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Magnetic behaviour of the MTbF$_6$ fluoroterbates (M=Cd, Ca, Sr, (α/β)-Ba)

M. Josse [a,d], M. El-Ghozzi [a,*], D. Avignant [a], G. André [b], F. Bourée [b], O. Isnard [c]

[a] Laboratoire des Matériaux Inorganiques, UMR 6002 CNRS, Université Blaise Pascal, 63171 Aubière, France
[b] Laboratoire Léon Brillouin, CEA-CNRS, CEA-Saclay, 91191 Gif-sur-Yvette, France
[c] Institut Néel, CNRS/Université Joseph Fourier, UPR2940, 38042 Grenoble, France
[d] CNRS, Université de Bordeaux, ICMCB, Pessac, France

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ABSTRACT

Neutron powder diffraction has been performed on the MTbF$_6$ fluorides (M=Cd, Ca, Sr, (α/β)-Ba). Four of these fluorides (Cd, Ca, Sr, β-Ba) are built of a (pseudo-) tetragonal packing of $[\mathrm{TbF_6}]^{2-}$ chains and only differs by the chains relative orientations. Thus this series represents a valuable opportunity to evaluate the Tb^{4+}-Tb^{4+} magnetic interactions. All the compounds displayed antiferromagnetic order (T_N=2.70 K (Cd), 2.15 K (Ca), 2.60 K (Sr), 2.10 K (β-Ba)), except for the α form of BaTbF$_6$. The crystal structure of this latter fluoroterbate has also been investigated by means of high-resolution neutron powder diffraction. From Neutron Powder Diffraction data, CdTbF$_6$ and β-BaTbF$_6$ magnetic structures were determined, together with the metamagnetic behaviour of β-BaTbF$_6$ as a function of an external magnetic field. A tentative phase diagram is then given for β-BaTbF$_6$. Advantage was taken of the polymorphism of the BaTbF$_6$ fluoroterbate to analyse, on the basis of topological parameters such as bond distances and angles, the magnetic behaviour of its α and β forms. It was shown that superexchange interactions are present in β-BaTbF$_6$, and that these interactions may also rule the magnetic behaviour of the other MTbF$_6$ (M=Ca, Sr, Cd) tetravalent terbium fluorides.

1. Introduction

The magnetic properties of paramagnetic lanthanides ions are related to their partially filled 4*f* shell, which is known to have a pronounced internal character. Because of their limited spatial extension and of the screening of the 5*d* and 6*s* shells, 4*f* electrons hardly interact with the electronic shells of neighbouring atoms, especially with other 4*f* electrons. Thus chemical bonding of rare-earths in oxides and fluorides is predominantly ionic, and their magnetism is usually dominated by dipolar interactions, especially in fluorides.

However structural studies of tetravalent terbium fluorides suggest that the singular crystal-chemistry of this class of fluorides (a propensity of the Tb^{4+} ions to adopt an 8-fold coordination) may be influenced by the half-filled 4*f* shell of the Tb^{4+} ion [1,2], i.e. that 4*f* electrons influence the Tb–F chemical bonding in these compounds.

Similarly, the magnetic behaviour of fluoroterbates, studied for many years in our laboratory, tends to demonstrate that non-dipolar interactions occur in these materials and may rule their magnetic behaviour [3–5], as for example, the recent study of the magnetic behaviour of M_2TbF$_6$ (M=Li, K, Rb) fluorides [6]. In these fluoroterbates incommensurate square-modulated magnetic structures are observed at low temperature (below 2.1 K). The ordering temperature observed have been correlated to the efficiency of the dipolar interactions to relay the frustration induced by the pseudo-hexagonal packing of magnetic $[\mathrm{TbF_6}]^{2-}$ chains, while the magnetic behaviour of Li$_2$TbF$_6$ suggests non-dipolar interactions in these chains.

To supplement our investigations, in order to bring further evidences of these non-dipolar interactions, we investigated the magnetic behaviour of the MTbF$_6$ (M=Cd, Ca, Sr, (α/β)-Ba) fluorides.

