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POWDER-DIAGRAM AND SPECTROSCOPIC STUDIES OF MIXED OXIDES OF LANTHANIDES AND QUADRIVALENT METALS

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Synopsis

Praseodymium and terbium occur predominantly as Pr(III) and Tb(III) in ZrO₂ whereas strongly coloured Pr(IV) and Tb(IV) is formed in ThO₂. The uncorrected optical electronegativities of these central atoms are 2.6 and 2.55 and found to agree with the general theory for 4fⁿ. The disordered fluorites M_{0.2}Zr_{0.8}O_{1.9} are studied spectroscopically and show a slightly weaker nephelauxetic effect than the C-M₂O₃. LaErO₃ and related materials such as La_{0.4}Er_{0.4}Zr_{0.2}O_{1.6} are further investigated. The new type NdYO₃ is found in a large variety of mixed La-Nd-Sm-Ti-Zr oxides prepared by ignition of co-precipitated hydroxides at 1000° C. Bi₂O₃ containing small amounts of Nd(III) or Er(III) is a disordered fluorite; the relations to senarmontite-Sb₂O₃ and M₂Bi₂₄O₄₀ are discussed. The absorption spectrum of Ce(IV) acetylacetonate is measured. Comparisons are made with the unusual octahedral 4f group and 5f group hexahalide complexes. The variable polarizability and optical electronegativity of oxide are discussed.

1. Miscibility and Superstructures of Fluorite

It is wellknown in geochemistry that trivalent lanthanides and certain quadrivalent metals such as thorium frequently replace each other in minerals. This is usually ascribed to comparable ionic radii and the stoichiometry is normally taken care of by charge compensation of other constituents, as is also often the case for aluminium (III) and silicon (IV) in common rocks. However, it is far more surprising that ZINTL and CROATTO [133] discovered that La_2O_3 is miscible to a large extent with CeO_2 retaining the cubic fluorite structure of the latter compound. This type of miscibility explains many tenacious impurities found in old days in rare earths, and may perhaps even explain why Urbain found traces of hafnium in fractions of Lu_2O_3 and called the new element celtium, firmly believing that it was trivalent.

From a crystallographic point of view, the miscibility may either be statistical, a surprisingly large number of oxygen vacancies (frequently above 12.5%) being formed, or new superstructures such as the C-type M_2O_3 or the pyrochlore $\text{A}_2\text{B}_2\text{O}_7$ are generated. No case seems to be known where the number of metal atoms deviate from that found in fluorite. In other words, in the unit cell characterized by the lattice parameter a_F (having the order of magnitude 5 Å), four metal atoms occur, whereas in the superstructures having the size $2a_F$, 32 metal atoms are found. They are arranged in cubic close-packing, and hence, on a Debye-powder diagram, the lines having the index $h^2 + k^2 + l^2 = 3, 4, 8, 11, 12, 16, 19, 24, \dots$ would occur anyhow, even if the oxygen atoms were neglected. In one sense, CaF_2 is a superstructure of CsCl containing half as many metal atoms, but we have found no trace of miscibility between these two types.

Small quadrivalent ions such as titanium (IV) favour distinct superstructures having the coordination number $N = 8$ for the lanthanides and $N = 6$ for Ti(IV). However, some C-oxides are miscible with TiO_2 to a certain extent [70] and $\text{Er}_{0.9}\text{Ti}_{0.1}\text{O}_{1.55}$ is distinctly C-type whereas $\text{Dy}_{0.9}\text{Ti}_{0.1}\text{O}_{1.55}$ seems to be a disordered fluorite with broadened diffraction lines. AULT and WELCH [3] found that a fluorite phase extends from $\text{Y}_{0.63}\text{Ti}_{0.37}\text{O}_{1.685}$ ($a_F = 5.135$ Å) to $\text{Y}_{0.76}\text{Ti}_{0.24}\text{O}_{1.62}$ ($a_F = 5.200$ Å) and a pyrochlore phase

from $Y_{0.45}Ti_{0.55}O_{1.775}$ ($2a_F = 10.088 \text{ \AA}$) to $Y_{0.59}Ti_{0.41}O_{1.705}$ ($2a_F = 10.127 \text{ \AA}$). The non-Daltonian behaviour of the pyrochlore casts a weak doubt on the stoichiometry of $ErTiO_{3.5}$ ($2a_F = 10.0762 \text{ \AA}$) which has been studied very carefully by X-ray and neutron diffraction [80]. The strongly distorted octahedron Ti-6 O has the internuclear distance 1.955 \AA whereas the compressed cube around erbium has two Er-O 2.1815 \AA ($= \sqrt{3}a_F/4$) and six Er-O 2.471 \AA . The distortions from fluorite ($x = 0.375$) can be expressed by the oxygen parameter $x = 0.420$ for $ErTiO_{3.5}$. If x were 0.4375 , the octahedron $Ti(IV)O_6$ would be regular. These figures illustrate the extraordinary liberality of ionic radius variation allowed in the superstructures. The two short Er-O distances represent the average value for A and B in $A_2B_2O_7$, whereas Er(III) otherwise seems to have an ionic radius some 0.4 \AA larger than Ti(IV). One would extrapolate a_F for a hypothetical fluorite TiO_2 to be 4.80 \AA whereas the (much safer) extrapolation to fluorite ZrO_2 gives 5.10 \AA . These values vary less than $(4/\sqrt{3})$ times the variation of the ionic radii for 6-coordination.

2. Zirconium Oxide

Excellent reviews on mixed oxides formed with Zr(IV) are written by Madame PEREZ Y JORBA [99], LEFÈVRE [84] and MÖBIUS [93]. Whereas pure ZrO_2 is not stable as fluorite, relatively small admixtures of trivalent or divalent ions stabilize the cubic form. There is an apparent discrepancy between our previous results [70] finding disordered fluorites $MZrO_{3.5}$ ($M = Nd, Sm, Eu, Dy, Ho, Er, Yb$) and COLLONGUES *et al.* [25] finding pyrochlores for $M = La, Ce, Nd, Sm$ and Gd in agreement with ROTH [109] for $M = La$ and Nd . The French authors prepared the pyrochlores under equilibrium conditions at 1300 to $1500^\circ C$ and noted that $SmZrO_{3.5}$ if heated above $2400^\circ C$ or $GdZrO_{3.5}$ if heated above $1550^\circ C$ transform to disordered fluorites, comparable to $DyZrO_{3.5}$ at all temperatures studied. Our technique of heating co-precipitated hydroxides for one to three hours at $1000^\circ C$ produces disordered Zr-fluorites (though Ti-pyrochlores) which must be metastable according to PEREZ Y JORBA [99]. The crystallization of the oxide formed from co-precipitated hydroxides takes place at a quite definite temperature, frequently around $500^\circ C$, whereas pure ZrO_2 is formed from the hydroxide at $370^\circ C$ according to LEFÈVRE [84]. The additional lines for pyrochlores ($a_P = 2a_F$) have indexes 3, 11, 19, 27, 35, . . .

We continued our studies by preparing $M_{0.2}Zr_{0.8}O_{1.9}$ of most of the lanthanides M. This concentration of M is well above what is normally

TABLE 1.

Unit cell parameters a_F in Å observed for cubic (and in the case of LaErO_3 , perhaps quasi-cubic) structures. F is fluorite, C the Er_2O_3 type, P pyrochlore (the actual unit cells have $a_C = a_P = 2 a_F$). The mixed La-Er-Zr oxides marked w and w^2 have the apparent fluorite-indexes 1.5 and 2.25, respectively. The calculated values a_F^* are obtained by linear combination of the constituents, the quantities for M(III) being obtained from eq.(1). +N indicates that the sample consists of two phases, the other being NdYO_3 of Table 2. As discussed in the text, the observation of the line w^2 may indicate N being present well.

| | Type | a_F | a_F^* | Ref. |
|---|---------------|--------|---------|------|
| $\text{La}_{0.55}\text{Er}_{0.45}\text{O}_{1.5}$ | C+N | ~ 5.36 | 5.57 | — |
| $\text{La}_{0.5}\text{Er}_{0.5}\text{O}_{1.5}$ (1000°C)..... | C+N | 5.29 | 5.55 | 70 |
| $\text{La}_{0.45}\text{Er}_{0.55}\text{O}_{1.5}$ | C+N | ~ 5.35 | 5.53 | — |
| $\text{La}_{0.4}\text{Er}_{0.6}\text{O}_{1.5}$ | C+N | ~ 5.41 | 5.51 | — |
| $\text{La}_{0.3}\text{Er}_{0.7}\text{O}_{1.5}$ | C+N | ~ 5.33 | 5.48 | — |
| $\text{La}_{0.2}\text{Er}_{0.8}\text{O}_{1.5}$ | C(+N) | 5.31 | 5.45 | — |
| $\text{La}_{0.1}\text{Er}_{0.9}\text{O}_{1.5}$ | C | 5.30 | 5.41 | — |
| $\text{ErO}_{1.5}$ | C | 5.274 | 5.38 | — |
| $\text{La}_{0.5}\text{Th}_{0.5}\text{O}_{1.5}$ (820°C)..... | C+N | 5.36 | 5.53 | — |
| $\text{La}_{0.5}\text{Yb}_{0.5}\text{O}_{1.5}$ (820°C)..... | C+N | 5.26 | 5.52 | — |
| $\text{Dy}_{0.9}\text{Zr}_{0.1}\text{O}_{1.55}$ | F or C | 5.32 | 5.39 | — |
| $\text{La}_{0.38}\text{Er}_{0.54}\text{Zr}_{0.1}\text{O}_{1.55}$ | F(w^2) | 5.345 | 5.47 | — |
| $\text{La}_{0.27}\text{Er}_{0.63}\text{Zr}_{0.1}\text{O}_{1.55}$ | F(w, w^2) | 5.29 | 5.44 | — |
| $\text{La}_{0.18}\text{Er}_{0.72}\text{Zr}_{0.1}\text{O}_{1.55}$ | F(w) | ~ 5.30 | 5.41 | — |
| $\text{La}_{0.09}\text{Er}_{0.81}\text{Zr}_{0.1}\text{O}_{1.55}$ | F(w) | ~ 5.28 | 5.38 | — |
| $\text{Er}_{0.9}\text{Zr}_{0.1}\text{O}_{1.55}$ | C | 5.26 | 5.35 | — |
| $\text{Sm}_{0.8}\text{Zr}_{0.2}\text{O}_{1.6}$ | F | ~ 5.40 | 5.44 | — |
| $\text{La}_{0.4}\text{Dy}_{0.4}\text{Zr}_{0.2}\text{O}_{1.6}$ | F+N | 5.38 | 5.48 | — |
| $\text{La}_{0.2}\text{Dy}_{0.6}\text{Zr}_{0.2}\text{O}_{1.6}$ | F+N | 5.34 | 5.40 | — |
| $\text{Dy}_{0.8}\text{Zr}_{0.2}\text{O}_{1.6}$ | F | 5.29 | 5.36 | — |
| $\text{La}_{0.4}\text{Er}_{0.4}\text{Zr}_{0.2}\text{O}_{1.6}$ | F(w^2) | 5.30 | 5.46 | — |
| $\text{La}_{0.32}\text{Er}_{0.48}\text{Zr}_{0.2}\text{O}_{1.6}$ | F(w^2) | ~ 5.29 | 5.43 | — |
| $\text{La}_{0.24}\text{Er}_{0.56}\text{Zr}_{0.2}\text{O}_{1.6}$ | F(w^2) | 5.275 | 5.41 | — |
| $\text{La}_{0.16}\text{Er}_{0.64}\text{Zr}_{0.2}\text{O}_{1.6}$ | F(w, w^2) | ~ 5.28 | 5.38 | — |
| $\text{La}_{0.08}\text{Er}_{0.72}\text{Zr}_{0.2}\text{O}_{1.6}$ | F(w) | 5.255 | 5.35 | — |
| $\text{Er}_{0.8}\text{Zr}_{0.2}\text{O}_{1.6}$ | C | 5.26 | 5.32 | 70 |
| $\text{Nd}_{0.67}\text{Zr}_{0.33}\text{O}_{1.67}$ | F+N | ~ 5.36 | 5.42 | — |
| $\text{La}_{0.33}\text{Sm}_{0.33}\text{Zr}_{0.33}\text{O}_{1.67}$ | F | ~ 5.37 | 5.45 | — |
| $\text{Sm}_{0.67}\text{Zr}_{0.33}\text{O}_{1.67}$ | F? | — | 5.38 | — |
| $\text{Dy}_{0.67}\text{Zr}_{0.33}\text{O}_{1.67}$ | F | 5.26 | 5.32 | — |
| $\text{Er}_{0.67}\text{Zr}_{0.33}\text{O}_{1.67}$ | C | 5.27 | 5.28 | 70 |
| $\text{La}_{0.25}\text{Nd}_{0.25}\text{Zr}_{0.5}\text{O}_{1.75}$ | F+N | 5.31 | 5.38 | — |
| $\text{Nd}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$ | P | 5.324 | — | 109 |
| | F | 5.30 | 5.35 | 70 |
| $\text{La}_{0.25}\text{Sm}_{0.25}\text{Zr}_{0.5}\text{O}_{1.75}$ | F | ~ 5.30 | 5.36 | — |

(contd.)

