Reflection Spectra of Lanthanides in Thorium (IV) Oxide and the Large Nephelauxetic Effect of Oxide Ligands or Vacancies

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Retaining the cubic structure, ThO_2 can accomodate large concentrations of lanthanides and the equivalent amount of oxygen vacancies. The reflection spectra are measured at 100 °K of Nd(III), Sm(III), Eu(III), Ho(III), Er(III), Tm(III) and Yb(III) in such samples. The excited *J*-levels correspond to rather broad bands in $Th_{1-x}M_xO_{2-0.5x}$ whereas Nd_2O_3 and Er_2O_3 have very detailed line groups. The visible spectra indicate a very large nephelauxetic effect in the oxide, the nephelauxetic ratio β being smaller than in the aqua ion to the extent of 0.033 for Nd(III), 0.019 for Sm(III), 0.017 for Ho(III), 0.016 for Er(III) and 0.013 for Tm(III). These values are roughly five times larger than those for the anhydrous chlorides and are quite unexpected.

Crystals with a large MADELUNG energy usually do not allow appreciable quantities of cations with another charge than that of the main constituent to be incorporated in the lattice, except by a charge-compensation process, e. g. when Mg(II) and Mn(IV) are simultaneously introduced in Al_2O_3. Hence, it was surprising when HUND and DÜRRWÄCHTER [1] found that La_2O_3 is miscible with ThO_2 to a great extent, concentrations as high as $Th_{0.48}La_{0.52}O_{1.74}$ being obtained. The cubic lattice parameter a of this substance is 5.645 Å (as compared to 5.592 Å for pure ThO_2) and the CaF_2-type of lattice contains 13% oxygen vacancies. We have prepared a similar material containing 50% $EuO_{1.5}$ and a series of $Th_{0.86}M_{0.14}O_{1.93}$ where M is Pr, Nd, Sm, Eu, Tb, Ho, Er, Tm and Yb. The lattice parameter a is for M =

$$\begin{array}{lll} \mathrm{Nd(III)}\ 5.61\ \text{Å} & \mathrm{Eu(III)}\ 5.59\ \text{Å} & \mathrm{Er(III)}\ 5.57\ \text{Å} \\ \mathrm{Yb(III)}\ 5.56\ \text{Å} & Th_{0.5}Eu_{0.5}O_{1.75} & 5.58 \pm 0.01\ \text{Å} \quad (1) \end{array}$$

The lattice showed no sign of macroscopic distortion from the cubic type, but the lines obtained with the GUINIER–DEWOLFF camera were broadened and indicated either very small crystallites, or a weak variation at different points of the local size of the unit cell *. The low-temperature C-form of rare earths M_2O_3 was identified by GOLDSCHMIDT [2] as derived from ThO_2 and lacking 25% of the oxygen atoms in an ordered fashion. The unit cell has twice as large a value for a as the corresponding ThO_2. Mixtures of ThO_2 containing Pr and Tb have previously been studied by MARSH [3], and mixtures containing Y, Nd, Sm and Gd by BRAUER and GRADINGER [4].

The purpose of our study is not so much a crystallographic as a spectroscopic one. We wanted to investigate the influence of eight oxide ligands arranged in a cube, or the corresponding defective coordinations with seven oxide ligands and an oxygen vacancy, or six oxide ligands and two vacancies, on the partly filled 4f shell of the lanthanides. This influence turned out to be much larger than in the corresponding aqua ions, giving a larger splitting (resolved in Nd_2O_3 and Er_2O_3, partly unresolved in $Th_{1-x}M_xO_{2-0.5x}$) of each *J*-level into sublevels [at most $(2J+1)$ for an even number of 4f electrons and $(J+\frac{1}{2})$ for an odd number of electrons, if we neglect possible co-excited vibrations]. However, the most conspicuous influence of the oxide

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[1] F. HUND and W. DÜRRWÄCHTER, Z. anorg. Chem. **265**, 67 [1951].

* Professor H. GRÄNICHER has drawn our attention to the possible effects of small grain size, as was thoroughly studied by M. ANLIKER, H. R. BRUGGER and W. KÄNZIG (Helv. Phys. Acta **27**, 99 [1954]) in the case of $BaTiO_3$. However, the grain size would have to be very small, about 200 Å, in order to explain our phenomena. Recent work on $MTiO_{3.5}$ (crystallizing in the superlattice pyrochlore, showing narrow DEBYE-lines) and $MZrO_{3.5}$ (disordered fluorite, showing broad lines, even broader than in the present case of thorium oxide) prepared under identical conditions (heated 30 minutes or 2 hours to 1000 °C) would rather suggest that the local size of the unit cell fluctuates, and that the local symmetry is distorted from the cubic one. It would not be easy to imagine that the intrinsic grain size of the pyrochlore samples would be so much larger than of the mixed oxides containing zirconium or thorium.

[2] V. M. GOLDSCHMIDT, F. ULRICH, and T. BARTH, Geochem. Verteil. Gesetze, IV. Norske Vid. Akad. Skr. Math. Nat. Klasse, no. 5, Oslo 1925.

[3] J. K. MARSH, J. Chem. Soc. **15** [1946].

[4] G. BRAUER and H. GRADINGER, Naturwiss. **38**, 559 [1951] and Z. anorg. Chem. **276**, 209 [1954].

