

# Crystal chemistry and magnetic structures of Tb(IV) fluorides

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## Abstract

This paper reviews the particular crystal-chemical properties of fluorides containing tetravalent terbium and emphasises the special case of the half-filled shell  $4f^7$  of the  $Tb^{4+}$  ion. To this end the crystal-chemical properties of  $Zr^{4+}$ ,  $Tb^{4+}$  and  $U^{4+}$  are compared. The way according to which the thermal decomposition of  $TbF_4$  is turned to account to synthesise mixed valence (III/IV) terbium fluorides is presented. The study of the magnetic interactions involving  $Tb^{4+}$  ions has been taken up through magnetic structures determination from neutron diffraction. The broad outlines of further work will be presented in the light of our recent results concerning the crystal chemistry of Tb(IV) fluorides. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Fluoride; Tetravalent terbium; Lanthanides

## 1. Introduction

Although the synthesis of terbium tetrafluoride has been reported as far back as half a century [1] the first fluoro complex of  $Tb^{4+}$ , namely  $Cs_3TbF_7$ , was prepared a few years later [2]. Then and for about three decades, only powdered samples of tetravalent terbium fluorides were synthesised [3–9], among which two were of the highest interest, i.e.  $Li_2TbF_6$  [3] and  $BaTbF_6$  [4] as representatives of new structural types whereas most of the other identified compounds proved to be isotypic with their tetravalent uranium or zirconium homologues. Then we had to wait until the end of the 20th century to see the first physical characterisations other than magnetic measurements to be investigated in order to characterise the 4+ oxidation state of the terbium. For instance the core-level spectroscopy of tetravalent lanthanide compounds was investigated in  $M_3LnF_7$  fluorides [10]. Finally as high power X-ray synchrotron sources were available and facilities offered to scientists, advanced spectroscopies such as XANES or XMCD became powerful tools for the solid state physicists to get deeper insight into the role played by the 4f orbitals in tetravalent lanthanides. With such perspectives the solid state chemists may introduce the flexibility of the chemistry to modify the environment interacting with the different parameters, either electronic or structural. In this framework

we undertook comprehensive research devoted to produce new materials to investigate their physical properties in narrow relationships with their structures. In particular we had envisaged to study the long range magnetic interactions possibly associated with superexchange interactions involving 4f orbitals in order to evaluate to what extent such orbitals may take part in such interactions through predictable relatively weak overlapping. To deal with this subject we chose to work on tetravalent terbium fluorides for several reasons. First because the predominant character in the bonding should be essentially ionic in these compounds. Secondly because the  $^8S_{7/2}$  ground state of the  $4f^7$  electronic configuration of the  $Tb^{4+}$  ion should be insensitive to crystal field effects. Finally, because the oxidation state 4+ of the Tb is one of the easier to reach under a fluorine atmosphere among the appropriate rare earth metals, i.e. Ce, Pr and Tb, anyway easier than for Pr which is much more easy to stabilise in the oxidation state 4+ in oxides than in fluorides.

The first part of our scientific approach was to prospect numerous systems to accumulate experimental results from which crystallographic data could be extracted using the well known Rietveld procedure of refinement of structures from X-ray or neutron powder diffraction data. However, the crystal chemistry of tetravalent terbium fluorides made a great leap forward when single crystals were obtained about 5 years ago and the first crystal structures determined and/or refined from single-crystal data [11–15]. These results and subsequent yet unpublished others allowed filled gap in the crystallographic data lack claimed by Shannon and Prewitt

