Reflection Spectra of Lanthanides in Cubic Oxides Containing Titanium (IV), Zirconium (IV), Indium (III), Tin (IV), Cerium (IV), and Thallium (III)

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Reflection spectra are measured at 100 °K of M = neodymium (III), samarium (III), europium (III), dysprosium (III), holmium (III), erbium (III), and ytterbium (III) in mixed oxides such as $M_xM'_{1-x}O_{1.5}$ [M′ = yttrium (III), indium (III), lanthanum (III), gadolinium (III) or thallium (III)] and $M_xM'_{1-x}O_{2-0.5x}$ [M′ = titanium (IV), zirconium (IV) (or mixtures of these two elements), tin (IV) or cerium (IV)]. Most of these oxides crystallize in the disordered fluorite structure or in the two superlattices C-type M_2O_3 and pyrochlore and relevant crystallographic parameters are measured. It was also attempted to introduce Er (III) in the perovskites $SrTiO_3$ and $BaTiO_3$. $LaErO_3$ and $LaYbO_3$ are distorted cubic (or have a very large unit cell) and certain Nd (III) Ti (IV) and Nd (III) Y (III) oxides present a new, non-cubic, structure. The nephelauxetic effect, the 4 f → 5 d and electron transfer bands in rare earths are theoretically discussed. A comparison is made with Cr (III) mixed oxides.

In the previous paper [1] we discussed the reflection spectra of lanthanides M in their mixed thorium oxides $M_xTh_{1-x}O_{2-0.5x}$. It was shown that the term distances in the partly filled 4 f-shells are decreased 1.3 to 3.3% below those of the corresponding aqua ions; i. e. that the nephelauxetic effect is far more pronounced than in other compounds of the rare earths.

We now wish to report optical and X-ray studies on similar mixed titanium, zirconium, tin and cerium oxides, where the lanthanide atom is surrounded by eight oxygen atoms in a cube, or in a cubic structure with oxygen vacancies statistically or systematically distributed on the eight positions. The fluorite lattice occurring in ThO_2 and CeO_2 has two common superlattices, the C-type M_2O_3 and the pyrochlore $A_2B_2O_7$. Both have the unit cell parameter a twice as large as a_F of the corresponding MO_2. Eight of the M atoms in the C-type unit cell are surrounded by a cube lacking a body-diagonal, whereas 24 M atoms are surrounded by six oxygen atoms in a cube lacking a face-diagonal. The various distances M – O are not so different as once supposed [2]; recent measurements by neutron diffraction have shown that all six distances on both sites are nearly identical [3, 4].

In the pyrochlore (koppite) each A atom is surrounded by six oxygen atoms in a cube lacking two oxygens on a body-diagonal (one may also call it an octahedron compressed by a factor of $\sqrt{3}$ along the trigonal axis) and each B has a complete cube of eight O. Each oxygen vacancy is surrounded by four A atoms.

1. Previous Studies on $MO_2 - M'O_{1.5}$ and $MO_{1.5} - M'O_{1.5}$ Systems

a) **CeO_2:** Zintl and Croatto [5] discovered that CeO_2 is miscible with La_2O_3 to the extent of forming $Ce_{0.56}La_{0.44}O_{1.78}$, while retaining the fluorite structure. McCullough and Britton [6] studied mixtures of CeO_2 with Sm_2O_3; Gd_2O_3; Y_2O_3 and indicate that the faint X-ray lines characterizing the C-type appear above some 50 – 60% concentrations of the trivalent ion. According to these authors the transition is gradual and the dividing line quite arbitrary. Brauer and Gradinger [7] discussed the general question whether the ordered superlattices are completely miscible with the fluorite type or not. Complete miscibility was assumed for CeO_2 containing Sm (III), Gd (III), Dy (III) and

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Y(III). CeO_2 and Ce_2O_3 are not completely miscible[8].

b) **ThO_2:** According to Brauer and Gradinger[7], ThO_2 is miscible with at most 50 atomic % Nd, 60% Sm and less than 25% Y. Recently it has been reported[9] that the relative miscibility of ThO_2 and Yb_2O_3 is rather small, at most $Th_{0.92}Yb_{0.08}O_{1.96}$ being obtained as disordered fluorite, whereas $C-Yb_2O_3$ dissolves even less ThO_2. On the other hand, $Eu_{0.5}Th_{0.5}O_{1.75}$ is still a fluorite[1, 9].

c) **TiO_2:** Giusca and Popescu[10] noted that $Sm_2Ti_2O_7$, $Y_2Ti_2O_7$, and Y_2TiO_5 crystallize in cubic lattices, whereas $La_2Ti_2O_7$, La_2TiO_5, $Nd_2Ti_2O_7$, Nd_2TiO_5, and Sm_2TiO_5 occur in rhombic crystals[10a]. These compounds do not contain isolated dititanate groups, but exemplify the pyrochlore structure, the small Ti(IV) occupying the six coordinated A position, and the lanthanides the eight-coordinated B position. Roth[11] made an extensive study of several other mixed oxides, finding that $Sm_2Ti_2O_7$, $Gd_2Ti_2O_7$, $Dy_2Ti_2O_7$, $Yb_2Ti_2O_7$, $Y_2Ti_2O_7$ all are cubic pyrochlores, whereas $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$ have an unindexed, distorted structure.

Black $EuTiO_3$ [presumably having electron transfer bands due to the transition Eu(II)Ti(IV) → Eu(III)Ti(III)] is known[12] to be a cubic perovskite with $a = 3.897$ Å.

d) **ZrO_2:** Very interesting reviews of the fluorite and superlattice types formed by ZrO_2 containing rare earths have recently been published by Perez y Jorba[13], Lefèvre[14], and Möbius[15].

e) **Mixed sesquioxides.** Reviews of this extensive subject have now been published by Brauer[16] and Roth[17]. Padurow and Schusterius[18] reported the orthorhombic perovskite $LaYO_3$. $LaInO_3$ and $LaYO_3$ are miscible to a great extent with cubic $SrTiO_3$, and tetragonally distorted $BaTiO_3$ becomes cubic by such admixtures. Schneider and Roth[19] found that $LaErO_3$, $LaTmO_3$, $LaYbO_3$ and $LaLuO_3$ are orthorhombic perovskites and that they are the only binary mixtures of rare-earths to form perovskites in equilibrium at 1650 or 1900 °C.

2. Preparations of Mixed Oxides

Table 1 gives the fluorite lattice parameter a (half the values of the actual a_P for pyrochlores and a_C for C-oxides) of the compounds we prepared.

a) **Mixed Er-oxides:** As seen from Table 1, we studied the influence of small amounts of titanium(IV) and zirconium(IV) on the C-type Er_2O_3. Our samples $Er_{0.95}Ti_{0.05}O_{1.525}$ and $Er_{0.9}Ti_{0.1}O_{1.55}$ are fairly compressed C-oxides. The sample $Er_{0.8}Ti_{0.2}O_{1.6}$ showed essentially the C-oxide lines with $a = 5.26_5$ Å. $Er_{0.67}Ti_{0.33}O_{1.67}$ contains two phases, one with $a = 5{,}27$ Å, probably the C-oxide grouping, and another, somewhat more intense, with $a = 5.11$ Å, comparable to the pyrochlore $ErTiO_{3.5}$ ($a = 5.04_2$ Å). In other words, the phase diagram $ErO_{1.5} : TiO_2$ must contain a miscibility gap between a C-oxide below some 25% Er and a fluorite (pyrochlore?) above some 35% Er.

The samples $Er_{0.8}Zr_{0.2}O_{1.6}$ and $Er_{0.67}Zr_{0.33}O_{1.67}$ are both C-oxides, whereas $Er_{0.5}Ti_{0.1}Zr_{0.4}O_{1.75}$ and $Er_{0.5}Ti_{0.25}Zr_{0.25}O_{1.75}$ only show the (broadened) lines appropriate for the fluorite structure. The a values vary in a fairly continuous way when compared with the disordered fluorite $ErZrO_{3.5}$ and pyrochlore $ErTiO_{3.5}$.

b) **Heat treatment in Hydrogen atmosphere:** We mentioned before that a cubic perovskite $EuTiO_3$ has been reported[12]. In this connection several of our samples were treated in hydrogen at ~ 1200 °C for two hours. No transformation to perovskites of the type $EuTiO_3$ were observed; $SmZrO_{3.5}$ and $DyZrO_{3.5}$ turned gray or purplish gray, whereas the colour of $EuTiO_{3.5}$, $EuZrO_{3.5}$ and even $YbZrO_{3.5}$ was not affected.