	λ	D	σ_{oxide}	σ_{aqua}	$\sigma_{\mathrm{oxide}} - \sigma_{\mathrm{aqua}}$	
$\mathrm{Pr(III)ThO_2}$ (at ~ 100°K)	2012	0.10				
	1845	0.05	5480	4950 ?	+ 530 ?	$^3F_2$
	1827	0.04				
	1805	0.03				
	1577	0.06	6450	6340	+ 90 ?	$^3F_3$
	1523 ?	0.07				
	1458	0.08	7040	6800	+ 240 ?	$^3F_4$
	1388 ?	0.05				
$\mathrm{Nd(III)ThO_2}$ (at ~ 100°K)	1980	0.05				
	1715	0.03	5840	5880	− 40	$^4I_{15/2}$
	885	0.11	11300	11580	− 280	$^4F_{3/2}$
	811	0.21	12330	12620	− 290	$^4F_{5/2}$
	750	0.22	13330	13580	− 250	$^4F_{7/2}$
	690	0.05	14490	14840	− 350	$^4F_{9/2}$
	593.5	0.23	16900	17400	− 500	$^2G_{7/2}$ $^4G_{5/2}$
	589	0.21				
	579	0.12				
	569.5	0.07				
	536.5	0.08	18690	19180	− 490	$^4G_{7/2}$
	533	0.06				
	516 broad	0.05	19380	19630	− 250	$^4G_{9/2}$
	482 broad	0.03	20750	21160 to 650		$^2D_{3/2}$, $^2G_{9/2}$, $^4G_{11/2}$
	435	0.02	22990	23400	− 410	$^2P_{1/2}$
	364.5	0.05	27430	28280	− 850	$^4D_{3/2}$
$\mathrm{Nd_2O_3}$ (at ~ 100°K)	1755	0.08	5950	5880	+ 70	$^4I_{15/2}$
	1730	0.12				
	1685	0.05				
	1610	0.17				
	1602	0.19				
	916.5	0.13	11190	11580	− 390	$^4F_{3/2}$
	903.5	0.31				
	897.5	0.38				
	890.5	0.28				
	884	0.33				
	823	0.60	12270	12620	− 350	$^4F_{5/2}$
	817	0.56				
	809	0.50				
	798	0.40				
	766 sh.	0.30	13250	13580	− 330	$^4F_{7/2}$
	762.5	0.48				
	754.5 sh.	0.58				
	751	0.61				
	695.5	0.15	14470	14840	− 370	$^4F_{9/2}$
	691.5 broad	0.16				
	687	0.15				
	682 sh.	0.09				
	639.4	0.08	15770	16030	− 260	$^2H_{11/2}$
	637.5	0.08				
	633.2	0.10				
	630.3	0.08				
	629.1	0.11				
	618.7	0.05				
	614.3	0.04				
	609.6	0.28				
	606.7	0.20				
	603.5	0.32				

Table 1. Continued next page.

	λ	D	σ_{oxide}	σ_{aqua}	$\sigma_{\text{oxide}} - \sigma_{\text{aqua}}$	
Nd_2O_3 (at ~ 100°K)	601.3 peak	0.82	16720	17400	−680	${}^2G_{7/2}$ ${}^4G_{5/2}$
	600.6	0.77				
	598.7	0.60				
	597.3	0.80				
	596.3 peak	0.81				
	593.6	0.37				
	591.2	0.44				
	588.3	0.58				
	584.6	0.49				
	582.5	0.31				
	581.6	0.30				
	579	0.30				
	578.3	0.25				
	575.2	0.20				
	569.6	0.08				
	564.4	0.04				
	546.3	0.07	18600	19180	−580	${}^4G_{7/2}$
	544.8	0.08				
	541.5	0.30				
	539.8	0.45				
	538.3	0.49				
	537.6	0.60				
	535 peak	0.66				
	530.3	0.16	19170	19630	−460	${}^4G_{9/2}$
	527.7	0.28				
	525.7	0.22				
	524.2 peak	0.37				
	521.7	0.40				
	520.2	0.40				
	519.3	0.43				
	512 broad	0.18				
	488.6	0.11	20700	21180	−480	${}^2D_{3/2}$ ${}^2G_{9/2}$
	487.2	0.25				
	485.7	0.39				
	483.7	0.19				
	481.6	0.25				
	478.9	0.23				
	471.1 broad	0.18	21300	21650	−350	${}^4G_{11/2}$
	468.1 peak	0.20				
	442.4	0.05				
	439.1	0.11				
	438.1	0.34	22840	23400	−560	${}^2P_{1/2}$
	437.6	0.38				
	430.1	0.05	23420	23900	−480	${}^2D_{5/2}$
	424.6	0.03				
	389.5	0.04	25740	26320	−580	${}^2P_{3/2}$
	387.2	0.03				
	369.7	0.08	27200	28280	−1080	${}^4D_{3/2}$
	367.6 peak	0.43				
	366.4 peak	0.59				
	360.5	0.44	27740	~ 28510 [a]	−770	${}^4D$
	357.2 peak	0.43	28000	~ 28840 [a]	−840	${}^4D$
	340.5	0.2	29370	~ 30400 [a]	−1030 ?	—
$NdAlO_3$ (at ~ 300°K)	882	0.19	11340	11580	−240	${}^4F_{3/2}$
	812	0.32	12320	12620	−300	${}^4F_{5/2}$
	749	0.29	13350	13580	−230	${}^4F_{7/2}$
	680	0.10	14710	14840	−130	${}^4F_{9/2}$
	628	0.03	15920	16030	−110	${}^2H_{11/2}$
	587	4 bands 0.35	17040	17400	−360	${}^4G_{5/2}$
	522	0.18	19160	19630 ?	—	${}^4G_{9/2}$
	432	0.07	23150	23400	−350	${}^2P_{1/2}$
Sm(III)ThO_2 (at ~ 100°K)	1992 broad	0.1	5010	5000	+ 10	${}^6H_{13/2}$

Table 1. Continued next page.