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in their pioneering article on the ionic radii [16] and kept without new developments for 25 years. This also brought out elements of explanation, if not of understanding at least for the rationalisation of the singular crystal chemical behaviour of  $\text{Li}_2\text{TbF}_6$  [9] which will be developed in a further section. Beyond the valuable contribution to the crystal chemical knowledge of the  $\text{Tb}^{4+}$  ion, the growth of single crystals also helped to remove uncertainties about the chemical stability of the tetravalent oxidation state of the terbium even if some fluorinated compounds containing tetravalent terbium are sensitive to moisture and/or decompose in time yielding trivalent terbium. We also took advantage of the thermal decomposition of  $\text{TbF}_4$  to synthesised mixed-valence (III/IV) terbium compounds. The obtaining of single crystals of pure tetravalent terbium fluorides and mixed-valence (III/IV) terbium fluorides incited us to reactivate research in this area in order to study physical properties studies relative to the  $\text{Tb}^{4+}$  ion. Some of the preliminary results are reported in the present paper and the lines of thought will be presented.

## 2. Synthesis of tetravalent terbium fluorides

### 2.1. Polycrystalline samples

In contrast to fluorides of  $\text{Pr}^{4+}$  and even 3d transition elements in their higher oxidation state such as  $\text{Ni}^{4+}$ , the synthesis of tetravalent terbium fluorides does not require the use of a high pressure of  $\text{F}_2$  gas. All the identified tetravalent terbium fluorides reported up to now can be prepared under a  $\text{F}_2$  gas flow at ambient pressure. Pure polycrystalline samples can be obtained from direct fluorination of starting mixtures of different compositions including either  $\text{Tb}_4\text{O}_7$ ,  $\text{Tb}_2\text{O}_3$  or  $\text{TbF}_3$  as source of terbium and fluorides or chlorides of the metal counterions in the case of binary, ternary, etc. fluorides. The only restrictive condition in synthesising tetravalent terbium fluorides in this way is the fact that fluorine brings up the elements with which it reacts to their higher oxidation state. So the synthesis of complex combinations including polyvalent elements such as Tl, *nd* and *nf* transition metals, In, Ce

for example, exhibiting more than one stable oxidation state cannot be envisaged for the lower oxidation states of these elements.

The preparation reaction may be carried out in alumina boats if the temperature does not exceed  $500^\circ\text{C}$ , otherwise side-products including  $\text{AlF}_3$  component may appear if the reaction temperature reaches values higher than this. Then highly passivated nickel boats should be used to rise the reaction temperature but with a certain risk of contamination by red  $\text{Ni}^{4+}$  side-products originating from vessel attack. Also the thermal decomposition of the tetravalent terbium fluoride may occur at high temperature but this aspect will be examined in a further section (see mixed-valence compounds).

### 2.2. Single crystals

Attempts to obtain single-crystals of fluorides, which easily decompose thermally, have discouraged people working in this field for a long time. But in the case of  $\text{TbF}_4$  a careful examination of the thermodynamic parameters governing the thermal decomposition reported by Gibson and Haire [17] suggested that terbium tetrafluoride was slightly more stable than previously predicted. Taking this into account and remembering suggestions made by Müller for growing  $\text{Cs}_2\text{CuF}_6$  [18], lead us to undertake experiments in progressively increasing the reaction temperature of the samples. This procedure was successful in several cases and seems to be all the more easy when tetravalent terbium is stabilised in combinations with alkaline or alkaline-earth metals. Examples of single crystals obtained by this way will be given in a further section (see below and Table 1).

### 2.3. Mixed-valence compounds

The first mixed-valence (III/IV) terbium fluoride mentioned in the literature was  $\text{TbF}_{3.75}$ , i.e.  $\text{Tb}_4\text{F}_{15}$  which is better represented by the formula  $\text{Tb}^{3+}\text{Tb}^{4+}\text{F}_{15}$  [19]. This compound appears as an intermediate stable phase which forms when terbium tetrafluoride partially decomposes thermally according to the reaction  $\text{TbF}_4 \rightarrow \text{TbF}_3 + 1/2\text{F}_2$  which takes place even under pure fluorine gas flow

Table 1  
Crystallographic data for Tb(IV) fluorides from single-crystal and/or neutron data<sup>a</sup>

