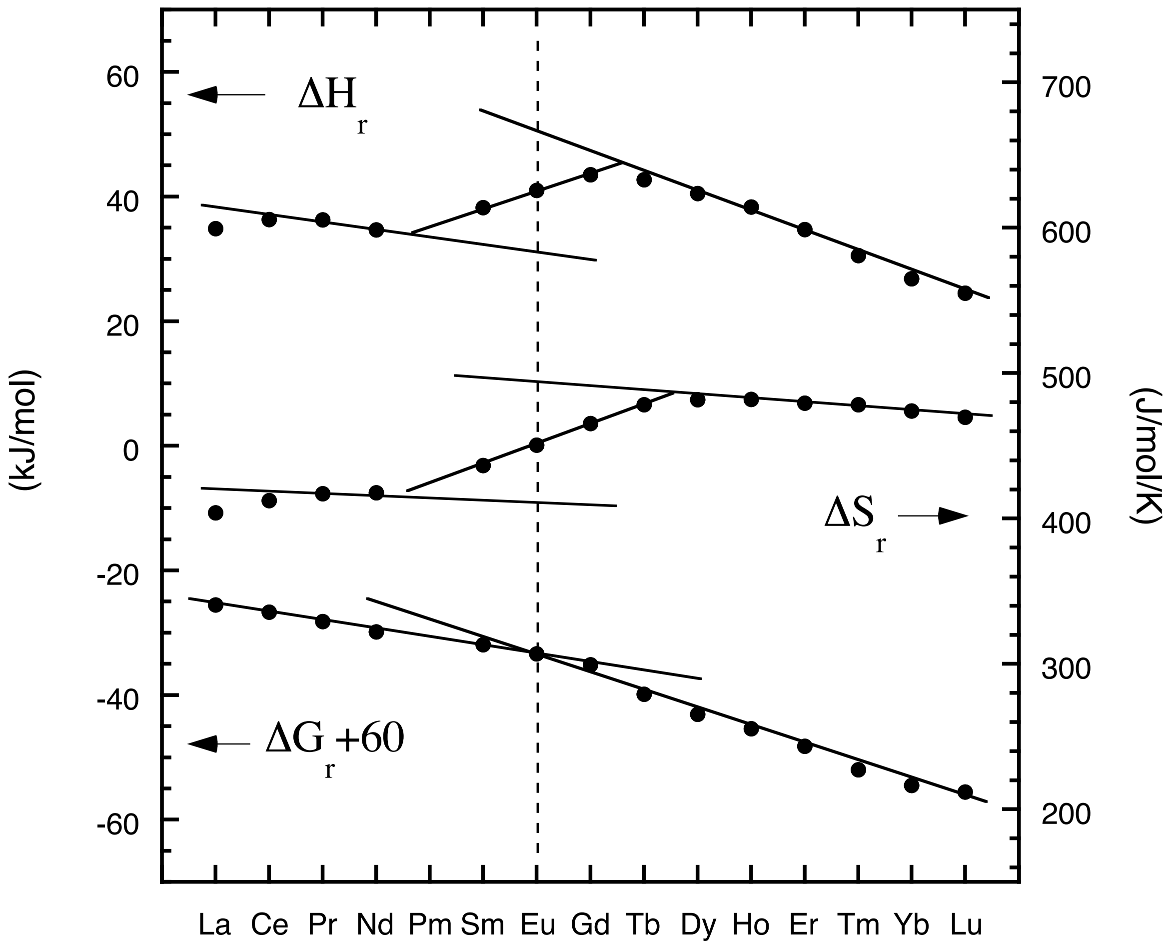

Fig. 2. Series variations of the thermodynamic data for the combined reactions of Ln(III)-EDTA complex formation (Mackey et al., 1962) with the solution of isomorphous crystalline series of Ln(III)-ethylesulphate nonahydrate, $Ln(ES)_3 \cdot 9H2O$, (Kawabe, 1999a). The series change of ΔG_r with a break at Eu and step-like changes of ΔH_r and ΔS_r centered approximately at Eu, suggest that the hydration states of Ln(III)-EDTA complex series are different between the light Ln (Ln=La to Nd) and heavy Ln (Ln=Dy to Lu), and that the intermediate members (Ln=Sm to Tb) are possibly the mixtures of the two distinguishable species of respective Ln(III)-EDTA. Auxiliary lines drawn here illustrate this situation with neglecting slightly curved features of the series changes.