The pyrochlore $YbTiO_{3.5}$ turned violet grey by this treatment, the Debye lines were very sharp and $\frac{1}{2}\,a$ only changed negligibly, to 5.01_5 Å. The a values obtained for $SmZrO_{3.5}$ treated the same way was 5.27_5 Å and for $DyZrO_{3.5}$, unchanged, 5.21 Å. The lines were sharper, but no traces of pyrochlore reflections were observed.

c) **Rare-earth doped $BaTiO_3$ and $SrTiO_3$:** Samples of nominal compositions $Ba_{0.9}La_{0.1}Er_{0.1}Ti_{0.9}O_3$ and $Sr_{0.8}La_{0.2}Er_{0.2}Ti_{0.8}O_3$ were also prepared; but were not perfectly homogeneous. The main component seems to be a cubic perovskite with $a = 4.00$ Å and $a = 3.91$ Å respectively. The average value of the parameters of the tetragonally distorted compound extrapolate[18] to 3.987 Å for $BaTiO_3$ and is 3.898 Å for $SrTiO_3$. A second component of the strontium containing mixture showed weak fluorite lines with $a = 5.09$ Å. This is probably the limiting phase $Er_{1+x}Ti_{1-x}O_{3.5-0.5\,x}$ discussed above[19a].

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[19a] The purpose of the La(III) was to keep Er(III) on the octahedral Ti sites (cf. the discussion of Sm(III) in $BaTiO_3$ by S. Makashima, K. Hasegawa and S. Shionoya, J. Phys. Chem. Solids **23**, 749 [1962]).

Fluorites		*Pyrochlores*	
$Ce_{0.9}Nd_{0.1}O_{1.95}$	5.41	$SmTiO_{3.5}$	5.22^{10}
$Ce_{0.9}Er_{0.1}O_{1.95}$	5.41		5.114^{11}
$Ce_{0.9}Yb_{0.1}O_{1.95}$	5.41		5.11_8
$NdZrO_{3.5}$	$5.324(P)^{11}$	$EuTiO_{3.5}$	5.09_8
	5.30	$DyTiO_{3.5}$	5.053^{11}
$SmZrO_{3.5}$	$5.288(P)^{13}$		5.06
	5.27	$HoTiO_{3.5}$	5.05_2
$EuZrO_{3.5}$	5.23	$ErTiO_{3.5}$	5.04_2
$DyZrO_{3.5}$	5.21	$YbTiO_{3.5}$	5.015^{11}
$HoZrO_{3.5}$	5.20		5.01_8
$ErZrO_{3.5}$	5.19		
$YbZrO_{3.5}$	5.17	*C-oxides*	
$Nd_{0.5}Ti_{0.25}Zr_{0.25}O_{1.75}$	~5.16 (F ?)	$Nd_{0.2}Yb_{0.8}O_{1.5}$	5.27
$Dy_{0.5}Ti_{0.25}Zr_{0.25}O_{1.75}$	5.18 (F ?)	$InErO_3$	5.19
$Er_{0.5}Ti_{0.1}Zr_{0.4}O_{1.75}$	5.16	$In_{0.8}Er_{0.2}O_{1.5}$	5.06_2
$Er_{0.5}Ti_{0.25}Zr_{0.25}O_{1.75}$	5.15	$Er_{0.95}Ti_{0.05}O_{1.525}$	5.26_5
$Dy_{0.9}Ti_{0.1}O_{1.55}$	5.32 (F ?)	$Er_{0.9}Ti_{0.1}O_{1.55}$	5.26
$Dy_{0.8}Ti_{0.2}O_{1.6}$	~5.32 (F ?)	$Er_{0.8}Zr_{0.2}O_{1.6}$	5.26
$Dy_{0.67}Ti_{0.33}O_{1.67}$	5.15 (F ?)	$Er_{0.67}Zr_{0.33}O_{1.67}$	5.27
$Er_{0.8}Ti_{0.2}O_{1.6}$	5.21 (F ?)		
$NdSnO_{3.5}$	$5.284(P)^{11}$	*C-similar*	
	5.29	$LaErO_3$	5.29
$EuSnO_{3.5}$	5.25	$LaYbO_3$	5.25
$ErSnO_{3.5}$	5.19		

Table 1. Unit cell parameters a in Ångström units for fluorites ($a/2$ for the two superlattices $C-M_2O_3$ and pyrochlore $A_2B_2O_7$). The letters F, P and C refer to fluorite, pyrochlore and C-oxide.

d) **$LaErO_3$ and $LaYbO_3$:** When we tried to prepare at 1000 °C the orthorhombic perovskite $LaErO_3$ and $LaYbO_3$, we observed a rather surprising DEBYE-powder diagram. The main features are those of a fluorite with the remarkably small values of $a = 5.29$ and 5.25_5 Å, respectively, about 0.2 Å smaller than the values extrapolated for C-oxides. Then, weak superstructure lines appear which must either belong to a very large unit cell (the d-values corresponding to the index square sum $h^2 + k^2 + l^2 = 9$ and 24 for a cubic unit cell with the parameter $4a$ are quite conspicuous) or a distortion from cubic symmetry. This phenomenon is comparable to the very large hexagonal unit cells reported for mixtures of ZrO_2 with [13] Gd_2O_3 and with [14] Sc_2O_3 and shall be discussed in a subsequent paper. If samples of $LaErO_3$ or $LaYbO_3$ prepared at lower temperature are heated to 1200 °C for 3 hours, they transform irreversibly to the orthorhombic perovskite previously mentioned [19].

e) **Mixed Nd-oxides:** We obtained a powder diagram of $Nd_{0.2}Gd_{0.8}O_{1.5}$ with numerous lines rather analogous to that of B-type [20] Sm_2O_3 and Gd_2O_3. On the other hand, as seen in Table 2, our five samples $Nd_{0.2}Y_{0.8}O_{1.5}$; $Nd_{0.5}Y_{0.5}O_{1.5}$; $Nd_{0.9}Ti_{0.1}O_{1.55}$; $Nd_{0.8}Ti_{0.2}O_{1.6}$, and $Nd_{0.67}Ti_{0.33}O_{1.67}$ have closely similar, and simpler, powder diagrams, which do not correspond neither to the A and B forms given in literature, nor to ROTH's [11] low symmetry $NdTiO_{3.5}$. It is obvious that our type is not cubic, though the ratio between the d-values 2.84 and 2.00 Å is close to $\sqrt{2}$.

$Nd_{0.5}Y_{0.5}O_{1.5}$	3.44	3.12	2.85	2.59	2.01
$Nd_{0.2}Y_{0.8}O_{1.5}$	3.42	3.09	2.82	2.57	1.98
$Nd_{0.9}Ti_{0.1}O_{1.55}$	3.44	~ 3.13	2.84	2.59	2.01
$Nd_{0.8}Ti_{0.2}O_{1.6}$	3.45	3.09	2.84	2.59	2.01
$Nd_{0.67}Ti_{0.33}O_{1.67}$	3.46	~ 3.13	2.86	2.61	2.02

Table 2. d-values for the strongest DEBYE-lines of certain mixed oxides, in Å.

According to SCHNEIDER and ROTH [19], one would expect our mixed Nd(III)Y(III) oxides to show B-type behaviour. However this may be caused by the higher tendency to formation of A- and B-types at 1650 °C than at 1000 °C.

f) **Tl_2O_3:** The brownish black Tl_2O_3 is a C-oxide [21]. Compared to the lemon-yellow [22] In_2O_3 and all the C-rare earths, thallium(III) oxide has highly unexpected physical properties. BAUER [23] found that it is a good electric conductor, only an order of magnitude more resistant than thallium metal. The very weak dependence of the conductivity on temperature indicates metallic behaviour or a semi-conductor with very low energy gap. BAUER [23] also reported that thin films are transparent at 9000 cm^{-1} and absorb infra-red radiation both at lower and higher wavenumbers. We con-

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firmed this result insofar our Tl_2O_3 has a broad absorption band centered around 7400 cm^{-1} at 100 °K. However, this phenomenon is probably connected with non-stoichiometry. Scatturin, Zannetti and Censolo [24] described the black compound as $TlO_{1.52}$, and other samples were reported with oxygen excess, up to $TlO_{1.75}$, and showing paler colours.