Compounds	Symmetry; space groups; unit cell parameters (pm)	Coordination	
		Number	Polyhedra geometry
$\text{Li}_2\text{TbF}_6$	Monoclinic; $P2_1/c$ ; $a = 758.5(1)$ , $b = 496.5(1)$ , $c = 1111.6(2)$ , $\beta = 106.96(1)^\circ$	8	D
$\text{KTbF}_5$	Triclinic; $P\bar{1}$ ; $a = 744.6(1)$ , $b = 856.7(1)$ , $c = 1083.4(3)$ , $\alpha = 76.02(2)^\circ$ , $\beta = 72.51(2)^\circ$ , $\gamma = 67.03(2)^\circ$	8	AA, BTP, D
$\text{CsTbF}_5$	Orthorhombic; $Cmca$ ; $a = 1406.7(1)$ , $b = 816.3(2)$ , $c = 816.1(2)$	8	D
$\text{Li}_2\text{CaTbF}_8$	Tetragonal; $I\bar{4}$ ; $a = 514.3(1)$ , $c = 1067.1(2)$	8	D
$\text{KTb}_3\text{F}_{12}$	Tetragonal; $I4/m$ ; $a = 771.6(1)$ , $c = 752.8(1)$	8	D
$\alpha\text{-BaTbF}_6$	Triclinic; $P\bar{1}$ ; $a = 734.4(1)$ , $b = 844.8(1)$ , $c = 867.7(1)$ , $\alpha = 101.63(8)^\circ$ , $\beta = 96.89(1)^\circ$ , $\gamma = 114.62(1)^\circ$	8	D, AA
$\beta\text{-BaTbF}_6$	Orthorhombic; $Cmma$ ; $a = 776.1(1)$ , $b = 1151.3(3)$ , $c = 552.3(1)$	8	D

<sup>a</sup> AA: square antiprism; BTP: bicapped trigonal prism; D: dodecahedron.

at ambient pressure. On the basis of this mechanism, mixed-valence (III/IV) terbium compounds may be formed when tetravalent terbium is in excess in binary systems. For instance, in the  $\text{KF-TbF}_4$  binary system, the well-defined compound corresponding to the higher content in  $\text{TbF}_4$  is  $\text{KTbF}_5$ , the structure of which was solved from X-ray single-crystal diffraction data [14]. For compositions richer in  $\text{TbF}_4$  than the equimolar  $1\text{KF} + 1\text{TbF}_4$  composition ( $\text{KTbF}_5$ ), the powdered samples consist of a diphasic domain involving  $\text{KTbF}_5$  and  $\text{TbF}_4$ . As  $\text{TbF}_4$  undergoes a thermal decomposition on heating above  $550^\circ\text{C}$ , an annealing carried out at higher temperature yields  $\text{TbF}_3$  that can react to lead to intermediate phases in the ternary system  $\text{KF-TbF}_3\text{-TbF}_4$ . The first mixed-valence (III/IV) terbium fluoride obtained in this way, starting from  $1\text{KF} + 3\text{TbF}_4$  composition was  $\text{KTb}_3\text{F}_{12}$ , the structure of which has been determined using both single-crystal X-ray diffraction and powder neutron diffraction [15]. By doing so from a  $1\text{KF} + 2\text{TbF}_4$  starting mixture and heating up to  $650^\circ\text{C}$  a second mixed-valence (III/IV) terbium fluoride with formula  $\text{K}_2\text{Tb}_4\text{F}_{17}$  has been filled. Although  $\text{Tb}^{3+}$  and  $\text{Tb}^{4+}$  are all in 8-coordination in both  $\text{KTb}_3\text{F}_{12}$  and  $\text{K}_2\text{Tb}_4\text{F}_{17}$  structures, the  $\text{Tb}^{3+}$  sites can be unambiguously distinguished from those of  $\text{Tb}^{4+}$  by performing a bond valence analysis of the structure using the Brese and O'Keeffe's model [20]. Precise enough values of the local charge on the cations were obtained using the  $R_{ij}$  bond valence parameter for the  $\text{Tb}^{4+}\text{-F}$  bond which could have been evaluated from single crystal X-ray diffraction data [14].