TABLE 1 (contd.)

| | Type | a_F | a_F^* | Ref. |
|--|------|-------------|------------|------|
| $\text{Sm}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$ | P | 5.288 | — | 99 |
| | F | 5.27 | 5.32 | 70 |
| $\text{Eu}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$ | F | 5.23 | 5.30 | 70 |
| $\text{La}_{0.25}\text{Dy}_{0.25}\text{Zr}_{0.5}\text{O}_{1.75}$ | F+N | 5.27 | 5.33 | — |
| $\text{Dy}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$ | F | 5.21 | 5.26 | 70 |
| $\text{Ho}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$ | F | 5.20 | 5.25 | 70 |
| $\text{La}_{0.2}\text{Er}_{0.3}\text{Zr}_{0.5}\text{O}_{1.75}$ | F | ~ 5.24 | 5.31 | — |
| $\text{La}_{0.15}\text{Er}_{0.35}\text{Zr}_{0.5}\text{O}_{1.75}$ | F | 5.23 | 5.29 | — |
| $\text{La}_{0.1}\text{Er}_{0.4}\text{Zr}_{0.5}\text{O}_{1.75}$ | F | 5.22 | 5.27 | — |
| $\text{La}_{0.05}\text{Er}_{0.45}\text{Zr}_{0.5}\text{O}_{1.75}$ | F | 5.205 | 5.255 | — |
| $\text{Er}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$ | F | 5.19 | 5.24 | 70 |
| $\text{Yb}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$ | F | 5.17 | 5.21 | 70 |
| $\text{Pr}_{0.4}\text{Zr}_{0.6}\text{O}_{2-x}$ | F | 5.265 | (IV)5.225 | — |
| | | | (III)5.31 | — |
| $\text{Pr}_{0.2}\text{Zr}_{0.8}\text{O}_{2-y}$ | F | 5.17 | (IV)5.16 | — |
| | | to 5.25 | (III)5.205 | — |
| $\text{Nd}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ | F | 5.19 | 5.20 | — |
| $\text{Sm}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ | F | 5.17 | 5.19 | — |
| $\text{Eu}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ | F | 5.155 | 5.18 | — |
| $\text{Tb}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ | F | 5.15 | (III)5.17 | — |
| $\text{Dy}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ | F | 5.15 | 5.16 | — |
| $\text{Ho}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ | F | 5.147 | 5.16 | — |
| $\text{Er}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ | F | 5.145 | 5.16 | — |
| $\text{Tm}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ | F | 5.135 | 5.15 | — |
| $\text{Yb}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ | F | 5.13 | 5.15 | — |

needed to induce the fluorite structure, and indeed, we find a very smooth variation of a_F as seen in Table 1. The samples form unusually large (about 1 mm³) crystals; the spectroscopic properties are discussed in chapter 8. The behaviour of praseodymium and terbium is particularly interesting. When incorporated in CeO₂, ThO₂ and in C-oxides, these two elements readily oxidize to Pr(IV) and Tb(IV) by heating in air. However, this is not at all true in ZrO₂. The value $a_F = 5.15 \text{ \AA}$ for M = Tb interpolates nicely in the series of the other trivalent M. An even stronger argument is the amber-yellow colour of the sample suggesting that nearly all terbium occurs as Tb(III) since we see in chapter 6 that Tb(IV) is far more intensely coloured in such lattices. The case for M = Pr is a little more complicated. The powder diagram here corresponds to a superposition of two components having $a_F = 5.25$ and 5.17 \AA ; and when heated in ethanol vapour, $a_F \sim 5.23 \text{ \AA}$

and the lines are asymmetrically broadened. The sample is yellow-brown before the reduction and turns pale grey. The black $\text{Pr}_{0.4}\text{Zr}_{0.6}\text{O}_{2-x}$ turns light olive-brown by reduction in ethanol vapour, but retains the value $a_{\text{F}} = 5.265 \text{ \AA}$. $\text{Pr}_{0.5}\text{Zr}_{0.5}\text{O}_{2-x}$ is black and has $a_{\text{F}} = 5.31 \text{ \AA}$. When compared with $a_{\text{F}} = 5.39 \text{ \AA}$ for PrO_2 [16, 45] this indicates lattice constants some $0.05\text{--}0.07 \text{ \AA}$ above Vegard's linear rule. The most probable conclusion is that most, but not all, praseodymium occurs as Pr(III) in these samples.

We also prepared some lanthanide-rich mixtures. Several of these preparations belong to a new type described in chapter 3 and which is remarkably common for lanthanum and neodymium oxides containing some Ti(IV), Y(III) or Zr(IV). However, some disordered fluorites are also found. As seen in Table 1, lanthanum substitution $\text{La}_x\text{Er}_{1-x}\text{ZrO}_{3.5}$ increases a_{F} from 5.19 \AA for $x = 0$ to 5.24 \AA for $x = 0.4$. Three other disordered fluorites are $\text{Nd}_{0.67}\text{Zr}_{0.33}\text{O}_{1.67}$, $\text{La}_{0.33}\text{Sm}_{0.33}\text{Zr}_{0.33}\text{O}_{1.67}$ and $\text{Dy}_{0.67}\text{Zr}_{0.33}\text{O}_{1.67}$ whereas $\text{Er}_{0.67}\text{Zr}_{0.33}\text{O}_{1.67}$ previously [70] was found to be a C-oxide with slightly larger a_{F} . $\text{Sm}_{0.8}\text{Zr}_{0.2}\text{O}_{1.6}$ has broader diffraction lines than $\text{Dy}_{0.8}\text{Zr}_{0.2}\text{O}_{1.6}$ but both seem to be disordered fluorites, whereas $\text{Dy}_{0.9}\text{Zr}_{0.1}\text{O}_{1.55}$ shows ambiguous and $\text{Er}_{0.8}\text{Zr}_{0.2}\text{O}_{1.6}$ certain signs of being C-oxides. We discuss nine mixed La-Er-Zr oxides in chapter 4 because of the relations to the problem of LaErO_3 .

3. The New Type NdYO_3

Since GOLDSCHMIDT's identification [36] of the A-, B- and C-types of the rare earths, there has been an extensive discussion of the influence of temperature and pressure on the equilibria and kinetic behaviour of the transformations (*cf.* the review by BRAUER [17]). FOEX and TRAVERSE [33] have recently found two new hexagonal forms of M_2O_3 which only occur above 2000°C . SCHNEIDER and ROTH [112] studied mixed lanthanide oxides prepared mainly at 1650°C and concluded in the presence of Goldschmidt's three forms and of an orthorhombic perovskite LaYbO_3 . As we shall see in chapter 4, this is a high-temperature form. When prepared at 600° or 800°C , two other types are observed.

As seen in Table 2, our technique produced [70] $\text{Nd}_{0.5}\text{Y}_{0.5}\text{O}_{1.5}$ and $\text{Nd}_{0.2}\text{Y}_{0.8}\text{O}_{1.5}$ not having the B-type expected [112] but a rather simple powder-diagram which has also been found in a large number of mixed oxides of lighter lanthanides containing some Ti(IV) or Zr(IV). Among the pure examples of this type are $\text{Nd}_{0.9}\text{Ti}_{0.1}\text{O}_{1.55}$, $\text{Nd}_{0.8}\text{Ti}_{0.2}\text{O}_{1.6}$, $\text{Nd}_{0.67}\text{Ti}_{0.33}\text{O}_{1.67}$, $\text{Nd}_{0.8}\text{Zr}_{0.2}\text{O}_{1.6}$, $\text{La}_{0.4}\text{Nd}_{0.4}\text{Zr}_{0.2}\text{O}_{1.6}$, $\text{La}_{0.45}\text{Sm}_{0.45}\text{Zr}_{0.1}\text{O}_{1.55}$ and $\text{La}_{0.45}\text{Dy}_{0.45}\text{Zr}_{0.1}\text{O}_{1.55}$. The purpose of making the ternary mixed oxides is to

TABLE 2.

d -values in Å for diffraction lines of the new type NdYO₃. The normalization factor n for the unit cell is indicated. +F indicates the simultaneous presence of another, fluorite-type, phase. “v” indicates the presence of additional lines, the strongest of which has $d = 2.12$ Å, and probably corresponding to a perovskite phase.

| | | | | | n | Ref. |
|---|-------|-------|-------|-------|-------|------|
| Nd _{0.5} Y _{0.5} O _{1.5} | 3.44 | 2.85 | 2.59 | 2.01 | 1.00 | 70 |
| Nd _{0.2} Y _{0.8} O _{1.5} | 3.42 | 2.82 | 2.57 | 1.98 | 0.99 | 70 |
| Nd _{0.9} Ti _{0.1} O _{1.55} | 3.43 | 2.84 | 2.59 | 2.01 | 1.00 | 70 |
| Nd _{0.8} Ti _{0.2} O _{1.6} | 3.45 | 2.84 | 2.59 | 2.01 | 1.00 | 70 |
| Nd _{0.67} Ti _{0.33} O _{1.66} | 3.46 | 2.86 | 2.61 | 2.02 | 1.005 | 70 |
| La _{0.45} Sm _{0.45} Zr _{0.1} O _{1.55} | 3.525 | 2.905 | 2.63 | — | 1.02 | — |
| La _{0.45} Dy _{0.45} Zr _{0.1} O _{1.55} | 3.525 | 2.905 | 2.63 | 2.06 | 1.02 | — |
| La _{0.4} Nd _{0.4} Zr _{0.2} O _{1.6} | 3.525 | 2.9 | 2.625 | 2.06 | 1.02 | — |
| La _{0.2} Nd _{0.6} Zr _{0.2} O _{1.6} | 3.505 | 2.875 | 2.62 | 2.04 | 1.015 | — |
| Nd _{0.8} Zr _{0.2} O _{1.6} | 3.45 | 2.855 | 2.595 | 2.02 | 1.005 | — |
| La _{0.4} Sm _{0.4} Zr _{0.2} O _{1.6} | 3.515 | 2.905 | 2.625 | 2.06 | 1.02 | — |
| La _{0.2} Sm _{0.6} Zr _{0.2} O _{1.6} (+F) | 3.505 | 2.885 | 2.615 | 2.04? | 1.015 | — |
| La _{0.4} Dy _{0.4} Zr _{0.2} O _{1.6} (+F) | 3.525 | 2.91 | — | 2.06 | 1.02 | — |
| La _{0.2} Dy _{0.6} Zr _{0.2} O _{1.6} (+F) | 3.515 | 2.895 | — | 2.06 | 1.02 | — |
| La _{0.33} Nd _{0.33} Zr _{0.33} O _{1.67} (+F) | 3.515 | 2.885 | 2.625 | 2.05 | 1.015 | — |
| Nd _{0.67} Zr _{0.33} O _{1.67} (+F) | 3.445 | 2.85 | 2.585 | — | 1.00 | — |
| La _{0.33} Dy _{0.33} Zr _{0.33} O _{1.67} (+F) | 3.535 | 2.915 | — | 2.06 | 1.025 | — |
| La _{0.25} Nd _{0.25} Zr _{0.5} O _{1.75} (+F) | 3.525 | 2.915 | 2.635 | 2.06 | 1.02 | — |
| La _{0.5} Y _{0.5} O _{1.5} (600°C) | 3.535 | 2.915 | 2.64 | 2.065 | 1.025 | — |
| La _{0.5} Y _{0.5} O _{1.5} (1000°C) | 3.545 | 2.92 | 2.64 | 2.065 | 1.03 | — |
| La _{0.5} Ho _{0.5} O _{1.5} (1000°C) | 3.535 | 2.915 | 2.64 | 2.065 | 1.025 | — |
| La _{0.6} Er _{0.4} O _{1.5} (+v) | 3.535 | 2.92 | 2.64 | 2.06 | 1.025 | — |
| La _{0.55} Er _{0.45} O _{1.5} (+v, +C) | 3.525 | 2.90 | 2.63 | 2.06 | 1.02 | — |
| La _{0.5} Er _{0.5} O _{1.5} (600°C) | 3.54 | 2.92 | 2.645 | 2.065 | 1.03 | — |
| — (1000°C, N-component) | 3.53 | 2.90 | — | 2.055 | 1.02 | — |
| La _{0.45} Er _{0.55} O _{1.5} (+v, +C) | 3.525 | 2.91 | ~2.63 | 2.06 | 1.02 | — |
| La _{0.4} Er _{0.6} O _{1.5} (+C) | 3.525 | 2.91 | ~2.65 | 2.065 | 1.02 | — |
| La _{0.5} Tm _{0.5} O _{1.5} (600°C) (+C) | 3.535 | 2.92 | ~2.65 | 2.065 | 1.025 | — |
| La _{0.5} Yb _{0.5} O _{1.5} (600°C) (+C) | 3.53 | 2.91 | ~2.64 | 2.065 | 1.02 | — |
| — (1000°C, N-component) | 3.535 | 2.91 | — | 2.06 | 1.025 | — |

investigate to what extent a mixture of two lanthanides imitates the actual lanthanide having the ionic radius equal to the average radius of the mixture. Other samples, containing heavier lanthanides such as dysprosium, or containing more zirconium, consisted of two phases, one fluorite and one NdYO₃ type. However, LaYO₃ and LaHoO₃ prepared at 600° or 1000°C, or LaErO₃ prepared at 600°C also belong to the NdYO₃ type.