However, the composition is slightly suspect because hydrogen peroxide was used in their preparation.

It is by no means a trivial task to prepare mixed oxides of Tl(III) with Er(III), In(III) or Y(III). The point is that even the slightly hydrated precipitate from aqueous thallium(III) solutions to which alkali is added has the C-oxide lattice [25] but readily looses oxygen by heating in air (though the equilibrium pressure [26] seems first to reach 1 atm at 896 °C) whereas erbium(III) hydroxide and similar compounds have to be ignited strongly in order to form C-Er_2O_3. Actually, our samples of nominal composition $Y_{0.9}Tl_{0.1}O_{1.5}$ (very pale chamois), $In_{0.9}Tl_{0.1}O_{1.5}$ (yellow) and $Er_{0.95}Tl_{0.05}O_{1.5}$ (pink) had none of the characteristics of the dark Tl_2O_3, and our only problem was to establish that the thallium had not evaporated from the crucibles. Actually, as seen in the experimental section, very serious losses of thallium did indeed occur.

3. Discussion of Reflection Spectra

a) *Correlation of reflection spectra with crystal structure*

The absorption bands caused by internal transitions in the partly filled 4 f shell observed in the reflection spectra (Tables 3 – 8) in the region 2000 to 350 mμ (5 000 – 28 600 cm^{-1}) corroborate a classification according to the crystal structures:

	$^4I_{13/2}$	$^4I_{15/2}$	$^4F_{3/2}$	$^4F_{5/2}$	$^4F_{7/2}$	$^4F_{9/2}$	$^2H_{11/2}$	($^2G_{7/2}$, $^4G_{5/2}$)	$^4G_{7/2}$	$^4G_{9/2}$	$^2P_{1/2}$	$^2D_{5/2}$	$^2P_{3/2}$	$^4D_{3/2}$	dσ	dβ %
$Nd(H_2O)_9^{+3}$(ref. [27])	(4030)	(5880)	11580	12620	13580	14840	16030	17400	19180	19630	23400	23900	26320	28280	0	0
Nd(III)$LaCl_3$(ref. [27])	4010	5930	11440	12480	13440	14720	15930	17210	19030	19440	23210	23770	26130	27970	−60	0.5
Nd_2O_3(type A, ref. [1])	—	5950	11190	12270	13250	14470	15770	16720	18600	19170	22840	23420	25740	27200	200	3.6
$Nd_{0.1}La_{0.9}O_{1.5}$(A)	—	—	11190	12300	13230	14470	—	16780	18680	19230	22880	—	—	—	100	3.2
$Nd_{0.2}Gd_{0.8}O_{1.5}$(B)	—	6020	11300	12350	13320	14510	15820	16920	18690	19230	22910	—	—	27470	200	3.4
$Nd_{0.2}Y_{0.8}O_{1.5}$(new)	—	6020	11310	12390	13330	14510	15820	16920	18690	—	22910	—	—	27470	200	3.4
$Nd_{0.2}Y_{0.5}O_{1.5}$(new)	—	6020	11360	12410	13350	14560	15870	17010	18710	—	22880	23280	—	27510	250	3.5
$Nd_{0.2}Yb_{0.8}O_{1.5}$(C)	—	(5760)	11360	12420	13390	14580	—	16950	18590	—	22880	—	—	—	150	3.2
$Nd_{0.1}Ce_{0.9}O_{1.95}$(F)	—	—	11390	12420	13460	—	—	17000	—	—	—	—	—	—	300	3.7
$Nd_{0.14}Th_{0.86}O_{1.93}$(F, ref. [1])	—	5840	11300	12330	13330	14490	—	16900	18690	19380	22990	—	—	27430	150	3.3
$Nd_{0.5}Zr_{0.5}O_{1.75}$(F)	—	—	11390	12420	13440	14660	15950	17090	18830	19490	23090	—	—	—	250	2.7
$Nd_{0.9}Ti_{0.1}O_{1.55}$(new)	4010	6020	11290	12380	13280	14520	15800	16950	18740	19270	22910	23500	25690	27570	200	3.2
$Nd_{0.8}Ti_{0.2}O_{1.6}$(new)	4010	6020	11310	12420	13330	14560	15850	17020	18780	19270	22910	23530	25690	27590	200	3.0
$Nd_{0.67}Ti_{0.33}O_{1.67}$(new)	4020	6020	11340	12390	13330	14580	15840	17040	18780	19310	22960	23530	25840	27550	200	2.8
$Nd_{0.5}Ti_{0.5}O_{1.75}$(dist.)	—	—	11420	12470	13420	14690	15920	17150	18870	19530	23160	—	—	—	200	2.2
$Nd_{0.5}Ti_{0.25}Zr_{0.25}O_{1.75}$(F ?)	—	6020	11350	12390	13330	14580	15860	17040	18800	19340	23000	—	25840	27590	200	2.9
$Nd_{0.5}Sn_{0.5}O_{1.75}$(F ?)	—	—	11290	12440	13420	—	—	16920	18780	—	—	—	—	—	250	3.7

Table 3. Baricenters (wavenumbers in cm^{-1}) of band groups at 100 °K in reflection spectra of neodymium (III) compounds.

	$^6H_{13/2}$	$^6F_{3/2}$	$^6H_{15/2}$	$^6F_{5/2}$	$^6F_{7/2}$	$^6F_{9/2}$	$^6F_{11/2}$	$^4G_{5/2}$	$^4G_{7/2}$		$^4I_{13/2}$	^6P		dσ	dβ %
$Sm(H_2O)_9^{+3}$(ref. [27])	(5000)	—	—	(7200)	(8000)	(9200)	(10500)	17900	—	20880	21550	24900	26700	0	0
Sm(III)$LaCl_3$(ref. [27, 29])	4990	6310	6710	7040	7900	9100	10460	17860	20010	20600	21560	24540	26330	—	—
Sm_2O_3(B)	—	6370	6620	7340	8050	9220	10500	17570	—	20750	21410	24390	26250	200	2.3
$Sm_{0.14}Th_{0.86}O_{1.93}$(F, ref. [1])	5010	6460	6740	7230	8100	9270	10580	—	20410	20850	21470	24630	26420	200	1.9
$Sm_{0.5}Zr_{0.5}O_{1.75}$(F)	—	6600	6830	7330	8200	9350	10700	—	20370	21010	21550	24630	26670	350	2.0
$Sm_{0.5}Ti_{0.5}O_{1.75}$(P)	—	6670	—	7380	8200	9370	10700	17530	—	—	—	24690	—	350	2.5

Table 4. Baricenters of band groups at 100 °K in reflection spectra of samarium(III) compounds. Assignments of certain excited levels in ref. [28].

	$^7F_1 \rightarrow {}^5D_0$	$^7F_0 \rightarrow {}^5D_0$	$^7F_1 \rightarrow {}^5D_1$	$^7F_0 \rightarrow {}^5D_1$	$^7F_0 \rightarrow {}^5D_2$	$^7F_0 \rightarrow {}^5D_3$	$^7F_0 \rightarrow {}^5L_6$
$Eu(H_2O)_9^{+3}$(ref. [27])	16880	17260	18630	19010	21490	—	25300
Eu(III)$LaCl_3$(ref. [30])	16890	17270	18650	19030	21500	24390	25270
Eu(III)Gd_2O_3(B, ref. [31])	—	17170	—	18930	21390	—	—
$Eu_{0.14}Th_{0.86}O_{1.93}$(F, ref. [1])	(16920)	(17240)	—	19030	21460	(24750)	25350
$EuZrO_{3.5}$(F)	17010	17270	18760	18990	21510	(24690)	25350
$EuTiO_{3.5}$(P)	16950	—	—	19000	21520	—	25320
$EuSnO_{3.5}$(F)	—	—	—	19010	21480	(24750)	25380

Table 5. Baricenters of band groups at 100 °K in reflection spectra of europium (III) compounds.