### 3. Crystal chemistry of tetravalent terbium fluorides

As stated in the introduction we had the opportunity to form the fluoride  $\text{Li}_2\text{TbF}_6$  the structure of which does not correspond to that which was expected within a series of homologous compounds [9]. As both the low pressure  $\beta$ -form of  $\text{Li}_2\text{ZrF}_6$  and  $\text{Li}_2\text{PrF}_6$  [21] are isostructural, the  $\text{Li}_2\text{TbF}_6$  fluoride was expected to belong to this structural type since the ionic radius of  $\text{Tb}^{4+}$  is, for equal coordination numbers, intermediate between those of  $\text{Zr}^{4+}$  and  $\text{Pr}^{4+}$ . Let us remember that in this  $\beta$ - $\text{Li}_2\text{ZrF}_6$  structural type [22] the  $\text{M}^{4+}$  cations are in 6-coordination. As regards  $\text{Li}_2\text{TbF}_6$ , it is the first and the only representative obtained at ambient pressure of another structural type known only through a high-pressure form, i.e.  $\alpha$ - $\text{Li}_2\text{ZrF}_6$  [23]. In this  $\alpha$ - $\text{Li}_2\text{ZrF}_6$  structural type the  $\text{M}^{4+}$  cations are in 8-coordination. In accordance with what is generally observed for fluorides of  $\text{A}_2^{1+}\text{M}^{4+}\text{F}_6$  stoichiometry, the structure consists of infinite chains of edge-sharing 8-coordination polyhedra further linked together by the  $\text{A}^+$  cations. The only alternative known up to now for the  $\text{A}_2\text{BX}_6$  compounds in which the anion is an infinite chain is the case of  $(\text{NH}_4)_2\text{ZrF}_6$  [24] where the  $(\text{MF}_6)^{2-}$  chains are built of corner-sharing dimeric  $(\text{Zr}_2\text{F}_{12})^{4-}$  units which are themselves made of two  $(\text{ZrF}_8)^{4-}$  polyhedra sharing a triangular face. This type of chain,

further encountered in the mixed-valence  $\text{K}_2\text{Tb}_4\text{F}_{17}$  fluoride, may also be regarded as built of alternating corners and faces sharing  $\text{MF}_8$  polyhedra. The inadvisability of trying to relate ionic size to coordination number is well illustrated by the structure of  $\text{Li}_2\text{TbF}_6$ . It is also well known that coordination numbers in essentially ionic crystals are determined by the balance between bonded and nonbonded forces and the constraints of the stoichiometry. In the case of  $\text{Li}_2\text{TbF}_6$  the 8-coordination of the  $\text{Tb}^{4+}$  ions is in agreement with the stoichiometry but beyond this observation the question arises as to why the  $\text{Tb}^{4+}$  ion adopts an 8-coordination by  $\text{F}^-$  in this structure. This feature seems to be in narrow relationship with the  $f^7$  electronic structure of the  $\text{Tb}^{4+}$  ion since the ionic radius is not the determinant factor. To provide elements of an explanation to this not yet fully understood crystal-chemical behaviour of the  $\text{Tb}^{4+}$  ion a comprehensive investigation of  $\text{MF-M}'\text{F}_4$ ,  $\text{MF}_2\text{-M}'\text{F}_4$  [25],  $\text{MF}_3\text{-M}'\text{F}_4$  and  $\text{MF-MF}_2\text{-M}'\text{F}_4$  ( $\text{M}' = \text{Zr, Tb, U}$ ) systems has been undertaken. From reliable results obtained by single-crystal X-ray diffraction or powder neutron diffraction it appears that the  $\text{Tb}^{4+}$  ion exhibits a strong propensity towards 8-coordination in a fluorinated environment whereas the octahedral coordination seems to be the usual coordination in an oxygenated environment. Our preliminary results tend to show that for fluorides of  $\text{Zr}^{4+}$  and  $\text{Tb}^{4+}$  the following empirical rule may be borne out: fluorozirconates and fluoroterbates of the same stoichiometry are isostructural when the  $\text{Zr}^{4+}$  ions are exclusively in 8-coordination; if in a fluorozirconate the  $\text{Zr}^{4+}$  ions exhibit simultaneously or exclusively coordination numbers other than 8, i.e. 6 or 7, then the homologous fluoroterbate does not exist or belongs to a different structural type. This observation can be applied to  $\text{U}^{4+}$  for which 8- and 9-coordinations are usual. To progress towards the knowledge of the role of the f orbitals in bonding, magnetic studies have been investigated.