The linear dimensions of the unit cells of the various compounds isotypic with NdYO_3 must be rather similar. It is seen in Table 2 that the d -values range from 1.025 ($\text{La}_{0.5}\text{Y}_{0.5}\text{O}_{1.5}$) to 0.99 ($\text{Nd}_{0.2}\text{Y}_{0.8}\text{O}_{1.5}$) times those characterizing NdYO_3 . It may be noted that in addition to our type, which we also find for Nd_2TiO_5 prepared by our technique, two other types M_2TiO_5 have been described. ROTH [109] found that $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{Nd}_2\text{Ti}_2\text{O}_7$ are not cubic pyrochlores (as are $\text{Sm}_2\text{Ti}_2\text{O}_7$ and heavier compounds) but have a very complicated powder-diagram not corresponding to our type. GUILLEN and BERTAUT [38] resolved the crystal structure of their orthorhombic La_2TiO_5 containing La(III)O_7 and unusual trigonal-bipyramidic Ti(IV)O_5 . QUEYROUX [103] studied Gd_2TiO_5 and Dy_2TiO_5 having essentially a fluorite structure, but an actual hexagonal unit cell with the volume $9a_F^3$. Professor E. F. Bertaut was so kind as to confirm that the powder-diagrams of these four types are all different.*

4. Mixed Lanthanum-Erbium Oxides

The C-type M_2O_3 solved by PAULING and SHAPPELL [98] is represented by a surprising variety of oxides, Sc_2O_3 , In_2O_3 , Tl_2O_3 in addition to rare earths (favoured by small ionic radii and low temperature). Obviously, the oxygen atoms do not contribute very strongly to the X-ray diffraction, and it is only after the refinement also using neutron diffraction [10] that it has become apparent that the M-O distances do not show as much spreading as first assumed (excepting Mn_2O_3 and the mineral bixbyite, which are rather atypical cases). Thus, 8 of the 32 indium atoms in the unit cell of In_2O_3 [88] have six oxygen neighbours at the distance 2.18 Å nicely situated at the corners of a cube lacking a bodydiagonal, whereas the 24 atoms deviate more from the idealized fluorite substructure (cube lacking a face-diagonal) by having each two distances In-O 2.13, two 2.19 and two 2.23 Å. It may be remarked that the average distance 2.183 Å is very closely that of fluorite $\sqrt{3}a_F/4 = 2.189$ Å.

Phenomenologically, the fluorite diffraction lines having the index $h^2 + k^2 + l^2 = 3, 4, 8, 11, 12, 16, 19, \dots$ become 12, 16, 32, 44, 48, 64, 76, \dots when the unit cell is doubled in C-oxides, and new, prominent lines have the indexes 6, 14, 18, 22, 26, 38, 46, \dots . It was noted [70] that samples of LaErO_3 and LaYbO_3 made at temperatures lower than 1000°C have the

* Dr. Paul Caro kindly attracted the writers' attention to the danger of forming very stable oxo-carbonates $\text{M}_2\text{O}_2(\text{CO}_3)$. However, the powder-diagrams of the two hexagonal forms $\text{M} = \text{La}$ and Sm do not correspond to ours, and a sample of $\text{LaYO}_3(1000^\circ\text{C})$ kept for half a year, only contains 2.6% CO_2 and not 13.75% CO_2 .

powder-diagram characterizing the C-type superposed very weak lines apparently having the fractional indexes 2.25 and 8.75 besides a few lines at lower d -values. One explanation of this behaviour would be a very large cubic unit cell having the size $4a_F$ ($\sim 20 \text{ \AA}$) and only showing appreciable diffraction intensity for the indexes 9, 24, 35, 48, 64, . . . which is not a very appealing idea. Another explanation would be an ordered distortion of the C-lattice, perhaps having a symmetry much lower than cubic, as has actually been found for Gd_2O_3 , Dy_2O_3 , Yb_2O_3 [99] and Sc_2O_3 [84] mixed crystals with relatively small amounts of ZrO_2 . However, these types do not correspond to our observations.

Here, we continued the study, and we found the same behaviour for LaTmO_3 and for $\text{La}_x\text{Er}_{1-x}\text{O}_{1.5}$ with $x = 0.2$ to 0.55 , and a rather unexpected variation of a_F as function of x , as seen in Table 1. We have adapted the suggestion by BRAUER and GRADINGER [15] to define an effective a_F^* parameter for C-oxides having the observed $a_C = 2a_F$:

$$a_F^* = a_F + 0.21295 (5.757 \text{ \AA} - a_F) \quad (1)$$

giving the values 5.62 \AA for Pr_2O_3 , 5.59 \AA for Nd , 5.53 \AA for Sm , 5.50 \AA for Eu , 5.45 \AA for Tb , 5.42 \AA for Dy , 5.40 \AA for Ho , 5.38 \AA for Er , 5.35 \AA for Tm , 5.33 \AA for Yb and 5.40 \AA for Y . These values, as well as the parameter $a_F^* = 5.72 \text{ \AA}$ for La_2O_3 , agree with the slopes extrapolated towards 100% lanthanide content in several oxides of quadrivalent metals. The reason why a_F is smaller than a_F^* in C- M_2O_3 (0.042 \AA for $\text{M} = \text{Pr}$, 0.115 \AA for $\text{M} = \text{Yb}$) is essentially the six-coordination in C-oxides. Goldschmidt argued that 8-coordination corresponds to 8% larger ionic radii than 6-coordination, which should hence decrease a_F^* of C- Pr_2O_3 (representing $(4/\sqrt{3})$ times the distance Pr-O) 0.27 \AA and of Yb_2O_3 0.23 \AA . Apparently $N = 6$ is unpleasantly low for lighter lanthanides, and equ. (1) corresponds to much smaller changes. POIX [100] compiled M-O distances for $N = 12$ and $N = 6$ in perovskites. Thus, $N = 12$ for Nd corresponds to 2.665 \AA , whereas the observed $a_F = 5.54 \text{ \AA}$ for C- Nd_2O_3 corresponds to 2.40 \AA (*cf.* the discussion of In_2O_3 above). Another example [100] is $N = 6$ for Ce 2.405 \AA whereas CeO_2 has the actual value (for $N = 8$) 2.338 \AA showing a larger rather than a smaller value for six-coordination.

Returning to our $\text{La}_x\text{Er}_{1-x}\text{O}_{1.5}$, the values for $(a_F^* - a_F)$ are 0.11 \AA for $x = 0$ and 0.1 ; 0.14 \AA for 0.2 ; and 0.15 \AA for $x = 0.3$. This shows that our samples are even more tightly packed than the ordinary C-oxide. For $x = 0.5$, this difference assumes the rather astonishing size 0.26 \AA . Apparently, these very high values are not perfectly reproducible. LaTmO_3 has $(a_F^* - a_F) = 0.17 \text{ \AA}$ and LaYbO_3 0.26 \AA .

However, most and probably all of these observations can be explained by the presence of two phases. It turned out that LaErO_3 prepared at 600°C is entirely of NdYO_3 -type (N), and that the effect of heating hence seems to be the formation of a mixture of much C- and some N at 1000°C and of perovskite at 1200°C . There are two unusual aspects of this interpretation. One is the w-line with the apparent fluorite index 9/16. Actually, it can be included in Table 2 at the position $d = n \cdot 6.7 \text{ \AA}$. This line is particularly strong in the mixed La-Er oxides, and it was apparently absent in several of the samples given in Table 2. However, a closer comparison showed that in all of these cases, it was due to insufficient exposure of the film. The other unexpected feature is that LaErO_3 prepared at 600°C has slightly larger d -values than LaYO_3 and LaHoO_3 . Actually, $n = 1.02$ seems to be a lower limit for the last entries in Table 2, and the N-component of LaYbO_3 has a slightly *larger* value of n than the N-component of LaErO_3 . This can be rationalized if the rearrangement typically taking place between 800 and 1000°C does not involve a complete transformation to the C-type, but that some N-phase remains containing somewhat less Yb in the former case compared to the proportion of Er in the latter case, whereas the C-type assumes a low value for a_{F} corresponding to less than 50% La. In many ways, the N-type assumes the same role as the B-type in SCHNEIDER and ROTH's studies [112] at 1650°C . We have found no case where the N-type survives at 1200°C .

The mixed La-Er-Zr oxides containing 10% Zr are not extremely different in behaviour. a_{F} for the C-type increases linearly until 18% La, whereas the samples containing 27 and 36% La also contain some N-phase. The samples containing 20% Zr tend to contain three phases, as is distinctly the case for $\text{La}_{0.48}\text{Er}_{0.32}\text{Zr}_{0.2}\text{O}_{1.6}$, viz. a fluorite with $a_{\text{F}} \sim 5.36 \text{ \AA}$, an N-phase and something giving sharp lines, the strongest of which at $d = 2.13 \text{ \AA}$. This third phase which can also be perceived in $\text{La}_{0.55}\text{Er}_{0.45}\text{O}_{1.5}$ and $\text{La}_{0.45}\text{Er}_{0.55}\text{O}_{1.5}$ prepared at 1000°C (strongest line $d = 2.12 \text{ \AA}$) is probably a perovskite.

Nearly all our disordered fluorites [70] $\text{MZrO}_{3.5}$ have $(a_{\text{F}} - a_{\text{F}}^{\bullet}) = 0.05 \text{ \AA}$, and this is also true for $\text{La}_x\text{Er}_{0.5-x}\text{Zr}_{0.5}\text{O}_{1.75}$ having $x = 0.05, 0.1$ and 0.15 . For $x = 0.2$, the fluorite lines are somewhat broadened and apparently, the phase breaks down by further lanthanum substitution.

The various oxides having C + N diffraction lines are all transformed irreversibly by heating for three hours to 1200°C . The powder-diagrams indicate clearly perovskites, the average cubic value for the strong multiplets of closely adjacent lines is $a_{\text{av}} = 4.23 \text{ \AA}$ for $\text{La}_{0.4}\text{Er}_{0.6}\text{O}_{1.5}$, 4.21 \AA for $\text{La}_{0.45}\text{Er}_{0.55}\text{O}_{1.5}$, 4.22 \AA for $\text{La}_{0.5}\text{Er}_{0.5}\text{O}_{1.5}$, 4.22 \AA for $\text{La}_{0.55}\text{Er}_{0.45}\text{O}_{1.5}$, 4.21 \AA for

$\text{La}_{0.5}\text{Tm}_{0.5}\text{O}_{1.5}$ and 4.19 \AA for $\text{La}_{0.5}\text{Yb}_{0.5}\text{O}_{1.5}$. It is highly probable that the homogeneity ranges for these orthorhombic perovskites are narrow, and that excess rare earth of one kind forms other phases. Thus, $\text{La}_{0.3}\text{Er}_{0.7}\text{O}_{1.5}$ when subject to 3 hours 1200°C seems to have superposed lines of a fluorite or C-oxide $a_{\text{F}} = 5.35 \text{ \AA}$ (pure Er_2O_3 5.274 \AA) and another phase. Though the perovskite LaErO_3 definitely is the stable thermodynamic form, the coordination number $N = 12$ for La is unusually high, and $N = 6$ for Er unusually low, and correspondingly, the value for $(a_{\text{av}}/\sqrt{2}) = 2.98 \text{ \AA}$ is considerably larger than POIR' value [100] for La-O 2.71 \AA , whereas $a_{\text{av}}/2 = 2.11 \text{ \AA}$ is smaller than expected for Er-O. Of course, because of the orthorhombic distortions, these two expressions do not correspond exactly to the M-O distances.

5. Bismuth Oxide

$\text{C-M}_2\text{O}_3$ has a highly distorted 6-coordination for 24 of the 32 M atoms in the unit cell. Among the most unusual properties of this type considered as a superstructure of fluorite is that the oxygen vacancies are surrounded by four (such six-coordinated) M-atoms without any metallic properties being apparent (with the exception of Tl_2O_3 [70]). One may ask whether a cubic structure is not feasible, where all M atoms adapt the coordination (cube lacking body-diagonal) characterizing the 8 remaining M-atoms in the C-type. Actually, senarmontite, one of the modifications of Sb_2O_3 , is cubic O_h^7 with $a = 11.14 \text{ \AA}$ and isotypic with arsenolithe As_2O_3 having $a = 11.074 \text{ \AA}$. This type can either be considered as a lattice of individual As_4O_6 molecules or as a superstructure of fluorite, all M-atoms being of the body-diagonal-vacancy class discussed above. The choice between these two descriptions is determined by the actual extent of three M-O distances being considerably shorter than the three others. The powder diagram lines have the indexes 3, 12, 16, 19, 24, 27, 32, 35, 36, 44, 48, 51, . . . [94] which obey the same selection rules as pyrochlore. However, in actual practice, confusion between the two types rarely occurs, because the intensity distribution is very different (19 stronger than 16; 51 comparable to 44; *etc.*).

LEVIN and ROTH [85] reviewed the many modifications reported of Bi_2O_3 . The two most common forms of high purity are monoclinic $\alpha\text{-Bi}_2\text{O}_3$ and tetragonal $\beta\text{-Bi}_2\text{O}_3$. SILLÉN [118] found a cubic form ($a = 10.08 \text{ \AA}$) having the composition $\text{M}_2\text{Bi}_{24}\text{O}_{40}$ where M is a quadrivalent impurity such as silicon (*e. g.* deriving from porcelain crucibles). SCHUMB and RITTMER [113] prepared the isotypic $\gamma\text{-Bi}_2\text{O}_3$ ($a = 10.245 \text{ \AA}$) which is definitely not a super-

structure of fluorite (like all other cubic structures discussed here) since it contains 26 Bi atoms per unit cell which can be written $\text{Bi}_{26}\text{O}_{39}$. LEVIN and ROTH [85] prepared many more "sillenites", mixed oxides 12 Bi: 1 M, where M = Pb, Cd, Rb, V, Zn, Ti, Ge, Al, P, Ge, B, Si, presenting a -values in the range from 10.258 to 10.104 Å. The strongest lines have indexes [113] 8, 10, 12, 14, . . . , 34, 36, 38, 46, . . .