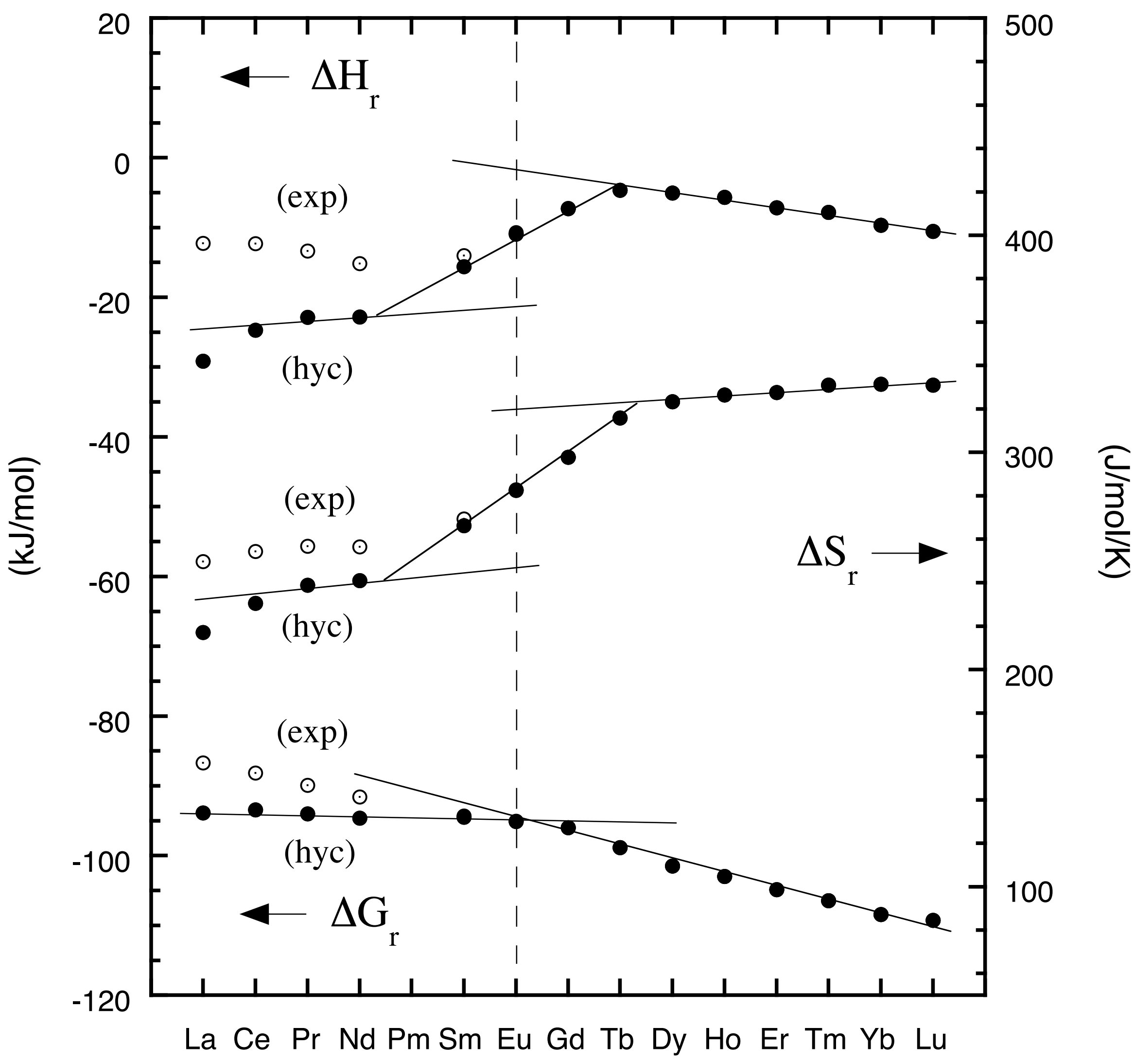

Fig. 3. The thermodynamic data for Ln(III)-EDTA formations (Mackey et al., 1962) with and without the corrections for the hydration changes of light Ln^{3+}(aq) relative to heavy Ln^{3+}(aq) of octahydrates (Kawabe, 1999a). The open circles are experimental data for light Ln series, and the filled circles are corrected ones. The experimental data for the heavy Ln series (Ln=Tb to Lu) are unaffected by the corrections, so that they are plotted as the filled circles. Auxiliary lines are drawn with neglecting slightly curved features of the series changes as in Fig. 2.