	λ	D	σ_{oxide}	σ_{aqua}	$\sigma_{\text{oxide}} - \sigma_{\text{aqua}}$	
Sm(III)ThO$_2$	1552	0.17	6460	~ 6400	+ 60	$^6F_{3/2}$
(at ~ 100°K)	1535	0.17				
	1484	0.17	6740	6800	− 60	$^6H_{1/52}$
	1383	0.25	7230	7200	+ 30	$^6F_{5/2}$
	1235	0.26	8100	8000	+ 100	$^6F_{7/2}$
	1079	0.18	9270	9200	+ 70	$^6F_{9/2}$
	945	0.04	10580	10500	+ 80	$^6F_{11/2}$
	490	0.01	20410	?		
	479.5	0.015	20850	20880	− 30	—
	468.5	0.01	21470	21550	− 80	—
	464	0.02				
	419	0.02	23870	24110	− 240	—
	406	0.15	24630	24900	− 270	^6P
	378.5	0.04	26420	26700	− 280	—
Eu(III)ThO$_2$	2000 broad	0.1	5000	5100	− 100	$^7F_6$
(at ~ 100°K)	525.5 broad	0.01	19030	19010	+ 20	$^5D_1$
	466.5	0.04	21460	21490	− 30	$^5D_2$
	465	0.03				
	404 sh.	0.01	24750	24390	+ 360 ?	
	394.5	0.07	25350	25360	− 10	
	384 peak	0.01	26040	26250 ?	− 210 ?	
	362.5	0.02	27580	27650 ?	− 70 ?	
Ho(III)ThO$_2$	1938	0.16	5190	5030	+ 160	$^5I_7$
(at ~ 100°K)	1910	0.10				
	1878	0.08				
	1138	0.07	8790	8530	+ 260	$^5I_6$
	884	0.02	11310	11140	+ 170	$^5I_5$
	650.5 sh.	0.08	15510	15420	+ 90	$^5F_5$
	642.5	0.18				
	540.5	0.25	18520	18370, 18520	—	$^5S_2$, $^5F_4$
	488.5	0.06	20560	20560	0	$^5F_3$
	487.5	0.10				
	486.2	0.10				
	483	0.06				
	473.5	0.07	21190	21030	+ 160 ?	$^5F_2$
	469.2	0.05				
	465	0.09	21570	21300	+ 270 ?	$^3K_8$
	462.5	0.10				
	455.2	0.32	22100	22200, 22300	—	$^3K_6$, $^5F_1$
	450.0	0.37				
	419.5	0.14	23910	24030	− 120	$^5G_5$
	416	0.10				
	387.5	0.03	25940	26000, 26200	—	$^5G_4$, $^3K_7$
	383	0.04				
	364.8	0.08	27560	27740	− 180	$^5G_6$
	361.2	0.1				
Er(III)ThO$_2$	1560	0.07	6640	~ 6600	—	$^4I_{13/2}$
(at ~ 100°K)	1531	0.23				
	1480 broad	0.12				
	973	0.09	10280	10220	+ 60	$^4I_{11/2}$
	797	0.06	12550	12520	+ 30	$^4F_{9/2}$ *
	654.5	0.16	15330	15350	− 20	$^4I_{9/2}$ *
	649	0.16				
	545.2	0.18	18350	18480	− 130	$^4S_{3/2}$
	524.2	0.31	19160	19230	− 70	$^2H_{11/2}$
	518.8	0.43				
	489.5	0.15	20430	20600	− 170	$^4F_{7/2}$
	451.5	0.03	22150	22270, 22610	—	$^4F_{5/2}$, $^4F_{3/2}$
	407.8	0.07	24540	24630	− 90	$^2H_{9/2}$
	405.8	0.03				
	381.5	0.29	26370	26490	− 120	$^4G_{11/2}$
	378.5	0.43				
	367.6 sh.	0.07	27390	27500, 28100[b]	—	$^2G_{9/2}$, $^2G_{7/2}$
	365.1	0.15				

Table 1. Continued next page.