GATTOW and SCHRÖDER [34] described the (disordered) fluorite δ - Bi_2O_3 ($a_{\text{F}} = 5.665$ Å) which is only stable in the interval from 730°C to the melting point 825°C. These authors also report δ^* mixed oxides such as $\text{Bi}_{12}\text{SiO}_{20}$ not being a sillenite, but again a disordered fluorite $a_{\text{F}} = 5.542$ Å. HUND [49] found that UO_2 is completely miscible with δ - Bi_2O_3 forming red-brown $\text{U}_x\text{Bi}_{1-x}\text{O}_{1.5+0.5x}$ and that ThO_2 and CeO_2 are miscible to a great extent with this fluorite.

When we melted Bi_2O_3 at 850°C for 30 minutes, the cooled product had a vitreous aspect. However, it does give a complicated powder-diagram. If oxides were carefully pre-mixed corresponding to the compositions $\text{Nd}_{0.04}\text{Bi}_{0.96}\text{O}_{1.5}$, $\text{Nd}_{0.08}\text{Bi}_{0.92}\text{O}_{1.5}$, $\text{Ho}_{0.04}\text{Bi}_{0.96}\text{O}_{1.5}$ and $\text{Er}_{0.04}\text{Bi}_{0.96}\text{O}_{1.5}$, the products have powder-diagrams exclusively corresponding to fluorites having $a_{\text{F}} = 5.545$, 5.515, 5.515 and 5.515 Å, respectively. Attempts to make $\text{Ho}_{0.08}\text{Bi}_{0.92}\text{O}_{1.5}$ produced a mixture of two phases. We conclude that these samples are essentially δ - Bi_2O_3 , and that the a_{F} -values extrapolate towards a value for pure Bi_2O_3 $a_{\text{F}} = 5.575$ Å. It must be remembered that Gattow and Schröder's 0.09 Å higher value was obtained at 750°C.

The two groups of cubic pure and impure bismuth(III)oxides are similar to γ - Bi_2O_3 having 26 metal atoms in an unit cell with $a \sim 10.2$ Å and δ - Bi_2O_3 having 32 metal atoms in eight unit cells, $2a_{\text{F}} \sim 11.1$ Å. The latter group might have a relation with senarmontite, the ordering of the body-diagonal vacancies having disappeared. It is not probable that δ - Bi_2O_3 is related to $\text{C-M}_2\text{O}_3$ since a_{F} is larger than for Nd_2O_3 . Thus, it is known from the discovery of europium that the (twelve-coordinated) $\text{Bi}(\text{NO}_3)_6^{-3}$ forms double salts having properties intermediate between those formed by $\text{Sm}(\text{NO}_3)_6^{-3}$ and $\text{Eu}(\text{NO}_3)_6^{-3}$, and for many other purposes, the ionic radius of Bi(III) seems to be even smaller than that of Eu(III). On the other hand, the possibility kept open in the senarmontite structure of three short and three long Bi-O distances would join other cases of strongly distorted s^2 -stereochemistry [96]. It may be remarked that a_{F}^* of fluorite Sm_2O_3 according to equ. (1) is 5.53 Å, and that Nd(III) and Er(III) contract our δ - Bi_2O_3 strongly.

6. Thorium Oxide and the Oxidation States of Praseodymium and Terbium

Zintl and Croatto's phenomenon of introduction of large quantities of $\text{LaO}_{1.5}$ in CeO_2 was found by HUND and DÜRRWÄCHTER [47] for ThO_2 to the surprising higher limit of $\text{La}_{0.52}\text{Th}_{0.48}\text{O}_{1.74}$. Under the conditions applied by BRAUER *et al.* [15, 35] (*i. e.* equilibria at 1200 to 1500°C) the miscibility is smaller for the heavier lanthanides and attains (at 1200°C) $\text{Eu}_{0.36}\text{Th}_{0.64}\text{O}_{1.82}$ and $\text{Yb}_{0.08}\text{Th}_{0.92}\text{O}_{1.96}$. We prepared [68] $\text{Eu}_{0.5}\text{Th}_{0.5}\text{O}_{1.75}$ and a variety of $\text{M}_{0.14}\text{Th}_{0.86}\text{O}_{1.93}$ (including $\text{M} = \text{Yb}$) by heating the coprecipitated hydroxides to 1000°C and we found single fluorite phases. The paradox is the same as discussed above for $\text{MZrO}_{3.5}$ that such a technique frequently produces samples which would only be thermodynamically stable at a much higher temperature. GINGERICH and BRAUER [35] report an increasing miscibility at increasing temperatures above 1200°C.

Since the spectroscopic and crystallographic behaviour of trivalent lanthanides in ThO_2 has been extensively treated, we are here going to discuss only the behaviour of praseodymium and terbium. These two elements have a far greater tendency to be oxidized to Pr(IV) and Tb(IV) in ThO_2 and CeO_2 than they have in ZrO_2 , as we saw in chapter 2. MARSH [89] demonstrated this tendency by analytical methods and found that the black $\text{Pr}_x\text{Th}_{1-x}\text{O}_2$ can be reduced by H_2 to Pr(III). A most extraordinary observation was that strong ignition in hydrogen again blackened the material and apparently produced Pr(II) quantitatively. Further on, C- Y_2O_3 was shown to allow full oxidation of Pr present to Pr(IV). On the other hand, Marsh could not confirm the claims by PRANDTL and RIEDER [102] that $\text{Pr}_x\text{Y}_{1-x}\text{O}_{1.5+0.5x}$ can be further oxidized to Pr(V). It is well-known by preparative rare-earth chemists that traces of Pr produce a dark-brown discoloration of C-oxides far easier than of A-oxides [131].

We observed a violet colour of $\text{Pr}_{0.0005}\text{Th}_{0.9995}\text{O}_2$ and a purple colour of $\text{Tb}_{0.001}\text{Th}_{0.999}\text{O}_2$. We are interested in the origin of these intense colours, and as we shall discuss in chapter 7, we are convinced that they are due to electron transfer from the adjacent oxide ligands to the Pr(IV) and Tb(IV) central atoms. It is not excluded that cubic oxides containing higher concentrations of Pr or Tb are black because of collective effects in mixed oxidation states, but the presence of monomeric chromophores at low concentration seems beyond doubt. The wavenumbers of these absorption bands increase slightly when the M-O distances decrease. Thus, $\text{Pr}_{0.0002}\text{Ce}_{0.9998}\text{O}_2$ is pink and $\text{Pr}_{0.01}\text{Ce}_{0.99}\text{O}_2$ brick-red [12,14] and Tb(IV) gives a

characteristic orange colour when present as traces in Y_2O_3 , which is the reason why Mosander already in 1843 could indicate the existence of this rare element. The Tb-O distance is presumably even shorter in the yellow perovskite ($a = 4.28 \text{ \AA}$) BaTbO_3 and yellow-brown K_2TbO_3 (disordered sodium chloride, $a = 5.11 \text{ \AA}$) reported by HOPPE [44]. It may be noted that this author has reported colourless K_2CeO_3 and pale brown K_2PrO_3 .

In the case of black oxides, we recommend the mineralogical technique of making coloured streaks on an unglazed tile. This has been quite informative in the study of mixed Ce-Th-U oxides.

The mixed Ce(III, IV), Pr(III, IV) and Tb(III, IV) oxides have a highly complicated crystal chemistry. The dark blue colours of $\text{CeO}_{1.65-1.81}$ [14] and $\text{Ce}_x\text{U}_{1-x}\text{O}_2$ [86] are certainly due to co-operative effects; but in the former case, a number of distinct phases such as Ce_7O_{12} , Ce_9O_{16} and $\text{Ce}_{11}\text{O}_{20}$ [11] (previously written as $\text{Ce}_{32}\text{O}_{55}$, $\text{Ce}_{32}\text{O}_{56}$ and $\text{Ce}_{32}\text{O}_{58}$) have been identified for higher oxygen content, whereas in the latter case, a fluorite smoothly changes a_F from 5.412 \AA for CeO_2 to 5.469 \AA for UO_2 . We are not going here to discuss the fascinating uranium oxides but only mention that UO_2 is miscible with $\text{YO}_{1.5}$ having a_F^* according to equ. (1) [32]. However, such samples are rapidly oxidized in air, diminishing a_F and turning black. The black, cubic Pr_6O_{11} (essentially fluorite with $a_F = 5.468 \text{ \AA}$, lacking 1/12 oxygen atoms and showing weak superstructure lines) [92, 39] is a well-defined, almost Daltonian, compound. An argument for the electronic ordering [definite atoms being Pr(III) and others being Pr(IV)] is Marsh' preparation of $\text{Pr}_4\text{La}_2\text{O}_{11}$ [89]. Electronic ordering has not been detected in many cases; spectroscopic studies of Sb(III) and Sb(V) in cubic crystals such as K_2SnCl_6 [27] and crystallographic investigation of K_2SbBr_6 [50] and $(\text{NH}_4)_2\text{SbBr}_6$ [83] have established the phenomenon. As one would expect, the electronic ordering is accompanied by fairly different M-X distances in the crystal.

We confirmed $a_F = 5.45 \text{ \AA}$ for our sample of Pr_6O_{11} . However, a minor component corresponds to $a_F = 5.39 \text{ \AA}$ and is probably PrO_2 (*cf.* BRAUER and PFEIFFER [19]). Several authors [126] have expressed doubts as to whether Goldschmidt's C- Pr_2O_3 exists. Actually, as discussed in the experimental section, we reduced Pr_6O_{11} at low temperature with ethanol or octanol vapour and obtained yellow-tan materials being C-oxides with $a_F = 5.57 \text{ \AA}$. The previously reported values of this parameter are 5.570 \AA [92] and 5.568 \AA by MAZZA and IANDELLI [91] who also measured reflection spectra. BRAUER and PFEIFFER [18] found complete miscibility between C- Pr_2O_3 ($a_F = 5.576 \text{ \AA}$) and C- Tb_2O_3 ($a_F = 5.365 \text{ \AA}$). However, it is highly probable that C- Pr_2O_3 is

thermodynamically unstable, relative to $\text{A-Pr}_2\text{O}_3$, even at room temperature.

HONIG, CLIFFORD and FAETH [43] pointed out that the distinct phases $\text{Pr}_n\text{O}_{2n-2}$ ($n = 4, 5, 6, 7, 9, 10, 11, 12$) have been observed.

Terbium oxides TbO_x exist in a surprising number of distinct phases [5]. The C-type Tb_2O_3 has $a_F = 5.364 \text{ \AA}$. Tb_7O_{12} is a rhombohedral phase, closely related to fluorite with $a_F = 5.319 \text{ \AA}$ and the rhombohedral unit cell having the volume $\frac{7}{4}a_F^3$ and systematically lacking one out of every seven oxygen atoms. When treated with oxygen, Tb_{1-812} is obtained, presumably a triclinic structure $\text{Tb}_{16}\text{O}_{29}$, and again, on a powder diagram, the fluorite lines are very conspicuous, but are separated in narrow doublets or triplets, much in the same way as non-cubic perovskites. It is more difficult to approach TbO_2 than PrO_2 ; TbO_{1-95} was reported [5] as a fluorite with $a_F = 5.220 \text{ \AA}$. Recently, BRAUER and PFEIFFER [19] have succeeded in making stoichiometric TbO_2 . This compound is dark red and not black as the intermediate phases. CHASE [24] studied the mixed oxide Y_6UO_{12} containing U(VI); it is isostructural with Tb_7O_{12} . In this connection, it may be mentioned that CHANG and PHILLIPS [21] reported $\text{La}_6\text{WO}_{12}$ ($2a_F = 11.18 \text{ \AA}$) and $\text{Sm}_6\text{WO}_{12}$ ($2a_F = 10.80 \text{ \AA}$) as disordered pyrochlores.

We found, as expected, that purple $\text{Tb}_{0.001}\text{Th}_{0.999}\text{O}_2$ has a value of $a_F = 5.59 \text{ \AA}$ which cannot be distinguished from that of ThO_2 made under the same conditions. As discussed in chapter 7, we believe that this material contains discrete Tb(IV)O_8 chromophores. Actually, BAKER *et al.* [6] studied the electron spin resonance, finding a value for the gyromagnetic factor $g = 2.0146$ surprisingly different from that theoretically calculated for a free Tb^{+4} ion in the groundstate $^8S_{7/2}$ of the configuration $4f^7$, *viz.* 1.9889. The opposite sign of the deviation from the Schwinger value for the free electron is ascribed to effects of covalent bonding, which are more pronounced in the strongly oxidizing Tb(IV) than in the isoelectronic Gd(III) and Eu(II) . Our black $\text{Tb}_{0.05}\text{Th}_{0.95}\text{O}_2$ and $\text{Tb}_{0.1}\text{Th}_{0.9}\text{O}_2$ have $a_F = 5.585$ and 5.57 \AA , respectively. At higher terbium concentrations, some Tb(III) seems to be formed [68].