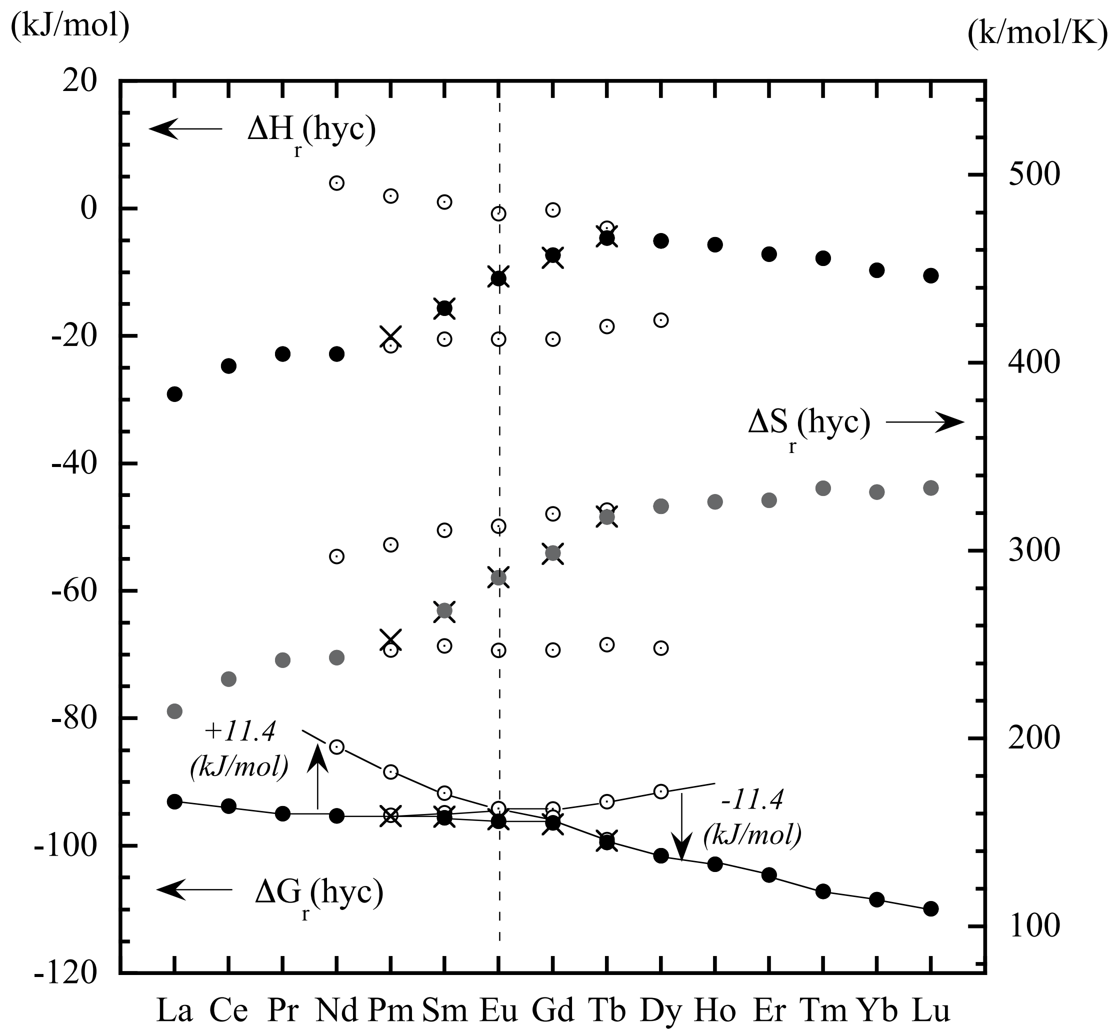

Fig. 4. Calculations of thermodynamic parameters for middle Ln(III)-EDTA complex formation. "hyc" means the corrections for the hydration change in light Ln^{3+}(aq) relative to heavy Ln^{3+}(aq) shown in Fig. 3. Filled circles: the experimental data with corrections of "hyc". Open circles: our estimates for middle Ln-EDTA complex formation belonging to the two different series. Crosses: the calculated points by eq. (16-1) using the pairs of our estimates for the two series. They are in good agreements with experimental data of filled circles. The dashed line at Eu indicates that $\Delta\Delta G_r \approx 0$ (kJ/mol) at Eu. The two vertical arrows indicate the approximate positions at which $\Delta\Delta G_r = +11.4(kJ/mol)$ and $-11.4(kJ/mol)$, respectively.