	λ	D	σ_{oxide}	σ_{aqua}	$\sigma_{\text{oxide}} - \sigma_{\text{aqua}}$	
Er_2O_3	1505	14 bands	6640	~ 6600	—	$^4I_{13/2}$
(at ~ 100°K)	976	6 bands	10250	10220	+ 30	$^4I_{11/2}$
	801	5 bands	12480	12520	— 40	$^4F_{9/2}$ *
	654	9 bands	15290	15350	— 60	$^4I_{9/2}$ *
	549	7 bands	18210	18480	— 270	$^4S_{3/2}$
	523.7	15 bands	19090	19230	— 140	$^2H_{11/2}$
	491	10 bands	20370	20600	— 230	$^4F_{7/2}$
	454	10 bands	22030	22270	— 240	$^4F_{5/2}$
	445.8	6 bands	22430	22610	— 180	$^4F_{3/2}$
	407.5	9 bands	24540	24630	— 90	$^2H_{9/2}$
	380.5	13 bands	26280	26490	— 210	$^4G_{11/2}$
	367.5	0.28	27210	27500[b]	— 290	$^2G_{9/2}$
(at ~ 300°K)	359	0.11	27850	28110[b]	— 260	$^2G_{7/2}$
	307	0.02	32570	32770[b]	— 200	$^2P_{1/2}$?
	294	0.01	34010	34070[b] ?	— 60 ?	$^4G_{7/2}$?
	289	0.01	34600	34820[c]	— 220 ?	—
	275	0.05	36360	36510[b]	— 150 ?	$^4G_{9/2}$?
	257.6	0.27	38820	39180[c]	— 360	^4D
$ErAlO_3$	974	0.19	10270	10220	+ 50	$^4I_{11/2}$
(at ~ 300°K)	807	0.11	12390	12520	— 130	$^4F_{9/2}$ *
	655	0.34	15270	15350	— 80	$^4I_{9/2}$ *
	524	0.55	19080	19230	— 150	$^2H_{11/2}$
	489	0.37	20450	20600	— 150	$^4F_{7/2}$
	452	0.14	22120	22270	— 150	$^4F_{5/2}$
	408	0.16	24510	24630	— 120	$^2H_{9/2}$
	380	0.57	26320	26490	— 170	$^4G_{11/2}$
	368	0.24	27170	27500[b]	— 330	$^2G_{9/2}$
Tm(III)ThO_2	1665	0.12	6030	5810[b]	+ 220	$^3F_4$*
(at ~ 100°K)	1657	0.11				
	1632	0.07				
	1210	0.13	8330	8230[d]	+ 100	$^3H_5$
	1196 peak	—				
	1160 broad	0.03				
	794	0.19	12610	12560[d]	+ 50	$^3H_4$*
	770	0.05				
	687	0.19	14560	14480[d]	+ 80	$^3F_3$
	682 sh.	0.09				
	660 ?	0.01	15150	15110[d]	+ 40	$^3F_2$
	472	0.04	21410	21280[d]	+ 130	$^1G_4$
	463.5	0.04				
	361	0.03	27850	27950[d]	— 100	$^1D_2$
	357.5	0.04				
Yb(III)	974 peak	0.38	10550	10300	+ 250	$^2F_{5/2}$
(at ~ 100°K)	945 sh.	0.14				
	925	0.18				

Table 1. Wavelengths λ in mμ and Optical Densities D above Background of Bands (sh. = shoulders) Observed in Reflection Spectra. The Wavenumbers in cm^{-1} of Baricenters are given and Compared with Those of the Aqua Ions [14], and the Difference ($\sigma_{\text{oxide}} - \sigma_{\text{aqua}}$) Indicated. The Final Column gives the Assignment [14] of the Excited J-level.

* We give a different order of the pairs of levels $^4I_{9/2}$ and $^4F_{9/2}$ in Er(III) and $^3H_4$ and $^3F_4$ in Tm(III) than that frequently found in literature. Whereas the squares of the coefficients of the L, S-terms in the appropriate wavefunctions of the J-levels are close to 50%, and no objective choice can be made, we find it more satisfactory to avoid partial inversion of the ground multiplet and to retain a width not very far from the RUSSELL–SAUNDERS value $(L + \frac{1}{2}) \zeta_{4f}$.

[a] D. C. STEWART, Light Absorption, AECD-2389. Berkeley 1948.

[b] S. HÜFNER, Z. Phys. **168,** 74 [1962].

[c] C. K. JØRGENSEN [28].

[d] E. Y. WONG and I. RICHMAN, J. Chem. Phys. **34,** 1182 [1961].

ligands is an apparent decrease of the parameters of interelectronic repulsion determining the distances between the different multiplet terms of the electron configuration $4f^q$. This effect corresponds to a relatively much larger tendency towards covalent bonding in these compounds, compared to the aqua ion, though this tendency is less pronounced than in the transition group complexes characterized by a partly filled 3d, 4d, or 5d shell.

Praseodymium. The sample is black and contains at the same time Pr(III) and Pr(IV). The reflection spectrum shows narrow bands in the near infrared (see Table 1) characteristic for Pr(III). All the visible bands are covered by the broad intense band due to Pr(IV) or to the simultaneous presence of the two oxidation numbers.

Neodymium. $Th_{0.86}Nd_{0.14}O_{1.93}$ is pale blue-grey and shows the characteristic bands (Table 1) caused by transitions from $^4I_{9/2}$ to the other *J*-levels of the electron configuration $4f^3$. However, most of these excited levels correspond only to one relatively broad band in our sample, whereas it has been known for a long time that pure Nd_2O_3 has a remarkable fine-structure in such bands[5]. We measured blue Nd_2O_3 and confirmed this observation. Thus at ~100 °K the band in the yellow shows 29 components, and the transition to $^2P_{1/2}$ at 437.6 mμ is very narrow and accompanied by three weaker components at 438.1, 439.1 and 442.4 mμ. Since no splitting of $^2P_{1/2}$ is expected, these are presumably caused by vibrationally or electronically excited sublevels of the ground-state, or by Nd(III) in strongly distorted (A-type?) sites.

Samarium. $Th_{0.86}Sm_{0.14}O_{1.93}$ is very pale yellow and shows the bands of Sm(III) in the near infrared and in the blue.

Europium. The absorption bands of

$$Th_{0.86}Eu_{0.14}O_{1.93} \quad \text{and} \quad Th_{0.5}Eu_{0.5}O_{1.75}$$

are narrow and very weak. The former mixture fluoresces bright pink, with line emission at

$$\begin{array}{lll} \left.\begin{array}{l} 628\ \mathrm{m}\mu = 15\,920\ \mathrm{cm}^{-1} \\ 611.5 \quad = 16\,350 \end{array}\right\} & {}^5D_0 \rightarrow {}^7F_2\ (\Gamma_3 \text{ and } \Gamma_5) & \\ 591 \quad = 16\,920 & {}^5D_0 \rightarrow {}^7F_1\ (\Gamma_4) & \\ (580) \quad = (17\,240) & {}^5D_0 \rightarrow {}^7F_0\ (\Gamma_1) & (2) \end{array}$$

whereas the latter mixture, as well as Eu_2O_3, do not fluoresce. For a calculation of the relative position of the Γ_3 and Γ_5 components, see the Appendix.