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	$^6H_{11/2}$	($^6H_{9/2}$, $^6F_{11/2}$)	($^6H_{7/2}$, $^6F_{9/2}$)	$^6H_{5/2}$	$^6F_{7/2}$	$^6F_{5/2}$	$^6F_{3/2}$	$^4F_{9/2}$	$^4I_{15/2}$	$^4G_{11/2}$	dσ	dβ %
$Dy(H_2O)_9^{+3}$(ref. [27])	—	—	(9100)	(10200)	(11000)	12350	13200	21050	22130	23420	0	0
Dy(III)$LaCl_3$(ref. [27])	5830	7670	9020	10150	10930	12320	13120	20960	21950	23300	−20	0.4
Dy_2O_3(C)	6100	8010	9460	—	11300	12580	13440	21120	22170	23560	500	1.8
$Dy_{0.5}Zr_{0.5}O_{1.75}$(F)	6080	7980	9420	10580	11390	12640	13500	21160	21940	23500	500	2.0
$Dy_{0.9}Ti_{0.1}O_{1.55}$(F ?)	6040	7970	9280	—	11190	12520	13160	21100	22170	23470	350	1.5
$Dy_{0.8}Ti_{0.2}O_{1.6}$(F ?)	6100	8030	9350	—	11350	12630	13480	21190	22150	23530	450	1.7
$Dy_{0.67}Ti_{0.33}O_{1.67}$(F ?)	6080	8000	9330	—	11340	12630	13460	21190	22200	23530	450	1.6
$Dy_{0.5}Ti_{0.5}O_{1.75}$(P)	6190	8100	9430	10650	11430	12640	13510	21100	21980	23590	550	2.0
$Dy_{0.5}Ti_{0.25}Zr_{0.25}O_{1.75}$(F ?)	6100	8030	9380	10550	11350	12620	13440	21190	22220	23530	500	1.8

Table 6. Baricenters of band groups at 100 °K in reflection spectra of dysprosium(III) compounds. Assignments of certain excited levels [28].

	$^5I_7$	$^5I_6$	$^5I_5$	$^5I_4$	$^5F_5$	($^5S_2$, $^5F_4$)	$^5F_3$	$^5F_2$	($^3K_6$, $^5F_1$)	$^5G_5$	($^5G_4$, $^3K_7$)	$^5G_6$	dσ	dβ %
$Ho(H_2O)_9^{+3}$(ref. [27])	5030	8530	11140	13250	15420	(18450)	20560	(21030)	(22250)	24030	(26100)	27740	0	0
Ho_2O_3(C)	5230	8800	11340	—	15500	18550	20530	21050	22220	23920	25970	27470	450	2.5
$Ho_{0.14}Th_{0.86}O_{1.93}$(F, ref. [1])	5190	8790	11310	—	15510	18520	20560	21190	22100	23910	25940	27560	350	1.7
$Ho_{0.5}Zr_{0.5}O_{1.75}$(F)	5190	8790	11350	—	15620	18620	20600	21160	22200	23950	26010	27590	500	2.3
$Ho_{0.5}Ti_{0.5}O_{1.75}$(P)	5190	8930	—	—	15760	18730	20660	21280	—	23950	—	—	600	2.4

Table 7. Baricenters of band groups at 100 °K in reflection spectra of holmium(III) compounds.

	$^4I_{13/2}$	$^4I_{11/2}$	$^4F_{9/2}$	$^4I_{9/2}$	$^4S_{3/2}$	$^2H_{11/2}$	$^4F_{7/2}$	$^4F_{5/2}$	$^4F_{3/2}$	$^2H_{9/2}$	$^4G_{11/2}$	$^2G_{9/2}$	$^2G_{7/2}$	dσ	dβ %
$Er(H_2O)_9^{+3}$(ref. [27])	(6600)	10220	12520	15350	18480	19230	20600	22270	22610	24630	26490	27500	28100	0	0
Er(III)$LaCl_3$(ref. [27])	6590	10220	12460	15280	18400	19150	20510	22180	22520	24560	26370	27610	27990	−30	0.3
Er_2O_3(type C, ref. [1])	6640	10250	12480	15290	18210	19090	20370	22030	22430	24540	26280	27210	27850	200	1.6
$Er_{0.002}La_{1.998}O_3$(A ref. [31])	—	—	—	—	18310	19100	—	—	—	—	—	—	—	—	—
$Er_{0.02}Gd_{1.98}O_3$(B, ref. [31])	—	—	—	15280	18290	19150	20470	—	—	—	—	—	—	—	—
$Er_{0.02}Y_{1.98}O_3$(C, ref. [31, 32])	6660	10280	12490	15270	18280	19140	20470	22100	22420	24510	26280	—	—	200	1.6
$Er_{0.1}Ce_{0.9}O_{1.95}$(F)	—	10280	—	15310	—	19160	—	—	—	—	—	—	—	250	1.7
$Er_{0.2}In_{0.8}O_{1.5}$(C)	6660	10310	12530	15280	18250	19120	20390	22030	—	—	—	—	—	300	2.4
$Er_{0.5}In_{0.5}O_{1.5}$(C)	6620	10270	12480	15250	18210	19140	20390	22050	22470	24540	26280	—	—	250	2.0
$Er_{0.95}Tl_{0.05}O_{1.5}$(C)	6640	10260	12500	15240	18210	19120	20390	22030	—	24510	26280	27210	—	200	1.8
$Er_{0.9}Tl_{0.1}O_{0\,5}$(C)	6640	10250	12470	15230	18180	19080	20370	(22030)	—	24450	26250	27170	—	200	1.9
$Er_{0.8}Tl_{0.2}O_{1.5}$(C)	6340	10260	12480	15230	(18300)	19120	20370	—	—	—	(26280)	—	—	250	2.1
$Er_{0.14}Th_{0.86}O_{1.93}$(F, ref. [1])	6640	10280	12550	15330	18350	19160	20430	22150	—	24540	26370	27390	—	250	1.6
$Er_{0.8}Zr_{0.2}O_{1.6}$(C)	6640	10260	12550	15270	18280	19140	20430	22080	22520	24510	26250	27230	27900	200	1.6
$Er_{0.67}Zr_{0.33}O_{1.67}$(C)	6690	10300	12550	15310	18330	19160	20450	22100	22520	24510	26320	27290	27930	250	1.7
$Er_{0.5}Zr_{0.5}O_{1.75}$(F)	6690	10300	12660	15360	18350	19160	20490	22170	22620	24570	26350	—	—	300	1.7
$Er_{0.95}Ti_{0.05}O_{1.525}$(C)	6630	10270	12500	15270	18280	19140	20410	22070	22470	24500	26250	27230	27900	200	1.7
$Er_{0.9}Ti_{0.1}O_{1.55}$(C)	6660	10260	12500	15280	18280	19130	20430	22090	22550	24510	26280	27230	—	200	1.7
$Er_{0.8}Ti_{0.2}O_{1.6}$(C)	6690	10280	12520	15290	18320	19160	20450	22080	22550	24520	26300	27250	—	250	1.7
$Er_{0.67}Ti_{0.33}O_{1.67}$(C + F)	6680	10300	12530	15310	18300	19140	20450	22080	22520	24540	26320	27280	27930	250	1.7
$Er_{0.5}Ti_{0.5}O_{1.75}$(P)	6650	10340	—	15430	18420	19230	20600	—	—	24630	—	—	—	250	1.3
$Er_{0.5}Ti_{0.1}Zr_{0.4}O_{1.75}$(F)	6680	10300	12580	15340	18350	19160	20500	22120	22570	24540	26320	27320	27970	250	1.5
$Er_{0.5}Ti_{0.25}Zr_{0.25}O_{1.75}$(F)	6700	10300	12580	15330	18350	19180	20490	22120	22570	24540	26320	27320	27900	250	1.6
$Er_{0.5}Sn_{0.5}O_{1.75}$(F)	6640	10280	12610	15360	—	19190	20490	—	—	24540	26390	—	—	200	1.3
$LaErO_3$(new quasi-cubic)	6660	10270	12520	15270	18280	19120	20410	22050	22510	24510	26320	27210	—	250	1.9
$La_{0\,2}Sr_{0.8}Er_{0.2}Ti_{0.8}O_3$ (perovskite + F)	—	10270	—	15340	18370	19160	20490	22120	—	24540	26330	—	—	200	1.4
$La_{0.1}Ba_{0.9}Er_{0.1}Ti_{0.9}O_3$ (mainly perovskite)	6670	10270	—	15350	—	19190	20580	22170	—	—	26460	—	—	150	0.9

Table 8. Baricenters of band groups at 100 °K in reflection spectra of erbium(III) compounds.