### 4. Magnetic ordering in tetravalent terbium fluorides

The only magnetic structures involving tetravalent terbium determined up to now are those of the perovskite-type oxides  $\text{ATbO}_3$  with  $\text{A} = \text{Sr}$  and  $\text{Ba}$  which exhibit an anti-ferromagnetic ordering below  $\sim 33\text{ K}$  [26]. From our preliminary studies on fluorides containing tetravalent terbium it has been observed that magnetic ordering may occur at very low temperatures, i.e. below  $4.2\text{ K}$ . We give here two examples to illustrate this and we shall be concerned only with  $\text{KTb}_3\text{F}_{12}$  and  $\text{Li}_2\text{TbF}_6$  compounds. Whereas the former which would be better written  $\text{KTb}^{3+}\text{Tb}^{4+}\text{F}_{12}$  is a mixed-valence (III/IV) terbium fluoride, the second is a pure tetravalent terbium representative. Both compounds are characterized by the presence of infinite chains  $(\text{TbF}_6)^{2-}$  of edge-sharing  $(\text{TbF}_8)^{4-}$  polyhedra. In  $\text{KTb}_3\text{F}_{12}$  the chains are arranged in a tetragonal packing and are held together by  $\text{K}^+$  ions alternating with the  $\text{Tb}^{3+}$  ions in a pseudo-cubic 8-coordination. In  $\text{Li}_2\text{TbF}_6$  the chains are arranged in a

pseudo-hexagonal packing and are held together by the  $\text{Li}^+$  ions in both octahedral and square pyramidal coordinations. For both  $\text{KTb}_3\text{F}_{12}$  and  $\text{Li}_2\text{TbF}_6$  compounds the magnetic structures have been determined by means of powder neutron diffraction.

$\text{KTb}_3\text{F}_{12}$  crystallizes in the tetragonal system with the space group  $I4/m$  and unit cell parameters  $a = 771.5(1)$  and  $c = 753.0(1)$  pm at 300 K. Below  $T_N = 3.6(1)$  K,  $\text{KTb}_3\text{F}_{12}$  exhibits a collinear magnetic structure characterized by ferromagnetic chains of edge-sharing  $(\text{TbF}_8)^{4-}$  dodecahedra with an antiferromagnetic ordering between the nearest chains (Fig. 1). Within these chains running along the  $c$ -direction of the tetragonal cell, the magnetic moments of the  $\text{Tb}^{4+}$  ions are equal to  $6.94(5) \mu_B$  at 1.4 K, are aligned parallel to this  $[001]$  direction. The magnetic structure belongs to the Shubnikov group  $Ip4'/m$  with  $k = (001)$  and the  $T_N$  temperature corresponds to a long range magnetic ordering of the  $\text{Tb}^{4+}$  moments. It is worthy of note that the  $\text{Tb}^{3+}$  ions do not present any spontaneous magnetic moment down to 1.4 K as they lie on a special position so that the resultant of all the superexchange fields is then equal to zero. However, it should be noted that above  $T_N$ , the observed Curie constant,  $27.97(1) \text{ emu K mol}^{-1}$ , is in very

good agreement with the value expected for two  $\text{Tb}^{4+}$  and one  $\text{Tb}^{3+}$  free ions.