Terbium. The sample is black similar to Tb_4O_7 which was studied by Vratny[6]. We find a band at 1790 mμ in the latter oxide, probably belonging to $^7F_6 \rightarrow {}^7F_1$ of Tb(III), a possible band at 2150 mμ and weaker absorption at 1958 and 1715 mμ.

Holmium. The very pale brown $Th_{0.86}Ho_{0.14}O_{1.93}$ has a detailed spectrum as indicated in Table 1.

Erbium. The pink $Th_{0.86}Er_{0.14}O_{1.93}$ has all the *J*-levels expected for Er(III), and again, the bands are relatively broader than those of Er_2O_3 which show a detailed fine-structure[7, 8]. Many of the lines of Er_2O_3 must be due to co-excited vibration in the excited level and possible splitting in the ground-level, because even $^4S_{3/2}$ shows seven narrow bands. We also measured the electronic spectrum of Er_2O_3 in the near ultra-violet using a hydrogen lamp as light source (Table 1).

Thulium. The pale grey $Th_{0.86}Tm_{0.14}O_{1.93}$ has bands somewhat more narrow than the bands of the aqua ion at room temperature.

Ytterbium. The nearly colourless $Th_{0.86}Yb_{0.14}O_{1.93}$ shows a narrow and a broader band in the near infra-red, as all other Yb(III) compounds.

Discussion

Ephraim and Bloch[9] discovered the nephelauxetic effect[10] in the lanthanides, i. e. that the apparent values of the interelectronic repulsion parameters separating the multiplet terms of $4f^q$ are smaller in supposedly more covalent compounds (such as the anhydrous chlorides, bromides and iodides) than in the aqua ions and fluorides. This effect is much weaker in the 4f shell of lanthanide complexes than in the 3d, 4d and 5d shells of ordinary transition group complexes, though it is quite perceptible in Pr(III), Nd(III), Sm(III) and Gd(III)[11].

Schäffer[12] pointed out that oxides of Cr(III) frequently have a much larger nephelauxetic effect than one would expect from the reducing character of oxide (though it is to be remembered that O^{--} is highly unstable in the gaseous state). Actually, this phenomenon is far more pronounced in the lanthanides, and Boulanger[13] found that the high-temperature form of Pr_2O_3 is yellow and has the three levels $^3P_0$, $^3P_1$ and $^3P_2$ at 5.7% lower wavenumber than the apple-green aqua ion. The similar figure (l. c. [9, 11]) for anhydrous PrI_3 which should be more covalent by most standards is only 2.9%.

The present study seems to be the first in demonstrating a nephelauxetic effect in the second half of the lanthanides, viz. in Ho(III), Er(III) and Tm(III). The order of magnitude of the effect seems to be some five times larger than in anhydrous

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$LaCl_3$ containing such ions, where the nephelauxetic influence hardly can be recognized [14].

Since the total splitting into sub-levels of the ground-level, some 100 to 300 cm^{-1}, is not much smaller than the general shift of all the excited levels due to the nephelauxetic effect, it is very useful that all the sub-levels of nearly all the *J*-levels recently have been identified for Pr(III) in

$$Pr(H_2O)_9(C_2H_5SO_4)_3\ ^{15};$$
$$LaCl_3;\quad PrCl_3;\quad GdCl_3\ ^{16,17}$$

and in $$LaBr_3 \text{ and } PrBr_3\ ^{16,17}.$$

Analogous identifications have been made for Nd(III) in $LaCl_3$ and $NdBr_3$ [18]. Hence, it is now recognized that the differences in the nephelauxetic ratio β are somewhat smaller than previously assumed, some 0.5% decrease going from the chromophore $Pr(III)Cl_9$ to $Pr(III)Br_9$ and 0.38% going from $Nd(III)Cl_9$ to $Nd(III)Br_9$. Comparing the Pr(III) aqua ion and the anhydrous chlorides, β is some 0.8% smaller in the latter case **. It is interesting to note that most of the excited levels correspond to roughly the same value of β. However, the singlet levels $^1G_4$ and $^1D_2$ vary less in Pr(III) than the eight triplet levels known, and the difference of β for $^2H_{9/2}$ going from the Nd(III) chloride to bromide [18] is only 0.10% and for $^2H_{11/2}$ only 0.21%. It might perhaps be connected with the fact that the position of these particular *J*-levels of Nd(III) is determined partly by the non-diagonal element of the two-electron operator with a level of a lower value (11) of Racah's quantum number *U*.

In our thorium oxide preparations, one can determine the difference of β between the aqua ion and the oxide, $d\beta$, by plotting the wavenumber difference $\sigma_{oxide} - \sigma_{aqua}$ for the baricenters (of intensity of the absorption bands) as a function of σ_{aqua}. One then observes a rough linear relation

$$\sigma_{oxide} - \sigma_{aqua} = d\sigma - (d\beta)\ \sigma_{aqua}. \qquad (3)$$

The physical significance of this equation is that $d\sigma$ represents the stabilization of the lowest sub-levels (populated at 100 °K) of the oxide minus the similar stabilization of the aqua ion in the crystalline ennea-aqua ethylsulphates. Table 2 combines the results for a series of our mixtures, and for oxides, in terms of equ. (3). Due to the scattering of the data in Table 1 the straight lines are somewhat uncertain, as the reader may verify.