1. *Disordered fluorites* such as $M_xCe_{1-x}O_{2-0.5x}$ and $MZrO_{3.5}$ have relatively broad absorption bands without much fine-structure of each distinct *J*-level. The nephelauxetic effect is very pronounced.

2. *Superlattices of the fluorite type*, such as the numerous C-oxides, the pyrochlores such as $MTiO_{3.5}$ (except M = Nd) and the new quasi-cubic type $LaErO_3$ show many components of each *J*-level and have a nephelauxetic effect about as large as the disordered fluorites, except certain cases of M = Er.

3. *Other symmetries* usually, but not always, have broad absorption bands corresponding to each *J*-level and relatively much weaker nephelauxetic effect. One might have imagined that the octahedral sites in perovskites would induce a stronger nephelauxetic effect than the fluorite-like types. However, $La_{0.1}Ba_{0.9}Er_{0.1}Ti_{0.9}O_3$ in Table 8 shows about half as large a nephelauxetic effect as the other mixed

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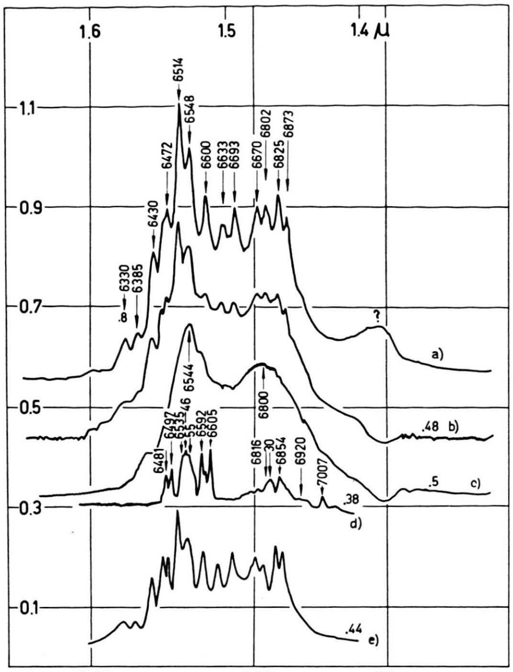

Fig. 1. Transition $^4I_{15/2} \rightarrow {}^4I_{13/2}$ in various systems. Reflection spectra at ~ 100 °K. a) $Er_{0.95}Ti_{0.05}O_{1.525}$; b) $Er_{0.8}Zr_{0.2}O_{1.6}$; c) $Er_{0.5}Ti_{0.25}Zr_{0.25}O_{1.75}$; d) $ErTiO_{3.5}$; e) $Er_{0.95}Tl_{0.05}O_{1.5}$. Because of loss of thallium by evaporation, the latter sample may more closely correspond to Er_2O_3.

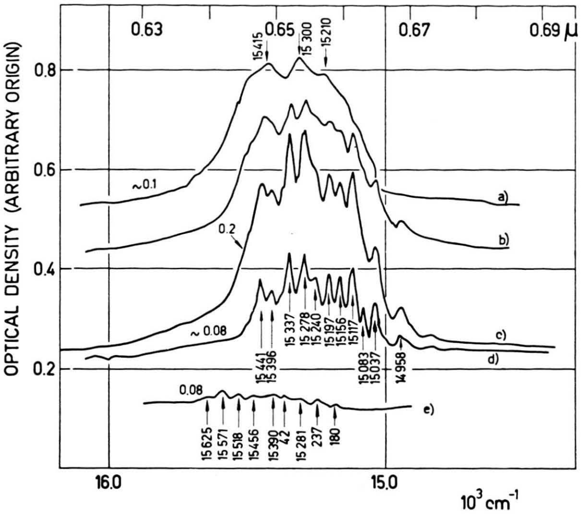

Fig. 2. Reflection spectra at ~ 100 °K for various systems. Transition $^4I_{15/2} \rightarrow {}^4I_{9/2}$. Please note for this figure and the following ones an inversion in the direction of scanning. a) $Er_{0.5}Ti_{0.25}Zr_{0.25}O_{1.75}$; b) $Er_{0.8}Zr_{0.2}O_{1.6}$; c) $Er_{0.95}Ti_{0.05}O_{1.525}$; d) $Er_{0.95}Tl_{0.05}O_{1.5}$; e) $ErTiO_{3.5}$.

Er(III) oxides. The sample $La_{0.2}Sr_{0.8}Er_{0.2}Ti_{0.8}O_3$ has a larger nephelauxetic effect, but contains also a part of the erbium in a fluorite-phase.

We are not yet going to discuss the observed fine-structure of the individual *J*-levels. An impression of the relative width of the sub-level absorption components can be had from Fig. 1 showing the spectra of Er(III) compounds in the infra-red close to the first excited level $^4I_{13/2}$, Fig. 2 Er (III) in the red

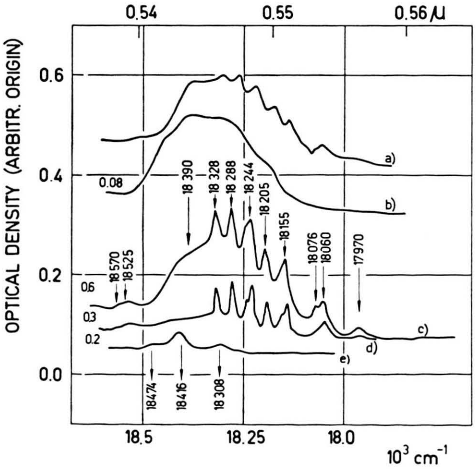

Fig. 3. Reflection spectra at ~ 100 °K for various systems. Transition $^4I_{15/2} \rightarrow {}^4S_{3/2}$. a) $Er_{0.8}Zr_{0.2}O_{1.6}$; b) $Er_{0.5}Ti_{0.25}Zr_{0.25}O_{1.75}$; c) $Er_{0.95}Ti_{0.05}O_{1.525}$; d) $Er_{0.95}Tl_{0.05}O_{1.5}$; e) $ErTiO_{3.5}$.

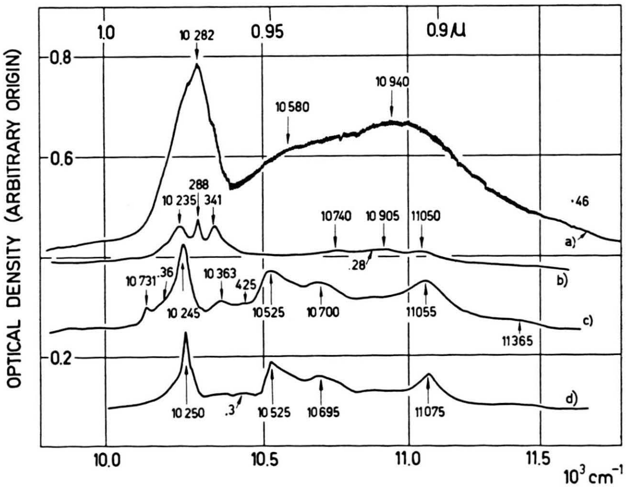

Fig. 5. Transition $^2F_{7/2} \rightarrow {}^2F_{5/2}$ in various systems. Reflection spectra at ~ 100 °K. Operating slit-widths in mm units. a) $YbZrO_{3.5}$; b) $YbTiO_{3.5}$; c) $LaYbO_3$; d) Yb_2O_3.