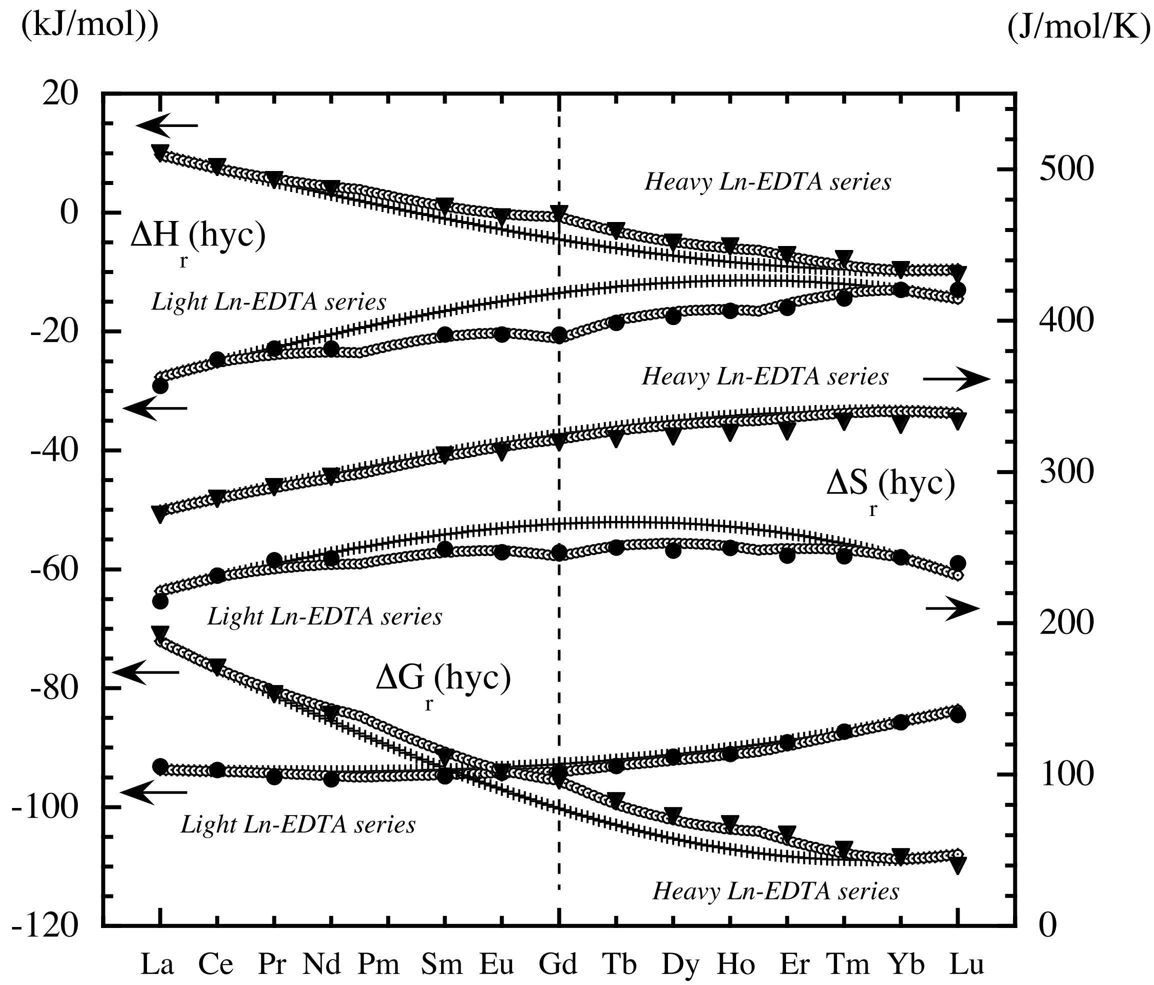

Fig. 5. Series variations of $\Delta H_r(hyc)$, $\Delta S_r(hyc)$, and $\Delta G_r(hyc)$ for the light Ln-EDTA series of $[LnEDTA(H_2O)_3]^-_{(aq)}$ (filled circles) and the heavy Ln-EDTA series of $[LnEDTA(H_2O)_2]^-_{(aq)}$ (inverted filled triangles), which are listed in Part A of Table 2. They are regressed by the improved RSPET equation (21). Each curve of small open circles shows the regressed result with the tetrad effect, and each curve of small crosses indicates the smooth variation separated from each tetrad effect variation. The parameters of tetrad effects of $\Delta H_r(hyc)$, $\Delta S_r(hyc)$, and $\Delta G_r(hyc)$ determined in the regressions are summarized in Table 4. Note that a vertical dashed line is placed at Gd, not at Eu.