The oxides seem quite generally to have a larger splitting for a given *J*-level into sub-levels than has the corresponding aqua ion. White [19] discussed the sub-levels in cubic chromophores MX_8. Kiss [20] indicates that the distance between the two sub-levels of the excited level $^2F_{5/2}$ of Yb(III) in CaF_2 ($a = 5.41$ Å) is 630 cm^{-1}. This distance corresponds to $8\,\sigma^*$ [the first and third line of eq. (9) of ref. [21] should read 13.33 and 17.77 rather than 13.81 and 17.30] in the description involving σ-anti-bonding effects [21]. However, our spectrum of Yb(III) in ThO_2 suggests that this distance is slightly smaller, about 500 cm^{-1}. This tends to show that the slightly smaller Yb – F distance in CaF_2 compensates the expected larger spectrochemical effect in Yb – O. If we apply White's results for $V_6 = -0.30\ V_4$ (this corresponds rather closely to the σ-anti-bonding case [21]) and $\sigma^* = 60\ cm^{-1}$ we obtain the stabilizations in cm^{-1} of the ground sub-levels in ThO_2:

$$\begin{array}{lll} \text{Nd(III) } 400 & \text{Sm(III) } 65 & \text{Ho(III) } 500 \\ \text{Er(III) } 620 & \text{Tm(III) } 680 & \text{Yb(III) } 600 \end{array} \qquad (4)$$

The stabilizations of the aqua ions are approximately 100 – 200 cm^{-1}. When this value is subtracted from those of equ. (4), the difference has the same order of magnitude as $d\sigma$ of Table 2 though no quantitative agreement is obtained.

The values of $d\beta$ show an unexpected variation with the atomic number. The decrease going from Pr(III) (where $d\beta$ certainly [11, 13] would be above 5%) over Nd(III) to Sm(III) might suggest that Tm(III) would experience the weakest nephelauxetic effect among all the trivalent lanthanides. On the other hand, there is a definite relation between oxidizing character and nephelauxetic effect [10, 14] and Tm(III) has electron transfer bands at lower wave-

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** Recently, E. Y. Wong, O. M. Stafsudd, and D. R. Johnston (J. Chem. Phys. **39**, 786 [1963]) reported the quantity $d\beta$ of equ. (3) to be 2.6% for Pr(III) in yttrium aluminum garnet $Y_3Al_2(AlO_4)_3$ whereas it has the opposite sign, –1.4%, for Pr(III) in LaF_3. However, these authors may have shifted the aqua ion 0.4% relative to our estimate.

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	dσ in cm^{-1}	dβ in percent
$Nd_{0.14}Th_{0.86}O_{1.93}$	+150	3.3
Nd_2O_3	+200	3.6
$NdAlO_3$	− 50	1.0
$Sm_{0.14}Th_{0.86}O_{1.93}$	+200	1.9
Gd_2O_3	0	0.8
$Ho_{0.14}Th_{0.86}O_{1.93}$	+350	1.7
$Er_{0.14}Th_{0.86}O_{1.93}$	+250	1.6
Er_2O_3	+200	1.6
$ErAlO_3$	+ 50	0.9
$Tm_{0.14}Th_{0.86}O_{1.93}$	+300	1.3

Table 2. The Parameters of Groundstate Stabilization dσ and Nephelauxetic Effect dβ Relative to the Aqua Ions, Defined in Equation (3).

number[22] than Gd(III) and Er(III). Actually, what was taken by one of the writers[23] as the beginning of $4f^{12} \rightarrow 4f^{11}5d$ transition in an aqueous solution of thulium(III) perchlorate is the tail of the broad electron transfer band (from the filled orbitals of the water molecules to 4f) as found in Eu(III) aqua ions[24].

We may discuss two definite problems in evaluating dβ. The position of $^4I_{13/2}$ in the Er(III) aqua ion is not well-known, and the value given in Table 1 is obtained by comparison with the results for Er(III) in $LaCl_3$[25] and in molten nitrates[26]. A more plausible value may be 6650 cm^{-1}.

Actually, the deviations of the individual points from a straight line eq. (3) are somewhat more severe for Er(III) than for most of the other lanthanides studied here.

The treatment of Er(III) in cubic symmetry previously suggested[27] can be adapted to $Er_{0.14}Th_{0.86}O_{1.93}$ though with other parameters, e. g. the ratio $(\mu/\lambda)_{15/2}$ would be -0.35. The overall width of the *J*-levels is predicted to be some 200 − 700 cm^{-1} in qualitative agreement with the spectra observed. However, we are not here making any detailed assignment of the individual sub-levels.

The aqua ion spectra of Er(III), Ho(III) and Dy(III) were previously discussed[28]. In the cases where it has been reported that the nephelauxetic effect of Er(III) anion complexes is absent or even slightly negative[11, 26] this is due to the accidental cancellation of dσ and (dβ)σ for transitions in the visible region. The observation of transitions in the near infra-red has allowed the independent evaluation of the rather large value of dσ.

Europium(III) complexes pose a most perplexing problem. It has previously been noted that the narrow and very weak transitions from $^7F_0$ to $^5D_0$, $^5D_1$ and $^5D_2$ hardly show any nephelauxetic effect[11, 22]. It is possible to give 0.1% as a higher limit for dβ, an order of magnitude smaller than in the other ThO_2 cases. There is no first-order contribution to dσ since the groundstate is not degenerate. [This is also true for Gd(III) where dβ for Gd_2O_3 is 0.8%.] The answer may again be connected with the fact that very large non-diagonal elements of the two-electron operator connect ^5D with the two other ^5D one of which has decreased seniority number[29]. If such non-diagonal elements were particularly strongly decreased in relatively more covalent $4f^q$ complexes, this effect would compensate the nephelauxetic effect to a large extent. One may also consider the behaviour of Eu(III) as an extreme case of a general tendency of spin-forbidden transition to show a weaker nephelauxetic effect[15, 16]. However, there is no theoretical support at present to explain such phenomena.