$\text{Pr}_{0.05}\text{Th}_{0.95}\text{O}_2$ was found to have $a_F = 5.59 \text{ \AA}$ and $\text{Pr}_{0.1}\text{Th}_{0.9}\text{O}_2$ 5.57 \AA . An attempt to make $\text{Pr}_2\text{Th}_4\text{O}_{11}$ by ignition of the co-precipitated hydroxides at 1000°C produced a black material with $a_F = 5.56 \text{ \AA}$. This must contain both Pr(III) and Pr(IV) since reduction produces a grey colour and $a_F = 5.595 \text{ \AA}$. Nd(III) is known to expand ThO_2 [68].

The pronounced stability of the ThO_2 lattice would not be predicted by somebody concentrating his attention on the vacancies surrounded by eight

oxygen atoms. WILLIS [130] has shown by neutron diffraction of ThO_2 and UO_2 that the oxygen atoms vibrate more strongly than the metal atoms, and as temperature rises (towards 1100°C), the oxygen atoms tend to be displaced towards these large interstitial holes (which have always been made responsible for the ionic conductance of doped ZrO_2 at higher temperature [93]). There is little doubt that disordered UO_{2+x} actually contain excess oxygen atoms at these very interstitial sites, and that O_9 clusters hence are formed. AURIVILLIUS and LUNDQVIST [4] showed that BiF_3 has the orthorhombic YF_3 structure whereas $\text{BiO}_{0.1}\text{F}_{2.8}$ is tysonite (LaF_3) which has recently been shown by MANSMANN [87] to contain very distorted chromophores La(III)F_{11} (or perhaps rather La(III)F_9 , since two of the La-F distances are very long). Whereas BiOF and BiOCl are of the tetragonal PbFCl type [4] a cubic phase with $a_{\text{F}} = 5.84 \text{ \AA}$ was found, which is cited [87] as $\text{Bi}_4\text{O}_2\text{F}_8$ having ten rather than eight anions in each fluorite unit cell. All our disordered fluorites have anion deficit rather than anion excess; but it is worth remembering that both alternatives are possible. We have not studied the mixed oxide-fluorides of compositions such as $\text{LaO}_{0.56}\text{F}_{1.88}$ [79], $\beta\text{-YOF}$ [46] and $\text{ThO}_{1.6}\text{F}_{0.8}$ [28] which are fluorites, frequently with anion excess. Similar pure fluorides are known*, *e. g.* NaCaCdYF_8 [48] and hightemperature forms of NaYF_4 and $\text{Na}_5\text{Y}_9\text{F}_{32}$ [124]. One would expect such compounds to be more numerous, because the conditions for forming fluorites (and their superstructures and disordered phases) obviously are appropriate stoichiometry combined with sufficiently large ionic radii and oxidation states of the metallic atoms *relative* to the anions. This is also why only oxide and fluoride are normally found. Lanthanum(III) is one of the few central atoms which is nearly *too* large forming fluorites as can be seen from the persistence of $\text{A-La}_2\text{O}_3$. At this point, it is interesting that the 5f group dioxides PaO_2 , UO_2 , NpO_2 , PuO_2 , AmO_2 and CmO_2 are particularly stable, supporting Goldschmidt's ideas of "thorides".

Niobium(V) and tantalum(V) are too small to participate in disordered fluorites and favour pyrochlore formation. In the cases of LaNbO_4 , LaTaO_4 , DyNbO_4 and DyTaO_4 , monoclinic fergusonites containing isolated groups Nb(V)O_4 and Ta(V)O_4 are even formed [107 a]. Smaller quadrivalent metals such as Tc(IV) [92 b], Ru(IV) and Ir(IV) [92 a] form pyrochlores $\text{A}_2\text{B}_2\text{O}_7$ with the lanthanides. On the other hand, protactinium(V) is the only quinquevalent metal to form disordered fluorites. KELLER [77 a] described $\text{M}_{0.5}\text{Pa}_{0.5}\text{O}_2$ of fifteen rare earths, having a_{F} ranging from 5.525 \AA for $\text{M} = \text{La}$

* Thus, ZINTL and UDGÅRD [134] reported miscibilities extending approximately to YCa_2F_7 , LaSr_2F_7 and $\text{ThCa}_3\text{F}_{10}$.

to 5.322 Å for M = Lu (and 5.257 Å for M = Sc). The value of α_F^* of eq. (1) thus obtained is 5.325 Å for Pa(V) somewhat smaller than the observed value 5.505 Å for PaO₂. KELLER [77a] also found a considerable miscibility with M₂O₃, arriving *e. g.* at $\alpha_F = 5.53$ Å for Nd_{0.75}Pa_{0.25}O_{1.87}.

7. Optical Electronegativity of Praseodymium(IV) and Terbium(IV)

Most intense absorption bands of d group complexes can be ascribed to electron transfer from filled molecular orbitals (M. O.) mainly localized on the ligands to the empty or partly filled d shell [57, 60, 63, 72]. „Inverted” electron transfer from the partly or completely filled d shell to low-lying, empty M. O. on the ligands is only common when the ligands are conjugated, carbon-containing molecules [129, 59, 67]. Electron transfer spectra caused by the transfer of electrons from filled M. O. to the 4f shell were difficult to observe, but were identified in solutions of bromide and dialkyl-dithiocarbamate complexes in ethanol [58] and in aqueous sulphate and ethanolic chloride solutions [7]. It is possible to define [60] *optical electronegativities* x_{opt} for the central atom M and the ligand X, where the values for X:

$$\text{F}^- 3.9 \quad \text{H}_2\text{O} 3.5 \quad \text{SO}_4^{--} 3.2 \quad \text{Cl}^- 3.0 \quad \text{Br}^- 2.8 \quad \text{I}^- 2.5 \quad (2)$$

agree with the values normally accepted on Pauling's scale, and where the central atom values for x_{opt} are corrected for spin-pairing energy in the partly filled shell. However, for our purposes, it is more convenient to consider the uncorrected electronegativities x_{uncorr} for the central atom, which are defined from the wavenumber σ of the first electron transfer band:

$$\sigma = [x_{\text{opt}}(\text{X}) - x_{\text{uncorr}}(\text{M})] \cdot 30000 \text{ cm}^{-1} \quad (3)$$

Table 3 gives the values obtained for trivalent lanthanides.

The octahedral hexachloride and hexabromide complexes MX₆⁻³, which are only stable in solvents such as acetonitrile [111] give values for x_{uncorr} some 0.1 to 0.2 units higher. This may be ascribed to the smaller M-X distances for $N = 6$, which seem to be further decreased in such solvents [61] besides the grouptheoretical fact that the highest filled M. O. in octahedral hexahalides have four angular node-planes (like g-orbitals) and are destabilized by ligand-ligand anti-bonding effects. Similar effects were found in the 5f by RYAN and one of the writers [110] studying U(IV), Np(IV) and Pu(IV) hexahalides. In aqueous solution, x_{uncorr} is somewhat smaller; and in

TABLE 3.

Uncorrected optical electronegativities $x_{\text{uncorr}}(\text{M})$ for trivalent lanthanides.

| Electron configuration | Sm(III) 4f ⁵ | Eu(III) 4f ⁶ | Tm(III) 4f ¹² | Yb(III) 4f ¹³ | Ref. |
|--|----------------------------|----------------------------|-----------------------------|-----------------------------|------|
| MCl ⁺⁺ in ethanol | 1.48 | 1.79 | — | 1.63 | 7 |
| MCl ₆ ⁻³ | 1.56 | 1.89 | — | 1.78 | 111 |
| MBr ⁺⁺ in ethanol | 1.46 | 1.76 | 1.32 | 1.62 | 58 |
| MBr ₆ ⁻³ | 1.63 | 1.98 | 1.51 | 1.83 | 111 |
| MSO ₄ ⁺ in water | 1.60 | 1.81 | — | 1.72 | 7 |
| M(H ₂ O) ₉ ⁺³ | — | 1.73 | — | ~1.53 | 65 |

uranyl complexes the situation is rather extreme [71]. In such anisotropic complexes, the ligands in the equatorial plane of UO₂X₄ or UO₂X₆ have so large distances U-X that the apparent x_{uncorr} of U(VI) seems to be 1.8. The analogous anisotropic neptunyl complexes indicate 2.1 for Np(VI). These values can be compared with $x_{\text{uncorr}} = 2.6$ for Np(VI) in NpF₆ [121] and 2.85 for Pu(VI) in PuF₆ [120]. It is possible to extrapolate $x_{\text{uncorr}} = 2.3$ for U(VI) in UF₆, though this means that this compound should have no electron transfer band before 48000 cm⁻¹ [71, 75 a].

It is now known from the spectra of CeCl₆⁻² and CeBr₆⁻² [111] that $x_{\text{uncorr}} = 2.1-2.15$ for Ce(IV). Previously, we measured the spectrum of the tetrakis-acetylacetonate Ce aca₄. This redbrown complex is chemically very unstable [51] but its crystal structure has recently been determined [90]. We find a shoulder at 21000 cm⁻¹ ($\epsilon \sim 700$) in the absorption spectrum. Since the ligand aca⁻ is known [59] to have $x_{\text{opt}} = 2.7$, this suggests $x_{\text{uncorr}} = 2.0$ for Ce(IV) in the chromophore Ce(IV)O₈.

Oxide is nearly the only ligand for which it has not been possible to establish a well-defined x_{opt} [60]. In the d group complexes, the main reason is the very strong π -anti-bonding effect on the partly filled d shell. This effect should be of minor importance in the 4f and 5f groups; but it is difficult to establish the value in a highly anisotropic complex such as UO₂⁺⁺. If $x_{\text{uncorr}} = 2.3$ for U(VI), $x_{\text{opt}} = 3.1$ for O⁻². A more direct determination comes from Eu(III) in Y₂O₃ having an electron transfer band [12 a, 22, 70] near 41000 cm⁻¹. Since most other Eu(III) compounds show $x_{\text{uncorr}} = 1.8$, this would mean $x_{\text{opt}} = 3.15$ for O⁻². This value can be expected to vary with the circumstances; thus, the maximum in the excitation spectrum [108] of fluorescence of Eu(III) has lower wavenumbers in Gd₂O₃ (38600 cm⁻¹) and La₂O₃ (33600 cm⁻¹) suggesting $x_{\text{opt}} = 3.1$ and 3.0, respectively. Cf. also the recent studies by BLASSE and BRIL [12 b].

The variation of x_{uncorr} as a function of the number q of electrons in the partly filled shell $4f^q$ is explained by a theory [58] taking into account the variation $-q(E-A)$ of the relative one-electron energies, as well as the spin-pairing energy contributing to the electron transfer $4f^q \rightarrow (\text{M. O.})^{-1}4f^{q+1}$:

$$\left. \begin{aligned} 0 < q \leq 6: & -8q D/13 \\ 13 > q \geq 7: & (8D) - 8q D/13 \end{aligned} \right\} \quad (4)$$

where the spin-pairing energy parameter D corresponds to $(9E^1/8)$ in terms of RACAH's parameters of interelectronic repulsion [104]. To this approximation, equ. (4) represents two parallel line segments jumping $8D$ at the half-filled shell $4f^7$. If other effects of interelectronic repulsion and first-order relativistic effects (spin-orbit coupling) are included [58, 110] the result is a decrease of the wavenumbers of the first electron transfer band from f^0 to f^2 , a roughly invariant wavenumber f^2 to f^4 , a decrease from f^4 to f^6 , a steep increase from f^6 to f^7 , and the zigzag curve is essentially repeated in the second half, f^{7+k} being comparable to f^k . The relative order of x_{uncorr} found for trivalent lanthanides agrees with this theory $f^6 > f^{13} > f^5 > f^{12} > \dots$. BARNES and PINCOTT [9] have recently pointed out that the difference between Eu(III) and Yb(III) complexes varies to some extent in solids. This difference is according to our theory [58, 110]:

$$\sigma_{\text{Yb(III)}} - \sigma_{\text{Eu(III)}} = -7(E-A) + \frac{4}{3} \frac{8}{3} D + \frac{3}{2} \zeta_{4f} (\text{Yb}) - 2\zeta_{4f} (\text{Eu}). \quad (5)$$

The observed value is roughly 5800 cm^{-1} for the aqua ions [65] and 4000 cm^{-1} for most complexes in solution. In the cyclopentadienides [97] $\text{M}(\text{C}_5\text{H}_5)_3$ it is only -500 cm^{-1} . Since D is a parameter of interelectronic repulsion, and since we know from the nephelauxetic effect to be discussed in chapter 8 that such parameters vary less than 6 percent in complexes, we can maintain a nearly constant value of $D = 6500 \text{ cm}^{-1}$ and ascribe the observed variation of equ. (5) to the (theoretically not very accessible) quantity $(E-A)$ increasing from 2800 cm^{-1} for the aqua ions to 3700 cm^{-1} for the cyclopentadienides. For comparison, it may be mentioned that $(E-A) = 6000 \text{ cm}^{-1}$ for 4d and 5d group hexahalide complexes [60, 72].