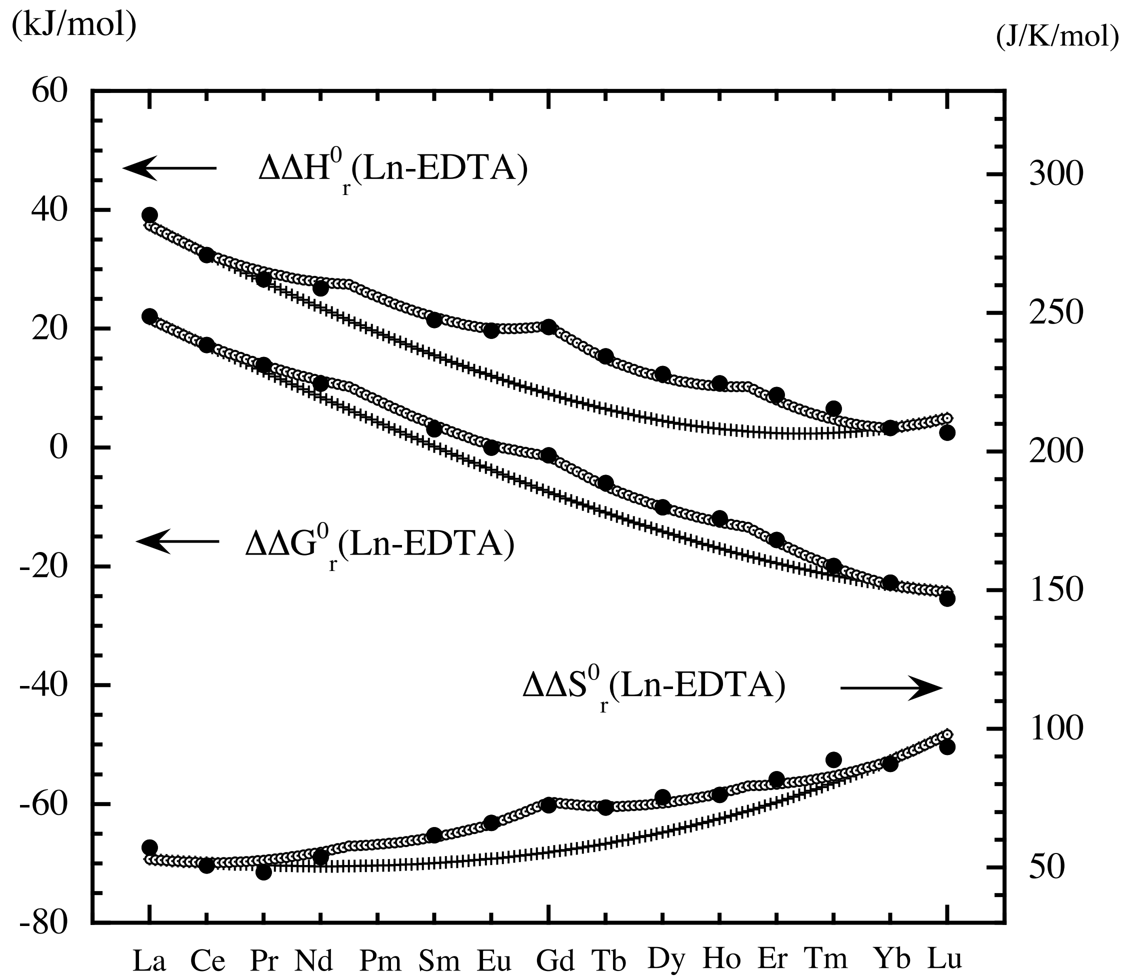

Fig.6. Thermodynamic quantities for the hydration change reaction between the two Ln-EDTA series species that $[LnEDTA(H_2O)_3]^-_{(aq)} = [LnEDTA(H_2O)_2]^-_{(aq)} + H_2O_{(l)}$, in which CN of Ln^{3+} is decreased from 9 to 8 and the nephelauxetic effect appears. They are regressed by the improved RSPET equation (21). Input data listed in Part B of Table 3 have been used in the regressions. The parameters of tetrad effects determined in the regressions are summarized in Table 5.