$\text{Li}_2\text{TbF}_6$  crystallizes in the monoclinic system with the space group  $P2_1/c$  and unit cell parameters  $a = 758.5(1)$ ,  $b = 496.5(1)$ ,  $c = 1111.6(1)$  pm and  $\beta = 106.96(1)^\circ$  at 300 K. Below  $T_N = 2.00$ – $2.05$  K and down to 1.43 K which is the lowest temperature which has been reached before recording the neutron powder pattern,  $\text{Li}_2\text{TbF}_6$  exhibits a spin wave modulated magnetic structure with a propagation vector  $k$  directed along the  $b$  direction with  $k_y = 0.016$  at 1.43 K. This incommensurate magnetic structure is characterized by a very long period (about 60 unit cells) along  $b$  and this period has been observed to be slightly temperature dependent. The magnetic moments of the  $\text{Tb}^{4+}$  ions are collinear and lie in the  $ac$  plane. At 1.43 K the components have been found to be  $M_x = 6.5 \mu_B$  and  $M_z = 2.1 \mu_B$  leading to a magnetic moment of  $6.2 \mu_B$ .

## 5. Conclusions

As 8-coordination seems to be the usual coordination arrangement of the  $\text{Tb}^{4+}$  ion in fluorinated compounds, we will direct our further researches toward the discovery of an exception, and when a fluorozirconate or a fluorouranate makes an exception to the empirical rule of the 8-coordination, then a re-examination of the crystal structure is envisaged as is the case for  $\text{CsU}_6\text{F}_{25}$  [27] where a short contact distance between fluorine atoms is suspicious and 9-coordination is reported for  $\text{U}^{4+}$  whereas homologous compound of terbium(IV) has been formed. Beyond the crystal chemistry of the tetravalent terbium fluorides development, the study of the magnetic interactions in these compounds will be also extended in order to analyse the role played by the 4f orbitals in this field.

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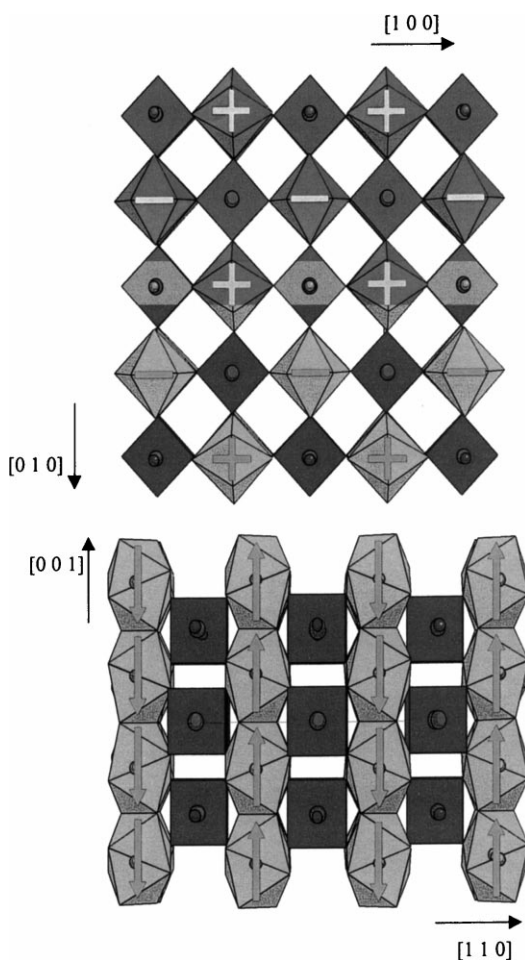


Fig. 1. Magnetic structure of  $\text{KTb}_3\text{F}_{12}$ .

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