Our thorium oxide mixtures seem to be quite extreme (together with the pure oxides M_2O_3) relative to other mixed oxides. Thus, the grey-blue[30] $NdAlO_3$ and pink $ErAlO_3$ are included in Table 1 and show much smaller values of dβ. If these compounds were cubic perovskites, the lanthanide atom would be tetradecahedrally coordinated with twelve oxygen atoms. However, our samples are distorted and did not give a cubic X-ray diagram. Bertaut and Mareschal[31] recently described a hexagonal $ErAlO_3$ transforming to the perovskite-structure above 1000 °C. Numerous distorted perovskites are formed by lanthanides[32, 33].

Keating and Drickamer[34] applied more than 100 000 atm. pressure to lanthanide compounds and obtained nephelauxetic effects corresponding

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to dβ about half a percent. This makes the behaviour of the ThO_2-samples with d$\beta \sim 2\%$ even more surprising. On the other hand, Sm(III) can be introduced[35] as well on the Ba as on the Ti site of $BaTiO_3$ (though the GOLDSCHMIDT ionic radii are very different: Ti(IV) 0.64 Å, Ba(II) 1.43 Å and Sm(III) 1.14 Å) and the fluorescence spectrum shows the unexpected phenomenon that dβ is 3% larger for Sm(III) on the compressed Ti site than for the Ba site.

The reason why the nephelauxetic effect is so pronounced in the thorium oxide samples may be that the partly filled 4f shell delocalizes, to the extent of $\sim 1\%$, on the adjacent oxygen vacancies forming a sort of F centers. It would be interesting to perform electron spin or nuclear spin resonance experiments on lanthanide-containing ThO_2 made from oxygen 17 in order to show the interaction of the partly filled shell with the oxygen nuclei. It is doubtful whether the natural abundance of oxygen 17 allows nuclear spin resonance on the ordinary materials[36].

Our conclusions are that we have a five times more extensive nephelauxetic effect in a trivalent lanthanide atom in thorium dioxide than in anhydrous lanthanum chloride, which may be compared to SCHÄFFER's phenomenon[12] that Cr_2O_3 is slightly more nephelauxetic than $CrCl_3$. However, the quantitative extent is astonishing in the lanthanide case where EPHRAIM's effect[9, 10] usually is much less pronounced even in anhydrous iodides, acetylacetonates and dialkyldithiocarbamates[22].

Experimental

Compounds. Stock solutions of 0.5 or 0.1 M rare earth perchlorates were prepared from American Potash (Lindsay Division, West Chicago) 99.9% or better oxides and Merck's p. a. perchloric acid. The oxides dissolve in a weak excess of 2 M acid by gentle heating, except Tb_4O_7 which needs strong boiling with 8 M $HClO_4$. A solution of 0.1 M $Th(NO_3)_4$ (Fluka) and the adequate amount of lanthanide perchlorate solution were mixed, and a 50% excess of aqueous ammonia, p. a., was added. The hydroxide precipitate was kept in the supernatant solution for four hours, filtered, washed with water, and ignited in new unglazed porcelain crucibles in an electric furnace (oxidizing conditions) at 1000 °C for 30 minutes. We did not observe the red coloration of ThO_2 occurring when heated to 1800 °C and caused by oxygen deficiency[37].

$NdAlO_3$ and $ErAlO_3$ were prepared in a similar way from $Al(ClO_4)_3$ (Fluka) and the same stock solutions. Though we may not have succeeded in preparing the perovskite, the reflection spectrum is widely different from that of Nd_2O_3 and Er_2O_3.

The oxides Nd_2O_3 and Er_2O_3 of which reflection spectra were taken were heated to 500 °C for a few minutes in order to remove water and carbon dioxide. A comparison with the spectra (to be discussed later) of $Nd_{0.1}La_{0.9}O_{1.5}$ (A type) and $Nd_{0.2}Yb_{0.8}O_{1.5}$ (C type) shows that the sample of Nd_2O_3 predominantly belongs to the hexagonal A-type, whereas Er_2O_3, of course, is the cubic C-type.

X-ray measurements were made with a GUINIER–DEWOLFF camera (Enraf-Nonius, Delft) using copper Kα-radiation. Silicon was used as standard substance. The films, though showing broadened lines of the $CaF_2(ThO_2)$ lattice, indicated no additional phases in the $MO_{1.5} - ThO_2$ mixtures.

Reflection spectra were measured of samples kept in contact with brass blocks at room temperature and 78 °K on a Cary 14 Spectrophotometer suitably modified for taking reflection spectra. However, thermocouple measurements show that the actual temperature at the surface is about 340 °K and 100 °K, respectively. The light from a powerful tungsten lamp is sent, by means of a system of lenses, both on the sample to be studied and on a plane mirror or a plane surface of $MgCO_3$. After that the two beams are focussed into the instrument. In the case of the ultraviolet reflection spectrum of Er_2O_3, the spectrophotometer was used as a single-beam instrument with the usual hydrogen lamp.

The mixtures having the composition $NdAlO_3$ and $ErAlO_3$ were measured by Messrs. GEORGES CASARO and BERNARD DUSONCHET on the reflection attachment to the Beckman DU spectrophotometer.