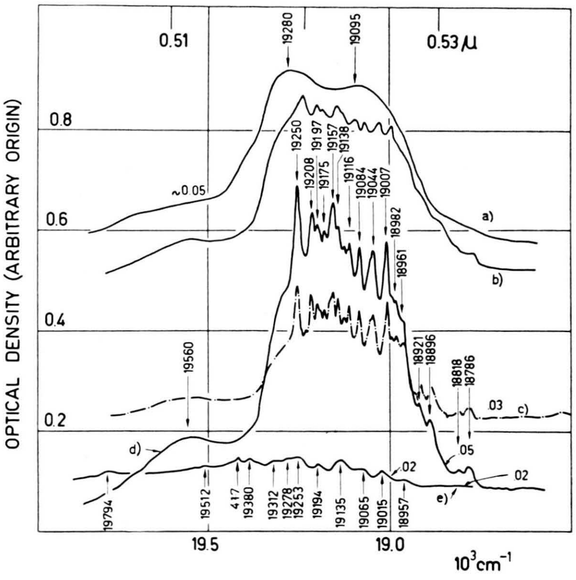

Fig. 4. Reflection spectra at ~ 100 °K. Transition $^4I_{15/2} \rightarrow {}^2H_{11/2}$. a) $Er_{0.5}Ti_{0.25}Zr_{0.25}O_{1.75}$; b) $Er_{0.8}Zr_{0.2}O_{1.6}$; c) $Er_{0.95}Tl_{0.05}O_{1.5}$; d) $Er_{0.95}Ti_{0.05}O_{1.525}$; e) $ErTiO_{3.5}$.

around $^4I_{9/2}$ (most authors [33] call this level $^4F_{9/2}$), Figs. 3 and 4 Er(III) in the green representing the two levels $^4S_{3/2}$ and $^2H_{11/2}$, and finally the reflection spectra of Fig. 5 showing the transition $^2F_{7/2} \rightarrow {}^2F_{5/2}$ of Yb(III) compounds in the near infra-red region.

b) *Nephelauxetic effect*

We define now $d\sigma$, the relative stabilization of the lowest sub-level of the groundlevel of the mixed oxide, compared with the aqua ion, and the relative nephelauxetic effect, $d\beta$ as in ref. [1] and we write for the wavenumbers of the baricenters of the excited *J*-levels:

$$\sigma_{\text{oxide}} - \sigma_{\text{aqua}} = d\sigma - (d\beta)\ \sigma_{\text{aqua}} . \qquad (1)$$

Tables 3, 4, 6, 7 and 8 express the remarkably large nephelauxetic effect in the mixed oxides, the average values of $d\beta$ being 3.2% for the fifteen Nd(III) compounds studied and 1.6% for the twenty-four Er(III) cases. Actually, the sulphides to be discussed soon [33a] are the only known lanthanide compounds with sufficiently large energy-gaps as semiconductors (allowing the internal 4 f-transitions to be observed in the visible region) which show even slightly larger nephelauxetic effect.

One of the reasons why the nephelauxetic effect is so pronounced in rare earth mixed oxides is undoubtedly that the parameter σ^* characterizing the weak σ-anti-bonding influence [34] of the surrounding ligands on the partly filled 4 f shell is [1] some 60 – 100 cm⁻¹ in our oxides whereas it is [34] some 30 – 40 cm⁻¹ in the ennea-aqua ions and some 20 – 30 cm⁻¹ in $LaCl_3$. One can apply second-order perturbation theory to the WOLFSBERG–HELMHOLZ model and obtain the average value for the σ-anti-bonding influence on the seven *f* orbitals

$$N\sigma^* = N H_X^2\ (S^*_{MX})^2/(H_M - H_X) . \qquad (2)$$

N is the number of ligands in the chromophore MX_N; H_M is the diagonal element of energy of the unperturbed central atom orbitals; H_X the same quantity for the ligand σ-orbitals, and S^*_{MX} the overlap integral between the central atom orbital (providing a constant angular function) and the σ-orbital of one of the identical ligand atoms X. Incidentally, the sub-level stabilization $d\sigma$ in eq. (1) is also proportional * to σ^*. It is possible [ref. [35], eq. (68)] to demonstrate that a good approximation to the orbital ψ of the partly filled shell after the delocalization is

$$\psi \cong \psi_M \left[1 - \frac{N H_X^2 (S^*_{MX})^2}{2 (H_M - H_X)^2} - \frac{N H_X (S^*_{MX})^2}{(H_M - H_X)} \right] + \psi_X \left[\frac{\sqrt{N} H_X S^*_{MX}}{H_M - H_X} \right] . \qquad (3)$$

When ψ of eq. (3) is used instead of ψ_M in the determination of the interelectronic repulsion parameters of the *f*-shell, relevant energies will be decreased by a factor β related to the fourth-power of the coefficient of ψ_M in eq. (3). This is part of the nephelauxetic effect caused by symmetry restricted covalency [36]. Approximately one obtains:

$$\beta \cong 1 - 2[N (S^*_{MX})^2 H_X (2 H_M - H_X)/(H_M - H_X)^2] . \qquad (4)$$

This expression has the rather unpleasant property of being less than one only if H_M is more negative than $\frac{1}{2} H_X$. However, it represents only a lower limit

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[34] C. K. JØRGENSEN, R. PAPPALARDO, and H.-H. SCHMIDTKE, J. Chem. Phys. **39**, 1422 [1963].

* We may add here that σ^* for Dy(III) in eq. (4) of ref. [1] is 340 cm⁻¹.

[35] C. K. JØRGENSEN, Proc. Summer School in Theoretical Chemistry, Milano, October 1963 (Director: M. SIMONETTA), Accademia Nazionale dei Lincei, Rome 1965.

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to the nephelauxetic effect, since the expansion of the $4f$ radial function by central-field covalency[36] has not been taken into account. If $H_M = \frac{3}{4} H_X$, eq. (2) and (4) can be combined to

$$\beta \cong 1 - [N\sigma^*/(H_M - H_X)] \,. \tag{5}$$

The order of magnitude expected for $d\beta$ is correct since $N\sigma^* \sim 600$ cm^{-1} and $(H_M - H_X) \sim 40\,000$ cm^{-1}, implies $\beta = 0.985$.

c) *Determination of the factor β from electron transfer bands*

If it is assumed that $(1-\beta)$ is proportional to the parenthesis of eq. (5), one needs an estimate of $(H_M - H_X)$ in various compounds. One possible method is the study of the electron transfer bands (cf. [37, 38]) which are best known in the relatively most oxidizing trivalent lanthanide[39, 40] Eu(III). In this case, $\varkappa$ being a proportionality constant,

$$\begin{array}{lll}
(H_{Eu} - H_{H_2O}) = 53\,000, & N\sigma^* = 300 \text{ cm}^{-1}, & (1-\beta) = 0.57\,\varkappa; \\
(H_{Eu} - H_{Cl}) \;\; = 36\,000, & = 250 \text{ cm}^{-1}, & = 0.70\,\varkappa; \\
(H_{Eu} - H_{Br}) \;\; = 31\,000, & = 240 \text{ cm}^{-1}, & = 0.77\,\varkappa; \\
(H_{Eu} - H_{O}) \;\;\; = 38\,000, & = 700 \text{ cm}^{-1}, & = 1.84\,\varkappa;
\end{array} \tag{6}$$

indicating that $d\beta = 0.13\,\varkappa$ of Eu(III) in $LaCl_3$ should be about ten times smaller than $d\beta = 1.27\,\varkappa$ of $EuZrO_{3.5}$, which is not very far from the conditions we have found in the mixed lanthanide oxides.