The wavenumber difference between the $4f^7$ -system Tb(IV) and the $4f$ -system Pr(IV) should be

$$\sigma_{\text{Tb(IV)}} - \sigma_{\text{Pr(IV)}} = -6(E-A) + \frac{5}{1} \frac{6}{3} D + 9E^3 - \frac{3}{2} \zeta_{4f} (\text{Tb}) + \zeta_{4f} (\text{Pr}). \quad (6)$$

Figure 1 shows the reflection spectra of very dilute solid solutions of Pr(IV) (having a pronounced shoulder at 18500 cm^{-1} and a maximum at 24300 cm^{-1})

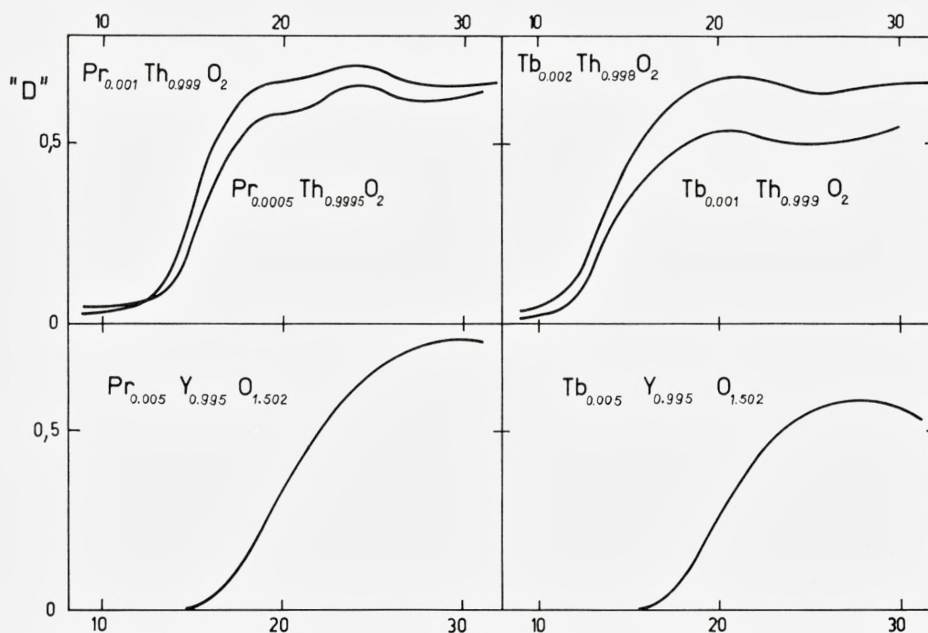


Figure 1. Reflection spectra of thorium and yttrium oxides containing minute amounts of praseodymium (IV) and terbium (IV). The optical density " D " = $\log_{10}(I_0/I)$ refers to the white reference material producing the light intensity I_0 and the compound I , and is given as a function of the wavenumber in the unit 1000 cm^{-1} .

and Tb(IV) in ThO_2 (band at 20300 cm^{-1}). The wavenumber difference of equ. (6) is 1800 cm^{-1} . It is not certain what are exactly the size of the parameters of spherical symmetry in quadrivalent as in trivalent lanthanides. At one side, it is nearly certain that gaseous M^{+4} would have D and Racah's E^3 some 20% larger than M^{+3} , but on the other hand, the nephelauxetic effect [110] is expected to be more pronounced in $M(\text{IV})$ than in $M(\text{III})$. Reasonable values seem to be $D = 7500 \text{ cm}^{-1}$ and $E^3 = 670 \text{ cm}^{-1}$. Hence, $(E-A) = 5700 \text{ cm}^{-1}$.

If $x_{\text{opt}} = 3.2$ for oxide in ThO_2 , x_{uncorr} turns out to be 2.6 for $\text{Pr}(\text{IV})$ and 2.55 for $\text{Tb}(\text{IV})$. Hence, one would expect $\text{Ce}(\text{IV})$ to have the first electron transfer band at 35000 cm^{-1} ($x_{\text{uncorr}} = 2.05$) quite in agreement with the very pale, lemon-yellow colour of pure CeO_2 . Our results are also compatible with the only other evidence available for quadrivalent lanthanides. Professors L. B. ASPREY and R. HOPPE were so kind as to inform one of the writers that Cs_3NdF_7 and Cs_3DyF_7 are orange compounds [2] both having

electron transfer bands at 26000 cm^{-1} , *i. e.* $x_{\text{uncorr}} = 3.05$. Our theory gives

$$\sigma_{\text{Dy(IV)}} - \sigma_{\text{Nd(IV)}} = -6(E-A) + \frac{5}{3}D + 3E^3 - \zeta_{4f}(\text{Dy}) + \frac{1}{2}\zeta_{4f}(\text{Nd}) \quad (7)$$

which is -1500 cm^{-1} with our parameters, in satisfactory agreement with experience. A corollary of this result is that if Nd(IV) or Dy(IV) could be prepared in ThO_2 , the first electron transfer band would occur already about 5000 cm^{-1} . This suggests that these two species cannot be prepared; though there is no absolute rule for how small a wavenumber the first electron transfer band can have in a stable species, there is not at present known any case below 9350 cm^{-1} in OsI_6^{--} [64].

The absorption bands of the oxides on Figure 1 are relatively broad. Pr(IV) shows two transitions having the distance 5800 cm^{-1} which is quite intelligible because the excited configuration (M. O.) $^{-1}4f^2$ have many adjacent energy levels. The situation is different in $4f^6$ systems such as Eu(III) or $4f^{13}$ systems such as Yb(III), where the two or three absorption bands observed [58, 97] must correspond to M. O. of differing energy.

We have disproved the hypothesis that the strong colours in ThO_2 necessarily indicate mixed oxidation states Pr(III, IV) and Tb(III, IV). The coherent description by the theory makes it highly probable that the colours are caused by monomeric Pr(IV) O_8 and Tb(IV) O_8 chromophores, and anyhow, one would have predicted the band positions observed. This does not exclude, of course, that genuine mixed-oxidation state colours are observed in CeO_x and $\text{Ce}_x\text{U}_{1-x}\text{O}_2$. It is not quite clear whether the dark blue colour in the second case is induced by the presence of Ce(III, IV) [simultaneously with U(IV, V)] or due to actual electron transfer from U(IV) to Ce(IV) comparable to the electron transfer from Ag(I) and Tl(I) to species such as OsCl_6^{--} and IrCl_6^{--} [63]. The prussian blue type compounds such as $\text{K}[\text{Fe}^{\text{II}}(\text{CN})_6\text{Fe}^{\text{III}}]$ are electronically ordered according to ROBIN [107] (*cf.* also SHRIVER [117] and BRATERMAN [13a]). ANDERSON [1] discussed the interesting question whether the many distinct phases in the systems CeO_x , PrO_x and TbO_x when brought to equilibrium at an appropriately low temperature, in contrast to the disordered fluorite structure of many mixed oxides containing tri- and quadrivalent metals, is not due to the fact that in the former cases, the complicated ordering is accompanied by electronic ordering of the same element, whereas in the second case, the metal atoms need to interchange their positions by diffusion; and it is known that this diffusion (as contrasted to that of oxide ions in deficient structures) needs a very high activation energy. Cf. also the review by BRAUER [19a].

We discussed above the somewhat varying colours of Pr(IV) and Tb(IV) in different oxides. The pink to chamois colour of Pr(IV) in CeO_2 corresponds, according to preliminary measurements, to an almost linear increase of the optical density (as a function of wavelength) between 15000 and 18000 cm^{-1} with a very broad shoulder at 20500 cm^{-1} , and a strong cut-off of the CeO_2 matrix above 28000 cm^{-1} . Figure 1 gives the reflection spectra of the orange $\text{Pr}_{0.005}\text{Y}_{0.995}\text{O}_{1.502}$ having a weakly pronounced shoulder at 21300 cm^{-1} and a broad maximum at 29800 cm^{-1} , and of the orange $\text{Tb}_{0.005}\text{Y}_{0.995}\text{O}_{1.502}$ having a broad band at 27400 cm^{-1} . Hence, Y_2O_3 seems to be less reducing than ThO_2 . If the values of $x_{\text{uncorr}} = 2.6$ for Pr(IV) and 2.55 for Tb(IV) are maintained, the first band of each sample indicate $x_{\text{opt}} = 3.3$ and 3.45, respectively, for the oxide ligands. It might seem more consistent to retain $x_{\text{opt}} = 3.2$ for oxide found from the absorption spectrum of Eu(III) in Y_2O_3 and if the main maxima are then considered, x_{uncorr} would be 2.2 for Pr(IV) and 2.3 for Tb(IV). However, this choice does not seem to be realistic. The low value for Pr(IV) would not interpolate satisfactorily between the values for Ce(IV) and Nd(IV) discussed above. Actually, one of the difficulties with these very broad absorption bands (which is accentuated in reflection spectra, relative to transmission spectra of liquid solutions) is that the position of the first electronic transition is not easily detected. The low symmetry of the two sites in Y_2O_3 may contribute to a superposition of closely adjacent bands.

It would be interesting to compare the spectra of dilute solutions of Pu(IV), Am(IV), Cm(IV), Bk(IV) and Cf(IV) in ThO_2 , though, in the case of the highly radioactive isotopes, one would have to be careful with colour centres induced by radiation damage. Our results once more stress the profound difference between the 4f and the 5f groups [26, 40, 71, 77]. The values 2.6 and 2.55 found for x_{uncorr} of Pr(IV) and Tb(IV) can be compared to the values 0.9 and 0.4 extrapolated [58] for the isoelectronic species Ce(III) and Gd(III) or to 1.1 and 0.8 for the lower oxidation states Pr(III) and Tb(III) of the same elements. In other words, x_{uncorr} increases more [71] than 1.5 unit when going from M(III) to M(IV) in the 4f group. On the other hand, the values (found for hexahalide complexes) Np(VI) 2.6; Pu(VI) 2.85; Np(IV) 1.9; and Pu(IV) 2.1 indicate half the effect when going from M(IV) to M(VI) in the 5f group, changing the oxidation numbers by two units. In the 4d and 5d groups, the variation of the optical electro-negativities as a function of the oxidation state is roughly the same as in the 5f group. This variation, and related problems are discussed in a recent review [75 a].

8. Internal f Transitions; the Nephelauxetic Effect and Intensities

Whereas the transitions $4f \rightarrow 5d$ correspond to rather broad and electron transfer (filled M. O.) $\rightarrow 4f$ to even broader absorption bands, the internal transitions in the configuration $4f^q$ correspond to groups of very narrow bands or absorption lines. Each such group normally represents one excited J -level of the corresponding gaseous ion M^{+3} in spherical symmetry, and the finestructure of the groups has been studied very extensively [54, 77, 132]. Originally, ligand field theory was applied in the form of BETHE's electrostatic model [41] but an alternative is the angular overlap model considering weak σ - and π -anti-bonding effects on the partly filled d or f shell [66, 74, 116].

However, there is another experimental fact about the $4f$ group compounds $M(\text{III})$ which has attracted relatively less attention. The *nephelauxetic effect* (the "cloud-expanding" effect according to a Greek word kindly suggested by Professor K. BARR) that the parameters of interelectronic repulsion are smaller in complexes than in the corresponding gaseous ions is quite conspicuous in the $3d$, $4d$ and $5d$ groups [114, 62, 76]. In the $4f$ group, the nephelauxetic effect has been recognized early as a shift of the narrow absorption bands towards smaller wavenumbers in the relatively more covalent compounds, the least covalent being the fluorides and the aqua ions. WÄEGNER [125] noted that the line groups of blue Nd_2O_3 have slightly lower wavenumbers than other pink $\text{Nd}(\text{III})$ compounds, and JOYE [52] made similar observations on Nd_2S_3 and anhydrous NdCl_3 . HOFMANN and KIRMREUTHER [42] found a red-shift in Er_2O_3 compared to other $\text{Er}(\text{III})$ compounds and invoked Stark's valency hypothesis assuming loosened ("ge-lockertes") valency electrons (this remark was made three years before N. BOHR's explanation of the hydrogen spectrum). EPHRAIM and BLOCH [29] made more systematic studies of the red-shift in $\text{Pr}(\text{III})$ and $\text{Nd}(\text{III})$ compounds and established the variation $\text{F}^- > \text{H}_2\text{O} > \text{Cl}^- > \text{Br}^- > \text{I}^-$. These authors suggested that the electronic orbits are contracted in highly electrovalent salts and expanded in covalent compounds. They suggested electron jumps between orbits of different radii, whereas we consider energy differences due to differing interelectronic repulsion, the groundstate having the lowest average value of the reciprocal interelectronic distance $\langle 1/r_{12} \rangle$; the excited levels of $4f^q$ have essentially the same average radius $\langle r \rangle$ of the partly filled shell as the groundstate. We can only retain the second half of EPHRAIM and BLOCH's explanation, *viz.* the expansion, though it was first in 1965 SUGAR [122] reported the energy levels belonging to $4f^2$ of gaseous Pr^{+3} showing that even the $\text{Pr}(\text{III})$ aqua ion has a red-shift amounting to

some 4 percent. That the expansion is relatively the most pronounced in compounds of the most reducing anions is quite expected; but EPHRAIM [30] found that Pr_2O_3 is unexpectedly covalent on this basis, even more than anhydrous PrI_3 . Similar effects have been found in d group compounds such as Cr_2O_3 [115] and in 4f group oxides studied by BOULANGER [13] and us [68, 70]. This is particularly striking when compared to the less pronounced nephelauxetic effect of oxygen-containing ligands in aqueous solution [13, 56]. On the other hand, solid sulphides, which are expected to be even more covalent, only show a nephelauxetic effect slightly stronger than the oxides [73]. EPHRAIM, JANTSCH and ZAPATA [31] noted that most Er(III) compounds show far weaker red-shifts than the analogous Pr(III), Nd(III) and Sm(III) compounds, and in a few cases, small blue-shifts are actually observed [56]. This anomaly can be explained by the term $d\sigma$ in equ. (8). Today, there is no doubt that the nephelauxetic effect occurs for all the lanthanides, though it is more pronounced in the beginning of the 4f group than for the later members such as Ho(III), Er(III) and Tm(III).

