



FLUOROTERBATES: CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES

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One of the topics under present investigation in LMI [Laboratoire des Matériaux Inorganiques], in collaboration with LLB and HMFL [High Magnetic Field Laboratory] deals with existing relationships between crystal structures and magnetic properties in fluoroterbates. This topic with an essentially basic character has been initiated to understand the singular behaviour of the Li_2TbF_6 representative of the Li_2MF_6 series (M. Guillot et al., J.S.S.C. 97, 2 (1992) 400) and instigated a growing interest both due to the originality and the diversity of the encountered structural types. Our approach consists in comparing the crystal chemistry of the Tb^{4+} ion with that of Zr^{4+} and U^{4+} ions, the ionic radii of which lie on each side of the Tb^{4+} ionic radius value for a given coordination number.

The singular crystal chemical behavior of the Tb^{4+} appears thus much more related to its half-filled $4f^7$ electronic configuration than to its ionic radius despite the ionic character of the fluorides. One of the most significant advance in the comprehensive crystal chemistry of the Tb^{4+} ion comes from its fitness for the 8-coordination as evidenced by numerous crystal structures determination. Indeed, with a set-back bearing over some thirty fluorides, the structures of which have been determined accurately from single-crystal X-ray diffraction and/or neutron powder diffraction, we may ascertain that the Tb^{4+} ions were always found in a F^- ions-8-fold surrounding, with either square antiprisms, dodecahedra or bicapped trigonal prisms as coordination polyhedra. The only exception to these observations comes out from M_3TbF_7 fluorides (M = K, Rb, Cs) where a $[\text{TbF}_7]^{3-}$ complex ion with a pentagonal bipyramid-like configuration and a dynamical fluorine disorder is expected by analogy with the isotypic $[\text{ZrF}_7]^{3-}$ ion.

The present knowledge about the crystal chemistry of the Tb^{4+} ion in fluorides leads us to lay down the following empirical rule, except for M_3TbF_7 (M=K, Rb, Cs) compounds: Fluoroterbates are isotypic to fluorozirconates with the same stoichiometry only if the Zr^{4+} ions are in 8-fold coordination exclusively. That is, if for a given stoichiometry the Zr^{4+} ions exhibit different

coordination numbers (in the 6-8 range), then the homologous tetravalent terbium fluoride does not exist; or, if it does, it crystallises in another crystal structure, being then built from 8-coordination polyhedra exclusively". This empirical rule does not apply to oxides despite the similar sizes of O^{2-} and F^- , thus strengthening the idea that the 4f orbitals play a determinant role in the crystal chemistry of the Tb^{4+} ion in fluorides.

Let us note that this part of our crystal structure investigations could not have been successfully carried out without using neutron diffraction, as small distortions of the anionic sublattice F (F^- is a "light" element, as compared to Tb) occurring either at room or low temperature have only been "seen" via neutron diffraction, in particular via High Resolution Powder patterns recorded on the 3T2 instrument.

To go further in the comprehensive role played by the 4f orbitals a study of the magnetic properties of the evidenced tetravalent terbium combinations was undertaken. Through the large panel of available compounds some general outstanding features relative to the magnetic behaviour of the Tb^{4+} ($4f^7$ electronic configuration and $^8\text{S}_{7/2}$ ground term) have been evidenced. Figure 1 gives a summary of the preliminary results obtained by neutron diffraction (on G4.1 instrument). In particular long range magnetic orderings have been observed in fluorides with edge-sharing $(\text{TbF}_8)^{4-}$ polyhedra. For instance, in both $\beta\text{-BaTbF}_6$ and $\text{KTb}_3\text{F}_{12}$ compounds, which are characterized by infinite $[\text{TbF}_6]^{2-}$ chains of edge-sharing $[\text{TbF}_8]^{4-}$ dodecahedra, ferromagnetic couplings are observed within the chains and the antiferromagnetic structures result from antiferromagnetic couplings between the nearest chains. In the case of $\beta\text{-BaTbF}_6$, let us mention that an applied magnetic field of a few hundred of oersteds (~ 200 oersteds) is sufficient to induce a ferromagnetic state. This emphasizes the weakness of the inter-chain couplings.

For some representatives of the M_2TbF_6 series (M=Li, K, Rb), incommensurate magnetic structures have been observed; for instance a square modulated magnetic structure with $\mathbf{k}=(0 \ 0.0162(1) \ 0)$ propagation vector is obtained



for Li_2TbF_6 from the position and intensity analysis of first, third and fifth order magnetic Bragg peaks down to 1.4K.

For compounds with a crystal structure built from edge- and corner-sharing coordination polyhedra (KTbF_5 , RbTbF_5 , $\text{K}_2\text{Tb}_4\text{F}_{17}$), the magnetic transition temperature is a function of the PCM (Polyhedra Connection Mode), the higher is the % of corner-sharing, the lower is the magnetic transition temperature (Figure 1).

In the near future this research will be developed

and extended to statistically disordered mixed-valence compounds obtained by taking advantage of the partial thermal decomposition of the tetravalent terbium tetrafluoride in terbium trifluoride and elemental fluorine which occurs in compositions rich in terbium tetrafluoride.

This work is associated to M. Josse PhD [2003]. And has already given rise to Communications either in National [1] and International [2] Conferences and to Publications in specialized reviews [3,4].

Compound	Structural characteristics		Long range magnetic order
	Polyhedral linking (CN ⁺ [8] for Tb ⁴⁺)	PCM ⁺	
Li_2TbF_6 (K_2TbF_6) (Rb_2TbF_6)		100% edges	$T_N = 2.00 \text{ K}$ $T_N = 1.60 \text{ K (K)}$ $T_N = 2.10 \text{ K (Rb)}$
$\beta\text{-BaTbF}_6$ (CaTbF_6) (SrTbF_6) (CdTbF_6)		100% edges	$T_N = 2.10 \text{ K}$ ($T_N \approx 2.15 \text{ K}$) ($T_N = 2.65 \text{ K}$) ($T_N \approx 2.75 \text{ K}$)
$\alpha\text{-BaTbF}_6$		66.6% corners and 33.3% edges	None down to 1.4K
KTbF_5 (RbTbF_5)		50% edges and 50% corners	$T_N = 1.60 \text{ K}$ ($T_N \approx 1.4 \text{ K}$)
CsTbF_5		80% corners and 20% edges	None down to 1.4K
$\text{Na}_7\text{Tb}_6\text{F}_{31}$		80% corners 20% edges	None down to 1.4K
$\text{Tb}^{\text{III}}\text{Tb}^{\text{IV}}_3\text{F}_{15}$		100% corners	None down to 1.4K
$\text{K}_2\text{Tb}^{\text{III}}\text{Tb}^{\text{IV}}_3\text{F}_{17}$		edges Corner	$T_N = 1.65 \text{ K}$
$\text{KTb}^{\text{III}}\text{Tb}^{\text{IV}}_2\text{F}_{12}$		100% edges ($\text{Tb}^{4+}\text{-Tb}^{4+}$) 100% corners ($\text{Tb}^{3+}\text{-Tb}^{4+}$)	$T_N = 3.65 \text{ K}$

References

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