However, it is a rather complicated question[27] whether one may accept the identification of $(H_M - H_X)$ with the wavenumbers of the first electron transfer bands, already because they are strongly influenced by spin-paring energy, having low wavenumbers in $4f^6$Eu(III) and $4f^{13}$Yb(III) and very high wavenumbers in $4f^7$Gd(III) at the half filled shell. There are several cases known where related properties show a pronounced discontinuity at Gd(III). Thus, the reflection spectra of the rare earths in the ultra-violet show absorption edges varying strongly with the lanthanide ion[41]. Table 9 gives the predicted position of the first $4f^q \to 4f^{q-1}$ 5d transitions with the parameters[37] $W_2 = 21\,000$ cm^{-1}, $D = 5\,200$ cm^{-1} and $(E-A)_2 = 3\,800$ cm^{-1} (as well as for the aqua ions, where the appropriate parameters are $W_2 = 31\,000$ cm^{-1}, $D = 6\,200$ cm^{-1} and $(E-A)_2 = 4\,700$ cm^{-1}) and the predicted positions of the $4f^q \to (2p_{oxide})^{-1}\,4f^{q+1}$ electron transfer transitions (essentially the values predicted[37] for bromide complexes in ethanol, increased by 5 000 cm^{-1}). It is seen from Table 9 that BORCHART's results[41] can be readily explained by these two types of transition and by a third mechanism, an edge occurring at 44 000 cm^{-1} of all rare earths not having any absorption at lower energy. This edge is presumably essentially a $2p^6 \to 2p^5 3s$ excitation of the oxide closed shell[42] analogous to that occurring in BaO. When CHANG[43] finds an actual

Absorption edge observed[41]		calculated oxide		assignment of edge	calculated aqua ions $4f \to 5d$
		$4f \to 5d$	$(2p_{oxide}) \to 4f$		
La_2O_3	44	—	74	$2p_{oxide} \to 3s_{oxide}$	—
(Ce_2O_3)	—	22	63	—	32
Pr_2O_3	31	32	55	$4f \to 5d$	45
Nd_2O_3	40	40	54	$4f \to 5d$	54
(Pm_2O_3)	—	43	54	—	57
Sm_2O_3	40	44	46	$4f \to 5d$?	58
Eu_2O_3	36	52	36	$2p_{oxide} \to 4f$	68
Gd_2O_3	43	61	75	$2p_{oxide} \to 3s_{oxide}$	79
Tb_2O_3	31	30	64	$4f \to 5d$	43
Dy_2O_3	40	41	55	$4f \to 5d$	57
Ho_2O_3	44	49	57	$2p_{oxide} \to 3s_{oxide}$	66
Er_2O_3	44	49	60	$2p_{oxide} \to 3s_{oxide}$	67
Tm_2O_3	44	48	51	$2p_{oxide} \to 3s_{oxide}$	66
Yb_2O_3	41	56	40	$2p_{oxide} \to 4f$	76
Lu_2O_3	46	67	—	$2p_{oxide} \to 3s_{oxide}$	88

Table 9. The wavenumbers in units of 10^3 cm^{-1} of $4f \to 5d$ and electron transfer bands in rare earths calculated using the parameters given in the text.

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absorption band at 255 mμ of Eu(III) in Y_2O_3, this is probably the first electron transfer band. The treatment used in Table 9 [44] has also been applied to McClure and Kiss' divalent lanthanides [45] in CaF_2 where the parameters describing the 4f → 5d transitions [46] are $W_2 = -17\,000$ cm^{-1}, $D = 5\,200$ cm^{-1} and $(E-A)_2 = 3\,800$ cm^{-1}.

d) *Possible explanation of the observed large nephelauxetic effect*

The most obvious, but not necessarily the unique explanation of why the "ligand field" influence $N\sigma^*$ and the nephelauxetic effect is so much larger in the mixed oxides than in the aqua ions and the anhydrous halides is that the oxides with coordination number 8 or smaller have somewhat smaller M – X distances (roughly Goldschmidt's lanthanide radii plus 1.22 Å in Dy_2O_3 and Tm_2O_3 (cf. [3]) whereas the six shortest distances in the ennea-aqua ions [47] are the lanthanide radii plus 1.32 Å) than the nine-co-ordinated aqua ions and halides. A corollary of this is that the twelve-co-ordinated positions such as Nd(III) in the perovskite $NdAlO_3$ should show relatively small $N\sigma^*$ and weak nephelauxetic effect [1]. Actually, since S_{MX} of eq. (2) is such a sensitive function [34] of the internuclear distance M – X, varying by a factor 1.3 when the distance is decreased by 0.1 Å under typical conditions, we obtain an expected variation of $N\sigma^*$ and $(1-\beta)$ of some 70%. Whereas this may be sufficient to explain the high-pressure effects [48] and McLaughlin and Conway's results [49] for Pr(III) in $LaCl_3$ and $GdCl_3$, it is not sufficient to explain the behaviour in the oxides, if it is not assumed that the 2p radial functions are more expanded and are much easier to deform than in the corresponding aqua ions.

e) *Comparison with mixed chromium oxides*

Schäffer [50] pointed out that chromium(III) mixed oxides frequently show a very large nephelauxetic effect, more than one would expect from the reducing character of oxide. It is instructive to compare our findings with the reflection spectra of Cr(III) containing perovskites [51], garnets [52] and other oxides [51]. Table 10 gives values for Racah's parameter B of interelectronic repulsion for such compounds. B is known to be 918 cm^{-1} in gaseous Cr^{+3}. The most convenient way [52a] to evaluate B in these compounds is to prepare Table 11, the distance between the two first spin-allowed bands $\sigma_2 - \sigma_1$ in units of B as function of the ratio σ_2/σ_1 obtained from Tanabe and Sugano's secular determinant of second degree [53]. Dr. D. Reinen was to kind as to inform us that he found identical values for B (cf. also ref. [54]).

$Al_{1.9}Cr_{0.1}O_3$	665	$MgAl_{1.7}Cr_{0.3}O_4$	670
$Al_{1.7}Cr_{0.3}O_3$	640	$MgAl_{1.6}Cr_{0.4}O_4$	640
$Al_{1.6}Cr_{0.4}O_3$	625	$MgAl_{1.4}Cr_{0.6}O_4$	650
$Al_{1.4}Cr_{0.6}O_3$	595	$MgAlCrO_4$	650
$Al_{1.2}Cr_{0.8}O_3$	590	$MgAl_{0.4}Cr_{1.6}O_4$	640
$Al_{0.8}Cr_{1.2}O_3$	550	$MgCr_2O_4$	620
$Al_{0.4}Cr_{1.6}O_3$	510	$Y_3Al_{4.8}Cr_{0.2}O_{12}$	670
Cr_2O_3	480	$Y_3Al_4CrO_{12}$	640
$LaAl_{0.7}Cr_{0.3}O_3$	505	$Y_3Al_3Cr_2O_{12}$	590
$LaAl_{0.5}Cr_{0.5}O_3$	510	$Y_3Ga_4CrO_{12}$	630
$LaAl_{0.3}Cr_{0.7}O_3$	505	$Y_3Ga_3Cr_2O_{12}$	630
$LaCrO_3$	510	$Y_3Al_{2.5}Ga_{0.5}Cr_2O_{12}$	590
$LaGa_{0.6}Cr_{0.4}O_3$	550	$Y_3Al_2GaCr_2O_{12}$	590
$LaGa_{0.3}Cr_{0.7}O_3$	525	$Y_3Al_{1.5}Ga_{1.5}Cr_2O_{12}$	595
$YAl_{0.5}Cr_{0.5}O_3$	555	$Y_3AlGa_2Cr_2O_{12}$	615
$YCrO_3$	540	$Y_3Al_{0.5}Ga_{2.5}Cr_2O_{12}$	620
		$Y_3Al_3GaCrO_{12}$	645
		$Y_3Al_2Ga_2CrO_{12}$	650

Table 10. Racah's parameter B of interelectronic repulsion evaluated from the Cr(III) absorption bands observed [51, 52].

As recently emphasized by several authors [55], the variation of B is approximately a linear function of x in the series $Al_{2-x}Cr_xO_3$.

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[44] There is a striking similarity between the variation of the Faraday rotation of lanthanide(III) phosphate glasses (cf. S. B. Berger, C. B. Rubinstein, C. R. Kurkjian, and A. W. Treptow, Phys. Rev. **133,** A 723 [1964]) and the reciprocal value of the last column of Table 9, except for minor details, such as the comparable Faraday rotation in Tb(III) and Dy(III). Similar observations have been made on borate glasses (C. B. Rubinstein, S. B. Berger, L. G. van Uitert, and W. A. Bonner, J. Appl. Phys. **35,** 2338 [1964]).