We proposed a linear relation [68, 70]:

$$\sigma_{\text{compound}} - \sigma_{\text{aqua}} = d\sigma - (d\beta)\sigma_{\text{aqua}} \quad (8)$$

where the difference between the wavenumbers of the baricenters (ideally of the sub-levels weighted with their degeneracy number; in actual practice frequently, the centers of intensity distribution) of the J -levels of the compound considered and of the aqua ions (which have now been studied in $\text{M}(\text{H}_2\text{O})_9(\text{C}_2\text{H}_5\text{SO}_4)_3$ at liquid helium temperature) is equalled the relative stabilization $d\sigma$ of the ground J -level of the compound (again compared with the lowest sub-level of the aqua ion) minus the relative nephelauxetic effect $(d\beta)\sigma_{\text{aqua}}$. There are several reasons why the linear relation (8) is not absolutely valid*. A closer analysis [119] of the wavenumber differences

* Recently, CHANG [23a] determined the actual positions of the baricenters of eighteen J -levels of Nd(III) in Y_2O_3 . When compared with the baricenters of $\text{Nd}(\text{H}_2\text{O})_9^{+3}$ [36a], $d\beta = 2.4\%$ is obtained. By the same token, KISLIUK, KRUPKE and GRUBER [78] determined sixteen J -baricenters for Er(III) in Y_2O_3 . When compared to $\text{Er}(\text{H}_2\text{O})_9^{+3}$, $d\beta$ turns out to be 0.9% . These two values are somewhat smaller than the parameters of equ. 8 ($d\beta = 3.2\%$ and $d\sigma = 150 \text{ cm}^{-1}$ for C-type $\text{Nd}_{0.2}\text{Yb}_{0.8}\text{O}_{1.5}$; $d\beta = 1.6\%$ and $d\sigma = 200 \text{ cm}^{-1}$ for Er_2O_3 [70]). This discrepancy is mainly caused by the negligible variation of the Landé parameter ζ_{4f} (the decrease relative to the aqua ions is 0.3% for Nd(III) in Y_2O_3) whereas the parameters of interelectronic repulsion E^1 and E^3 decrease 4.4 and 3.1% , respectively. The absolute values of $d\sigma$ would be calculated from the baricenters $(276-210) = 66 \text{ cm}^{-1}$ for Nd(III) and $(203-147) = 56 \text{ cm}^{-1}$ for Er(III). The differences between these quantities and the values for $d\sigma$ previously determined have the same order of magnitude as $\frac{7}{2}\zeta_{4f}(\text{Nd}) d\beta = 100 \text{ cm}^{-1}$ and $3\zeta_{4f}(\text{Er}) d\beta = 150 \text{ cm}^{-1}$ which would represent the first-order effect of the Landé parameter not being influenced by the nephelauxetic effect.

It is excluded that the variable extent of the shift of the excited levels is caused by dispersion

between gaseous Pr^{+3} and Pr(III) in LaCl_3 shows that the parameters of interelectronic repulsion, and in particular Racah's E^3 , are decreased more than twice as much than the Landé parameter ζ_{4f} . If the nephelauxetic effect was due to delocalization of weakly anti-bonding M. O. [66] one would expect E^k to decrease twice as much as ζ_{4f} . Empirically, one finds that certain levels, such as 5D_0 and 5D_1 of Eu(III) , or ${}^2H_{11/2}$ of Nd(III) and Er(III) , move much less than predicted by equ. (8) for the value of $d\beta$ satisfactorily describing the red-shift of most of the other band groups.

BARNES [8] performed a statistical analysis of the validity of equ. (8) and concluded that it was not possible to ascribe physical significance to the parameter $d\sigma$ obtained, and that only in the case of a few oxides (Nd_2O_3 $d\beta = 3.4 \pm 1.3\%$, Er_2O_3 $d\beta = 1.4 \pm 0.6\%$) it is possible to assign positive values of $d\beta$ at the confidence level 0.95. We do not agree that this statistical analysis indicates all the relevant aspects. If one draws best straight lines according to equ. (8) at two different occasions through the same set of experimental data, one normally has a scattering of 50 cm^{-1} in $d\sigma$ and 0.2% in $d\beta$. It may be that the confidence level 0.95 does not represent this feature well, and in particular, the scattering of the "misbehaving" points may not at all correspond to a Gaussian error-curve. In the extreme case of half of the points being on a straight line and half being widely scattered, one would recognize the straight line very readily with a transparent rule. However, it is of course worthwhile to devote some statistical analysis to such problems.

Dr. Romano Pappalardo took spectra at liquid nitrogen temperature (or more exactly, at 100°K) of our $\text{M}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ under conditions similar to those previously used [68]. Surprisingly enough, these highly compressed lattices generally show a less pronounced nephelauxetic effect than the oxides M_2O_3 . In order to obtain a more reliable comparison, we plotted $\sigma_{\text{mixed oxide}} - \sigma_{\text{oxide}}$ according to equ. (8) and obtained the values of $d\sigma$ and $d\beta$ (relative to aqua ions) given in Table 4. A list of baricenters of Nd(III) , Ho(III) , Er(III) and Tm(III) compounds are given in Table 5.

It had previously been noted [70] that pyrochlores $\text{MTiO}_{3.5}$ had a less pronounced nephelauxetic effect than our disordered fluorites $\text{MZrO}_{3.5}$. If it is argued that the extraordinary large nephelauxetic effect of oxides is mainly connected with short M-O distances [66], this phenomenon can be rationalized. One would expect four types of M sites in our mixed oxides:

effects dependent on the transition dipole moments. However, the experimental fact that the nephelauxetic effect is more pronounced for transitions in the visible than in the infra-red might be connected with second-order perturbations from continuum levels at high wavenumbers, though a more predominant factor seems to be the importance of the rather invariant Landé parameter for transitions in the infra-red.

cubic $M(III)O_8$; $M(III)O_7$ adjacent to one vacancy; $M(III)O_6$ lacking a face-diagonal like in the C-oxides; and $M(III)O_6$ lacking a body-diagonal. Of these sites, the first and the last have centres of inversion. The importance of this situation was not realized until quite recently, when octahedral MX_6^{-3} were prepared [111] and when KISLIUK, KRUPKE and GRUBER [78] after a careful study of Er(III) in Y_2O_3 were not able to detect any absorption lines originating in that quarter of the erbium atoms being on sites possessing a centre of symmetry. (However, the corresponding weak vibronic structures have recently been reported [36c]). Though the grain size of the sample and the experimental apparatus used in ref. [70] do not allow an absolute comparison of band intensities, one has the definite impression that the pyrochlores containing $M(III)O_8$ with centre of inversion have far weaker intensities than the disordered fluorites presumably containing a fair proportion of $M(III)O_7$. The reflection spectrum of the low-temperature form of $LaYbO_3$ [70] is very similar to that of $C-Yb_2O_3$ suggesting that the local symmetry of the sites is the same $M(III)O_6$ lacking a face-diagonal. The detailed structure of each J -group is also strikingly similar in $LaErO_3$ and a fairly compressed C-oxide such as $ErInO_3$.

A marked difference between cubic $M(III)O_8$ and the C-oxide site is the behaviour of the level 7F_1 observed in fluorescence ${}^5D_0 \rightarrow {}^7F_1$ of Eu(III). In ThO_2 [68], this level is not split, in accordance with the group-theoretical prediction for O_h , whereas in Y_2O_3 [23, 128] three sub-levels are observed 199, 359 and 543 cm^{-1} above the groundstate 7F_0 . Our $Eu_{0.2}Zr_{0.8}O_{1.9}$ fluoresced with red line emission. The strongest line (measured both at 4°K and 78°K by Dr. Romano Pappalardo) occurs at 16930 cm^{-1} surrounded by weaker shoulders at 16875 and 17000 cm^{-1} . Since the ${}^5D_0 \rightarrow {}^7F_0$ transition is observed as a very weak line at 17260 cm^{-1} , this corresponds to three different 7F_1 sub-levels at 260, 330 and 385 cm^{-1} . Since the 7F_1 level occurs at 320 cm^{-1} in $Eu_{0.14}Th_{0.86}O_{1.93}$ [68], the 330 cm^{-1} sub-level may very well correspond to an essentially cubic $Eu(III)O_8$ site in $Eu_{0.2}Zr_{0.8}O_{1.9}$ whereas the 260 and 385 cm^{-1} sub-levels, showing a smaller spreading than $Eu(III)$ in Y_2O_3 , corresponds to $Eu(III)O_7$ involving only one vacancy. It is not understood why 7F_0 and 7F_1 have a so relatively small energy difference in cubic crystals, whereas it is 380 cm^{-1} for $Eu(H_2O)_9^{+3}$ and $Eu(III)$ in $LaCl_3$. Our sample of $Eu_{0.2}Zr_{0.8}O_{1.9}$ shows weaker fluorescence lines at 16530 and 16370 cm^{-1} , corresponding to 7F_2 sub-levels at 730 and 890 cm^{-1} . This may be compared to the sub-level of symmetry type F_5 identified [68] at 890 cm^{-1} in ThO_2 . LINARES [85a] recently identified several sites for fluorescent $Eu(III)$ in partly charge-compensated CeO_2 and ThO_2 .

The reflection spectrum of $\text{Yb}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ shows bands at 10300, 10360 and 10480 cm^{-1} , a shoulder about 10700 cm^{-1} and a broad asymmetric maximum at 10990 cm^{-1} . Hence, the local symmetry deviates more from cubic than $\text{Yb}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$ [70] having a relatively narrow band at 10280 cm^{-1} and a very broad band at 10940 cm^{-1} . With regard to band positions (though not to intensities), $\text{Yb}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ shows certain analogies with the pyrochlore $\text{Yb}_{0.5}\text{Ti}_{0.5}\text{O}_{1.75}$ [Figure 5 of ref. 70] containing chromophores Yb(III)O_8 compressed along a body-diagonal but retaining a centre of inversion. According to the principle of holohedrized symmetry in the angular overlap model [116] one would expect the sub-level energy differences to have a certain similarity with those of Yb(III)O_7 .

As discussed in chapter 1, the internuclear distances are re-distributed in pyrochlores such as $\text{ErTiO}_{3.5}$ [80] in such a way that the six Ti-O distances are much shorter than six of the eight Er-O distances, the two remaining Er-O distances being adapted to the cubic lattice parameter. In disordered fluorites such as $\text{M}_{0.2}\text{Zr}_{0.8}\text{O}_{1.9}$ or $\text{M}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$, one might have expected that the decreasing values of a_{F} by introducing the small Zr(IV) would decrease the distance M-O and increase the nephelauxetic parameter $d\beta$. However, it is quite conceivable that the M(III)O_7 chromophores mainly responsible for the band intensities observed have longer M-O distances on the average than the Zr-O distances. ErCl_6^{-3} has $d\beta = 1.2\%$ [111] which is larger than 0.9% found for Er(III) in the six-coordinated YCl_3 [105] and 0.3% characterizing Er(III) in nine-coordinated LaCl_3 with much larger Er-Cl distances. Hence, one would expect that one of the rare cases where M(III)O_6 would show a more pronounced nephelauxetic effect than in C-oxides might be the octahedral site of perovskites (*cf.* Tables 4 and 5). This has not been satisfactorily detected until now; one reason may again be the comparatively low band intensities.

The concept of hypersensitive pseudoquadrupolar transitions [69] has been much discussed recently. It is beyond any doubt that those transitions (characterized by the selection rules $J \rightarrow J - 2$ and in Russell-Saunders coupling $L \rightarrow L - 2$ and $S \rightarrow S$) which would be relatively strong as electric quadrupole transitions are very sensitive to the nature of the adjacent ligands and frequently get very high intensities. In JUDD's parametrization [53] this corresponds to large matrix elements of the operator $U^{(2)}$, and the phenomenon was further studied by CARNALL, FIELDS and WYBOURNE [20] and KRUPKE and GRUBER [81]. Recently, JUDD [55] and NIEUWPOORT and BLASSE [95] discussed the influence of linear ligand-field contributions which are group-theoretically acceptable in low symmetries such as C_s, C_n and C_{nv}

TABLE 4.