Fluorescence spectra were measured on the Cary 14 by a technique shortly to be described[38].

Appendix

The multiplet term ^7F of f^6 [as represented by Eu(III)] has the particular property that only one electron is lacking in a half-filled totally symmetric shell ^8S. Hence it is possible to introduce the one-electron energies with opposite sign $-E_2$, $-E_4$ and $-E_5$ for odd $\gamma_2(a_{2u})$, $\gamma_4(t_{1u})$ and $\gamma_5(t_{2u})$ orbitals, re-

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spectively, and to use the fact that for a given J-level the baricenter is not moved by a first-order "ligand field" perturbation and the J-level hence has a perturbation energy directly related to the perturbation energy per electron of the complete shell i. e. $(E_2+3\,E_4+3\,E_5)/7$:

$$\begin{aligned}
{}^7\mathrm{F}_0(\Gamma_1):&\quad -\tfrac{1}{7}\,E_2-\tfrac{3}{7}\,E_4-\tfrac{3}{7}E_5\,,\\
{}^7\mathrm{F}_1(\Gamma_4):&\quad -\tfrac{1}{7}\,E_2-\tfrac{3}{7}\,E_4-\tfrac{3}{7}E_5\,,\\
{}^7\mathrm{F}_2(\Gamma_3):&\quad -a_1\,E_2-a_2\,E_4-a_3\,E_5\,,\\
(\Gamma_5):&\quad -b_1\,E_2-b_2\,E_4-b_3\,E_5
\end{aligned}\tag{5}$$

bound by the conditions

$$\begin{aligned}
&a_1+a_2+a_3=b_1+b_2+b_3=1,\\
&2\,a_1+3\,b_1=5/7\,,\\
&2\,a_2+3\,b_2=2\,a_3+3\,b_3=15/7\,.
\end{aligned}\tag{6}$$

Since the Γ_J components of

$$\begin{aligned}
{}^7\Gamma_2&=\Gamma_1+\Gamma_4+\Gamma_5\,,\\
{}^7\Gamma_4&=\Gamma_1+\Gamma_2+2\,\Gamma_3+2\,\Gamma_4+3\,\Gamma_5\,,\\
{}^7\Gamma_5&=\Gamma_1+\Gamma_2+2\,\Gamma_3+3\,\Gamma_4+2\,\Gamma_5\,,
\end{aligned}\tag{7}$$

do not comprise Γ_3 of ${}^7\Gamma_2$, the coefficient a_1 is zero. Equ. (6) then gives $b_1=5/21$. We may utilize the fact that in the electrostatic ligand field model, a level with $J=2$ is only perturbed by the ligand field components $\mathrm{A}_2\langle r^2\rangle$ (absent in cubic symmetry) and $\mathrm{A}_4\langle r^4\rangle$ but not $\mathrm{A}_6\langle r^6\rangle$, as for $J\geqq 3$ of f^q, and hence to write[39]

$$\begin{aligned}
{}^7\mathrm{F}_2(\Gamma_3):&\quad 3\,\delta=+3\,a_2\,\eta-a_3\,\eta\\
(\Gamma_5):&\quad -2\,\delta=-(5/21)\,6\,\eta+3\,b_2\,\eta-b_3\,\eta
\end{aligned}\tag{8}$$

from which the coefficients can be derived:

$$a_2=\frac{9}{14}\,;\;\; a_3=\frac{5}{14}\,;\;\; b_2=\frac{2}{7}\;\;\text{and}\;\; b_3=\frac{10}{21}\,.\tag{9}$$

It is worth remarking that this argument is entirely valid though the electrostatic model is inadequate in the description of lanthanide chromophores[21]. The point is that the energy levels expressed as linear combinations of one-electron energies have identical expressions in the more general M.O. theory of which the electrostatic model is a special case. Introducing[21]

$$E_2=(280/9)\,\sigma^*,\quad E_4=(224/27)\,\sigma^*\;\;\text{and}\;\;E_5=0\,,$$

equs. (5) and (9) reduce to

$$\Gamma_3:\quad -5.333\,\sigma^*\quad\text{and}\quad \Gamma_5:\quad -9.778\,\sigma^*\,.\tag{10}$$

The experimental results of equ. (2) can therefore be interpreted as the excited levels being

$$\begin{aligned}
{}^7\mathrm{F}_1(\Gamma_4)&\quad 320\ \mathrm{cm}^{-1}\\
{}^7\mathrm{F}_2(\Gamma_5)&\quad 890\ \mathrm{cm}^{-1}\\
{}^7\mathrm{F}_2(\Gamma_3)&\quad 1320\ \mathrm{cm}^{-1}
\end{aligned}\tag{11}$$

above the groundstate ${}^7\mathrm{F}_0(\Gamma_1)$. If second-order effects (spin-orbit coupling with other multiplets and "ligand field" non-diagonal elements with Γ_3 and Γ_5 components of other J-levels) can be neglected, σ^* of equ. (10) is seen to be close to 95 cm^{-1}. The baricentre of ${}^7\mathrm{F}_2$ is at 1060 cm^{-1} in ThO_2 whereas it is[40] at 1036 cm^{-1} in LaCl_3. Kingsley and Prener[41] find for Eu(III) in CdF_2 components of ${}^7\mathrm{F}_1$ between 307 and 400 cm^{-1} (hence the site is not perfectly cubic) and ${}^7\mathrm{F}_2$ components at 798, 826, 1334 and 1368 cm^{-1} comparable to equ. (11).

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