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[52a] *Note added in Proof:* C. P. Poole, J. Phys. Chem. Solids **25,** 1169 [1964] recently continued this study and gave also the explicit formula for

$$B = (2\,\sigma_1 - \sigma_2)\,(\sigma_2 - \sigma_1)/(27\,\sigma_1 - 15\,\sigma_2).$$

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σ_2/σ_1	$(\sigma_2-\sigma_1)/B$	σ_2/σ_1	$(\sigma_2-\sigma_1)/B$
1.26	10.946	1.46	9.444
1.27	10.890	1.47	9.340
1.28	10.833	1.48	9.231
1.29	10.775	1.49	9.118
1.30	10.714	1.50	9.000
1.31	10.652	1.51	8.878
1.32	10.588	1.52	8.750
1.33	10.522	1.53	8.618
1.34	10.454	1.54	8.478
1.35	10.385	1.55	8.333
1.36	10.312	1.56	8.182
1.37	10.238	1.57	8.024
1.38	10.161	1.58	7.857
1.39	10.082	1.59	7.684
1.40	10.000	1.60	7.500
1.41	9.916	1.61	7.308
1.42	9.828	1.62	7.105
1.43	9.737	1.63	6.892
1.44	9.643	1.64	6.667
1.45	9.546	1.65	6.428

Table 11. How to calculate B from the two spin-allowed absorption maxima σ_1 and σ_2 in octahedral d^3-systems.

Since the crystals have compressed $Cr-O$ distances[56] in ruby (small x), where B is largest, it is not possible to apply our arguments above. The reason is probably (ref. [57], p. 89) that Cr_2O_3 is a "softer" oxide with smaller $(H_{Cr}-H_O)$ in the sense of eq. (6). The two perovskite series $LaGa_{1-x}Cr_xO_3$ and $YAl_{1-x}Cr_xO_3$ also show decreasing B values when x increases, whereas $LaAl_{1-x}Cr_xO_3$ have nearly invariant B. The spinels $MgAl_{2-x}Cr_xO_4$ exhibit weakly decreasing B values.

f) *Discussion of optical properties of some individual systems*

In general, our results go in the opposite direction, the cubic titanium(IV) and zirconium(IV) mixed oxides decreasing the interelectronic repulsion parameters relative to those in the pure M_2O_3 whereas the relatively larger unit cells of thorium(IV) oxide mixtures produce a smaller nephelauxetic effect. Actually, the "compressed" $Nd_{0.1}Ce_{0.9}O_{1.95}$ and $Er_{0.2}In_{0.8}O_{1.5}$ show a very large nephelauxetic effect. It is not readily explained why the apparent value of $d\beta$ is only 0.1% in Eu(III) and 0.8% in Gd_2O_3, only a quarter of the value in Nd(III) and half the value of $d\beta$ in Er_2O_3. There seems to be a general tendency[1] for excited levels having lower total spin S or lower seniority number v or exceptional values of other among Racah's quantum numbers, to show less pronounced nephelauxetic effects than the excited levels of normal spin-allowed transitions.

Previously, Rosenberger[31] studied the absorption spectra of La_2O_3 (type A), Gd_2O_3 (type B) and Y_2O_3 (type C) containing minute amounts of Er(III). Rosenberger also concluded a general shift of the excited levels, relative to the ennea-aqua ions. Kisliuk, Krupke and Gruber[32] recently performed a more extensive study of Er(III) in Y_2O_3. With the nomenclature of eq. (1), Y_2O_3 yields $d\sigma = +200$ cm^{-1} and $d\beta = 1.6\%$, in complete agreement with Table 8 for Er_2O_3. Recently, the fluorescence in the visible of Eu(III)[58] and in the infra-red of Nd(III)[59] substituted in crystals of Y_2O_3 has been thoroughly studied. The detailed structure (at least five components of the Eu(III) emission spectrum[43, 58] in the 580 – 602 mμ region as contrasted to two components[1] in $Eu_{0.14}Th_{0.86}O_{1.93}$) demonstrate the relatively low micro-symmetry of the lanthanide sites in $C-M_2O_3$ and the presence of two different sites.

4. Experimental

Compounds. Stock solutions of 0.5 M or 0.1 M rare earth perchlorates were prepared from American Potash (Lindsay Division, West Chicago) 99.9% or better oxides and a weak excess of 2 M perchloric acid (diluted from Merck p. a.). A solution of 4 M $TiCl_4$ in 9 M HCl was made by slow addition of B. D. H. titanium tetrachloride to a cold mixture of water and concentrated hydrochloric acid. A solution of 0.5 M zirconyl chloride (Fluka) in 2 M HCl was freshly prepared before each series of preparations and filtered from small amounts of basic salts. A solution of 1 M Na_2SnCl_6, $6\,H_2O$ (B. D. H.) in 3 M HCl was also freshly prepared each time. The Ce(IV) mixed oxides were either prepared from a 1 M aqueous solution of $CeCl_3$, $7\,H_2O$ (Thorium Ltd., London) or by impregnation with the rare earth solution of cerium(IV) hydroxide powder (99.9%, Fluka) and subsequent ignition. A 0.05 M solution of Tl(III) in 2 M $HClO_4$ was made from $TlNO_3$ (AnalaR, B. D. H.) in perchloric acid oxidized with bromine and the brown

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hydrated oxide precipitated with aqueous sodium hydroxide. The filtered product was washed and dissolved on a sintered glass funnel in 2 M perchloric acid.

In all cases, appropriate amounts of the solutions were mixed, then added to equal (or larger, in the case of $MTiO_{3.5}$) amounts of water and to an amount of 12 M aqueous ammonia (Merck p. a.) 50% larger than necessary in order to neutralize all the acid and metal aqua ions present. It may be remarked that neodymium(III) hydroxide always shows a more bluish pink colour than the aqua ions, but that the co-precipitated mixtures containing titanium(IV) or zirconium (IV) are relatively more blue violet. In the case of lanthanum-containing samples, the excess of ammonia was four times as large. In all cases, the mixed hydroxides were left in the supernatant solution during one night, filtered, washed with water (it is recommendable to remove NH_4Cl if present) and ignited for one hour in an electric furnace at 1000 °C under oxidizing conditions (air).

It is remarkable that the mixed hydroxide containing nine times as much indium as thallium(III) is nearly colourless. This is also true for co-precitated zirconium(IV) and thallium(III) hydroxide in the same proportion, whereas yttrium or erbium are precipitated together with the brown hydrated Tl_2O_3. We analyzed the oxides of nominal composition $Tl_{0.1}In_{0.9}O_{1.5}$ and found it to correspond to $Tl_{0.027}In_{0.973}O_{1.5}$ only, and $Tl_{0.2}Er_{0.8}O_{1.5}$ to consist of $Tl_{0.028}Er_{0.972}O_{1.5}$. The remaining thallium must have evaporated during the preparation, as discussed in the text. The analysis method applied was: 100 mg mixed oxide was dissolved in 2 ml 6 M HCl, and 2 ml 0.1 M Na_2PtCl_6 was added. Subsequent addition of 50 mg ascorbic acid in 5 ml water produces an orange precipitate of Tl_2PtCl_6 which was allowed to stand for four hours, filtered, washed with ethanol and weighed.

The perovskites $Ba_{0.9}La_{0.1}Er_{0.1}Ti_{0.9}O_3$ and $Sr_{0.8}La_{0.2}Ti_{0.8}O_3$ were made from aqueous solutions of $BaCl_2$, $2\,H_2O$ and $SrCl_2$, $6\,H_2O$ (B. D. H.), $La(ClO_4)_3$, $Er(ClO_4)_3$ and $TiCl_4$ in HCl. However, a carefully calculated amount of 1 M aqueous Na_2CO_3 was added rapidly under efficient stirring in order to precipitate a mixture of hydroxides and $BaCO_3$ or $SrCO_3$ but avoiding amphoteric re-dissolution. The mixture was heated for two hours at 1000 °C.

X-ray measurements were made with a Guinier-DeWolff camera (Enraf-Nonius, Delft) using copper Kα-radiation. Silicon was used as standard substance.

Reflection spectra were measured with a Cary 14 Spectrophotometer, the sample temperature being approximately 100 °K, by the same technique as previously described[1].

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