Nephelauxetic parameters from eq.(8) for mixed oxides and for various halide complexes.

| | $d\sigma$ (cm ⁻¹) | $d\beta$ (°/a) | Ref. |
|---|-------------------------------|----------------|------|
| Nd(III)LaCl ₃ | -60 | 0.6 | 70 |
| NdCl ₆ ⁻³ | +50 | 2.2 | 111 |
| Nd ₂ O ₃ (type A) | +200 | 3.6 | 70 |
| Nd _{0.1} La _{0.9} O _{1.5} (A) | +200 | 3.4 | 70 |
| NdYO ₃ | +250 | 3.5 | 70 |
| Nd _{0.2} Yb _{0.8} O _{1.5} (C) | +150 | 3.2 | 70 |
| Nd _{0.1} Ce _{0.9} O _{1.95} (F) | +300 | 3.7 | 70 |
| Nd _{0.14} Th _{0.86} O _{1.95} (F) | +150 | 3.3 | 68 |
| Nd _{0.5} Zr _{0.5} O _{1.75} (F) | +250 | 2.7 | 70 |
| Nd _{0.2} Zr _{0.8} O _{1.75} (F) | +100 | 1.6 | — |
| BaNd ₂ S ₄ | +250 | 4.2 | 73 |
| Sm ₂ O ₃ (type B) | +200 | 2.3 | 70 |
| Sm _{0.5} Zr _{0.5} O _{1.75} (F) | +350 | 2.0 | 70 |
| Sm _{0.2} Zr _{0.8} O _{1.9} (F) | +200 | 1.5 | — |
| Dy ₂ O ₃ (C) | +500 | 1.8 | 70 |
| Dy _{0.5} Zr _{0.5} O _{1.75} (F) | +500 | 2.0 | 70 |
| Dy _{0.2} Zr _{0.8} O _{1.9} (F) | +500 | 1.9 | 70 |
| HoCl ₆ ⁻³ | +150 | 1.1 | 111 |
| Ho ₂ O ₃ (C) | +450 | 2.5 | 70 |
| Ho _{0.5} Zr _{0.5} O _{1.75} (F) | +500 | 2.3 | 70 |
| Ho _{0.2} Zr _{0.8} O _{1.9} (F) | +450 | 2.0 | — |
| Er(III)LaCl ₃ | -30 | 0.3 | 70 |
| Er(III)YCl ₃ | 0 | 0.9 | 105 |
| ErCl ₆ ⁻³ | +100 | 1.2 | 111 |
| Er ₂ O ₃ (C) | +200 | 1.6 | 70 |
| Er _{0.5} Ti _{0.5} O _{1.75} (P) | +250 | 1.3 | 70 |
| Er _{0.8} Zr _{0.2} O _{1.6} (C) | +200 | 1.6 | 70 |
| Er _{0.5} Zr _{0.5} O _{1.75} (F) | +300 | 1.7 | 70 |
| Er _{0.2} Zr _{0.8} O _{1.9} (F) | +250 | 1.1 | — |
| LaErO ₃ | +250 | 1.9 | 70 |
| La _{0.45} Er _{0.55} O _{1.5} (perovskite) | +200 | 1.7 | — |
| La _{0.2} Er _{0.3} Zr _{0.5} O _{1.75} (F) | +250 | 1.6 | — |
| TmCl ₆ ⁻³ | +100 | 1.3 | 111 |
| Tm ₂ O ₃ (C) | +300 | 1.5 | — |
| Tm _{0.2} Zr _{0.8} O _{1.9} (F) | +350 | 1.1 | — |
| LaTmO ₃ (perovskite) | +350 | 1.7 | — |

but previously were rejected with (invalid) arguments about energy minima for the position of the central atom. However, we feel that a somewhat more chemical explanation may be more appropriate. Our reasons are that

TABLE 5.

Baricenters of excited J -levels evaluated from the reflection spectra of mixed oxides measured at 100°K. The absolute baricenters are known from aqua ions in salts such as $M(H_2O)_9(C_2H_5SO_4)_3$.

| | Nd(H ₂ O) ₉ ⁺³ | Nd ₂ O ₃ (A) | Nd(III)Y ₂ O ₃ [23a] | Nd _{0.2} Zr _{0.8} O _{1.9} | | |
|---|---|------------------------------------|--|--|-----------------------------------|--|
| ⁴ I _{15/2} | (5880) | 5950 | 6160 | 5800 | | |
| ⁴ F _{3/2} | 11580 | 11190 | 11300 | 11420 | | |
| ⁴ F _{5/2} | 12620 | 12270 | 12300 | 12420 | | |
| ⁴ F _{7/2} | 13580 | 13250 | 13350 | 13420 | | |
| ⁴ F _{9/2} | 14840 | 14470 | 14630 | 14770 | | |
| ² H _{11/2} | 16030 | 15770 | 15840 | — | | |
| ⁴ G _{5/2} | 17330 | 16720 | 16970 | 17150 | | |
| ⁴ G _{7/2} | 19180 | 18600 | 18640 | 18940 | | |
| ⁴ G _{9/2} | 19630 | 19170 | 19330 | 19530 | | |
| ² P _{1/2} | 23400 | 22840 | 22910 | 23150 | | |
| | Ho(H ₂ O) ₉ ⁺³ | Ho ₂ O ₃ (C) | Ho _{0.2} Zr _{0.8} O _{1.9} | | | |
| ⁵ I ₇ | 5030 | 5230 | 5260 | | | |
| ⁵ I ₆ | 8530 | 8800 | 8850 | | | |
| ⁵ I ₅ | 11140 | 11340 | 11380 | | | |
| ⁵ F ₅ | 15420 | 15500 | 15650 | | | |
| ⁵ S ₂ , ⁵ F ₄ | 18450 | 18550 | 18640 | | | |
| ⁵ F ₃ | 20560 | 20530 | 20640 | | | |
| ³ K ₆ , ⁵ F ₁ | 22250 | 22220 | 22270 | | | |
| ⁵ G ₅ | 24030 | 23920 | 23980 | | | |
| ⁵ G ₄ , ³ K ₇ | 26100 | 25970 | 26040 | | | |
| ⁵ G ₆ | 27740 | 27470 | 27620 | | | |
| | Er(H ₂ O) ₉ ⁺³ | Er ₂ O ₃ (C) | Er _{0.2} Zr _{0.8} O _{1.9} | La _{0.2} Er _{0.3} Zr _{0.5} O _{1.75} (F) | LaErO ₃ (C-similar) | La _{0.45} Er _{0.55} O _{1.5} (perovskite) |
| ⁴ I _{13/2} | (6650) | 6640 | 6640 | 6680 | 6660 | 6580 |
| ⁴ I _{11/2} | 10220 | 10250 | 10360 | 10310 | 10270 | 10270 |
| ⁴ F(I) _{9/2} | 12520 | 12480 | 12580 | 12580 | 12520 | 12480 |
| ⁴ I(F) _{9/2} | 15350 | 15290 | 15380 | 15340 | 15270 | 15280 |
| ⁴ S _{3/2} | 18480 | 18210 | 18400 | 18350 | 18280 | 18300 |
| ² H _{11/2} | 19230 | 19090 | 19270 | 19210 | 19120 | 19230 |
| ⁴ F _{7/2} | 20600 | 20370 | 20530 | 20490 | 20410 | 20430 |
| ⁴ F _{5/2} | 22270 | 22030 | 22220 | 22150 | 22050 | 22080 |
| ⁴ F _{3/2} | 22610 | 22430 | 22680 | 22560 | 22510 | 22570 |
| ² H _{9/2} | 24630 | 24540 | 24570 | 24540 | 24510 | 24540 |
| ⁴ G _{11/2} | 26490 | 26280 | 26390 | 26350 | 26230 | 26390 |

(contd.)

TABLE 5 (contd.)

| | Tm(H ₂ O) ₉ ⁺³ | Tm ₂ O ₃ (C) | Baricenters for Tm _{0.05} Y _{0.95} O _{1.5} (36b) (³ H ₆ at 312 cm ⁻¹) | Tm _{0.2} Zr _{0.8} O _{1.9} | LaTmO ₃ (perovskite) |
|--------------------------------------|---|------------------------------------|---|--|------------------------------------|
| ³ F(H) ₄ | 5810 | 5880 | 5960 | 5990 | 5990 |
| ³ H ₅ | 8230 | 8370 | 8400 | 8460 | 8260 |
| ³ H(F) ₄ | 12560 | 12790 | 12810 | 12800 | 12800 |
| ³ F ₃ | 14480 | 14590 | 14660 | 14700 | 14640 |
| ³ F ₂ | 15110 | 15210 | 15170 | 15270 | (15200) |
| ¹ G ₄ | 21280 | 21460 | 21640 | 21550 | 21460 |
| ¹ D ₂ | 27950 | 27740 | 27830 | (27930) | 27780 |

octahedral MX₆⁻³ [111] and gaseous NdBr₃ and NdI₃ [37] show extreme effects of hypersensitivity, and that, quite generally, conjugated ligands such as acetate and acetylacetonate have a strong effect. It is interesting that KRUPKE [82] in a quantitative study of the band intensities of M(III) in Y₂O₃ also determined considerably larger values of U⁽²⁾ than for the aqua ions.

Several authors [127] have suggested a connection between the nephelauxetic effect and the electric polarizabilities α of the ligands. In our opinion [62] this is a somewhat secondary connection, because reducing ligands of low electronegativity, favouring M. O. delocalization, also tend to have rather large α . One might have connected the large nephelauxetic effect of oxide with high values of α . It is worth noting that though oxide(-II) does not have a sharply defined value for α (which would be infinite for gaseous O⁻), using the cation polarizabilities determined by TESSMAN, KAHN and SHOCKLEY [123] consistently, one obtains a fairly moderate variation, α being 1.1 Å³ for O(-II) in ClO₄⁻, 1.3 Å³ for Al₂O₃, 1.65 Å³ for MgO and 2.1 Å³ for BaO [75]. Anyhow, the main reason for the high nephelauxetic effect in our oxides, relative to aqua ions, must be the short M-O distances, as also discussed by POOLE [101] for Cr(III) and by REINEN [106] for Co(II), Ni(II) and other d group mixed oxides.

It is a fascinating question to what extent our oxides are covalent. The nephelauxetic effect is less informative in a numerical sense in the 4f group, where the empty 5d and 6s orbitals must be responsible for a much larger proportion of the covalent bonding than the partly filled 4f shell, than would be the case in the d groups [62, 76]. A chemical argument would be the very slow dissolution of C-oxides and fluorite-type dioxides in aqueous mineral acids, though, of course, the very large Madelung energy might

contribute to this high activation energy. What is perhaps more striking is the occurrence of O_9 clusters in UO_{2+x} as discussed at the end of chapter 6. The electronic density of the anions seems indeed to be depleted to an extent where one rather would talk about oxygen atoms than oxide ions from the point of view of fractional atomic charges [76]. Since this M. O. delocalization is connected with empty, rather than partly filled, central atom orbitals, we do not yet have sufficiently clear-cut physical methods to study the quantitative extent of covalent bonding. However, the nephelauxetic effect on the 4f shell indicates, at least indirectly, that the anhydrous halides are relatively more electrovalent than the oxides.

9. Experimental Section

The mixed oxides were prepared by ignition of co-precipitated hydroxides as discussed previously [70]. 0.5 M or 0.1 M lanthanide perchlorate solutions were prepared from 99.9% or better purity La_2O_3 , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 and Yb_2O_3 from American Potash (Lindsay Division, West Chicago) in a slight excess of 2 M Merck *p. a.* $HClO_4$ (diluted from 60%). Pr_6O_{11} and Tb_7O_{12} from the same supplier can only be dissolved by prolonged boiling with more concentrated perchloric acid. 1 M or 0.5 M zirconyl chloride (Fluka, Buchs, S. G., Switzerland) was dissolved in 2 M HCl and filtered from a small amount of white, insoluble material. 0.5 M aqueous thorium nitrate was made from American Potash code 103 and analyzed by gravimetry of ThO_2 formed by our technique. Appropriate amounts of such stock solutions (usually containing totally 5 millimoles of metal) were mixed in beakers and diluted to 100 ml with demineralized water. Excess (1.5 times the stoichiometric amount, except when La is present, thrice the stoichiometric amount) Merck *p. a.* aqueous ammonia was rapidly added. Next day, the mixed hydroxides were washed thoroughly with water, and ignited in new porcelain crucibles, first over a Bunsen burner for a few minutes until nearly all water had left, and then in an electric furnace, usually at 1000°C for 1 hour. $LaErO_3$ was made under similar circumstances, whereas $LaTmO_3$ and $LaYbO_3$ were heated to 820°C for 1 hour. The subsequent transformation to orthorhombic perovskites took place by heating to 1200°C for 3 hours. Merck *p. a.* Bi_2O_3 was heated to 850°C for 30 minutes, pure or pre-mixed with Nd_2O_3 or Er_2O_3 as described in chapter 5. Lindsay Pr_6O_{11} was heated gently with various reducing agents in order to study the formation of Pr(III) oxide (which turned out to be well-defined C- Pr_2O_3) at as low temperature as possible.

Thus, boiling with 1-octanol (200°C) or heating the contents in a test-tube to about 300°C produced very pale yellow-green products.

Cerium(IV) acetylacetonate was, after unsuccessful attempts with $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, made by shaking 2 millimoles of finely powdered, yellow $[\text{N}(\text{CH}_3)_4]_2\text{CeCl}_6$ [58] for 30 minutes in a flask (protected against light) with a solution of 8 millimoles anhydrous $\text{N}(\text{C}_2\text{H}_5)_3$ and 12 millimoles acetylacetonate in 50 ml 1,2-dichloroethane. The filtered red-brown solution shows molar extinction coefficients ε at various wavelengths which decrease to the extent of some 20% per hour.

The reflection spectra on Figure 1 were measured on the Beckman DU spectrophotometer. Y_2O_3 and BaSO_4 were used as references for Y- and Th-oxides, respectively. The internal $4f^a$ -transitions given in Table 5 were measured at 100°K on the Cary 14 spectrophotometer with the reflection apparatus previously constructed by Dr. ROMANO PAPPALARDO [68].

The powder-diagrams were made with a Guinier-De Wolff camera (Enraf-Nonius, Delft) applying copper $K\alpha$ -radiation. Silicon was used as internal standard; the three strongest lines at $d = 3.135$, 1.920 and 1.637 Å were invariantly found on the reading scale at 1.05% lower d -values during the two years the measurements were performed. We did not attempt to determine lattice parameters better than one part per thousand; all our measurements were made at 20–30°C.

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