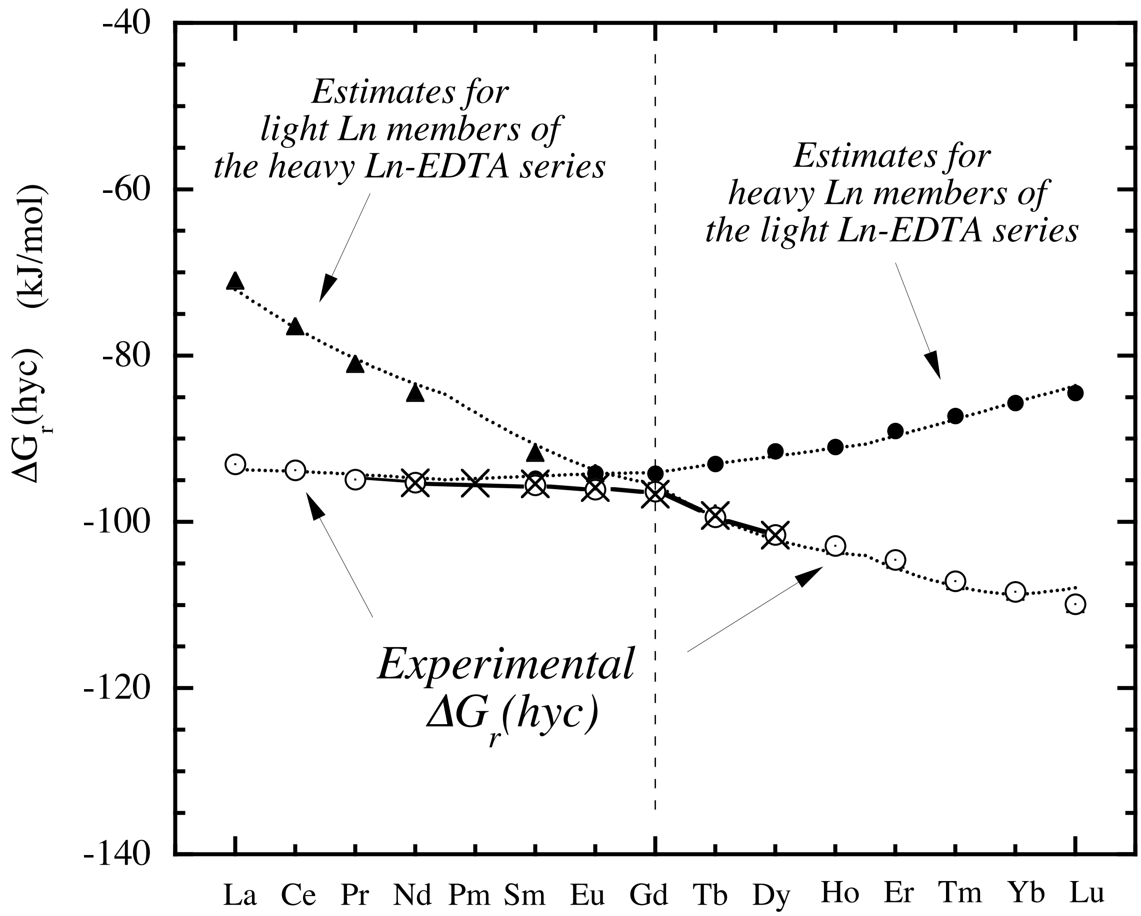

Fig. 7. "Experimental $\Delta G_r(hyc)$" values for Ln(III)-EDTA formation (open circles), which are the same as $\Delta G_r(hyc)$ in Fig. 4, are plotted in a more expanded scale. $\Delta G_r(hyc)$ values for middle Ln (Nd~Dy) are connected with thick lines. Crosses are the calculated $\Delta G_r(hyc)$ values for middle Ln by eq. (16-1). The two series variations of $\Delta G_r(hyc)$ for the light and heavy Ln-EDTA series intersect at Eu, but the experimental and calculated $\Delta G_r(hyc)$ values for middle Ln (Nd~Dy) are smaller than each of the two variations because of ΔG_{mixing} for the coexistence of two distinct hydrates. They indicate a Gd-break, but this is caused by the hydration change reaction between two Ln(III)-EDTA hydrates occurring at around Eu, not by the Gd-break as an octad-like variation of the lanthanide tetrad effect.