The crystal structures of α and β polymorphs of BaTbF$_6$ were the first, among fluoroterbates, to be determined from single-crystal X-ray diffraction (XRD) [7,8]. SrTbF$_6$ was reported to be isomorphic to β-BaZrF$_6$ [9]. CaTbF$_6$ and CdTbF$_6$ adopt an anti-KSbF$_6$ [2] and are, after Li$_2$TbF$_6$ [1], new examples of the singular crystal-chemistry of fluoroterbates. The remarkable feature of the MTbF$_6$ fluorides is that they are all, except α-BaTbF$_6$, built of $[\mathrm{TbF_6}]^{2-}$ chains (Fig. 1). These chains adopt different orientation, depending on the size of the associated alkaline earth, yielding different symmetries for the corresponding crystal structure. This series represents a valuable opportunity to evaluate the Tb^{4+}–Tb^{4+} magnetic interactions, due to the homogeneity of the polyhedral frameworks ($[\mathrm{TbF_6}]^{2-}$ chains) on one hand, and to the polymorphism of BaTbF$_6$ on the other hand, which should allow more insight the structural parameters influencing the magnetic behaviour of fluoroterbates.

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[*] Corresponding author.
E-mail address: Malika.EL-GHOZZI@univ-bpclermont.fr (M. El-Ghozzi).

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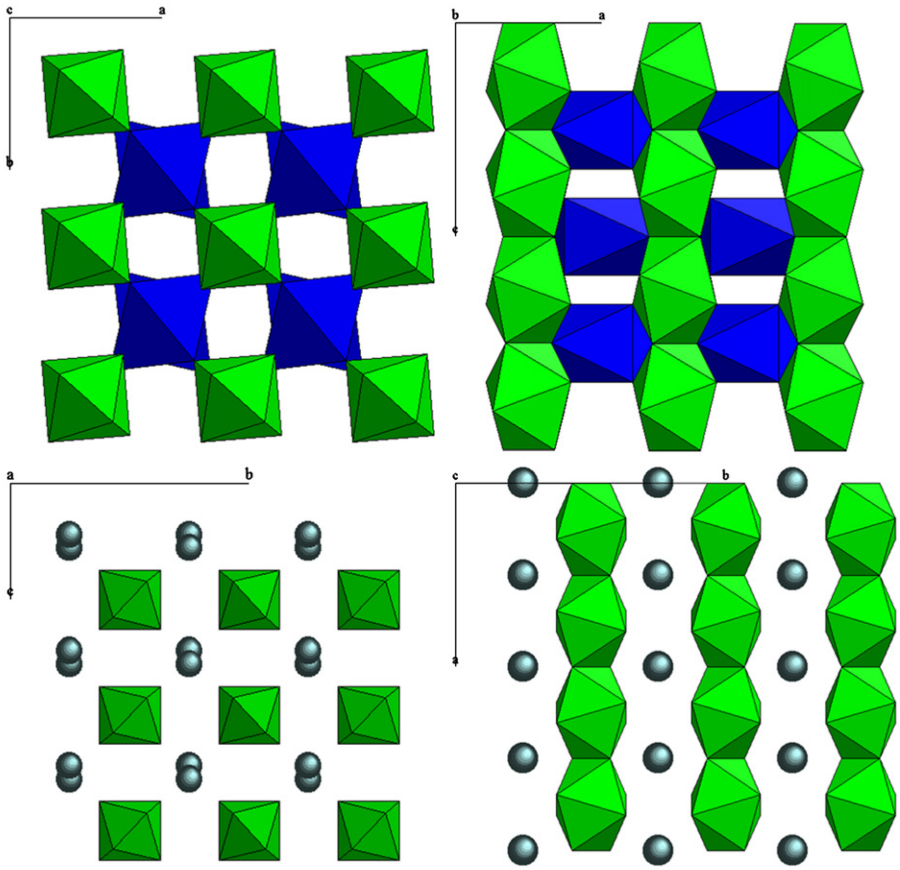

Fig. 1. Crystal structure of $CaTbF_6$ and $CdTbF_6$ viewed along the *c*-axis (top left) and the *b*-axis (top right), Tb^{4+} polyhedra in green, Ca^{2+}/Cd^{2+} polyhedra in blue. Crystal structure of $SrTbF_6$ and β-$BaTbF_6$ viewed along the *a*-axis (bottom left) and the *c*-axis (bottom right), Tb^{4+} polyhedra in green, Sr^{2+}/Ba^{2+} as spheres. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The present work deals with a neutron diffraction study of the magnetic behaviour of the titles compounds. The magnetic structures of $CdTbF_6$ and β-$BaTbF_6$ were determined. The crystal structure of α-$BaTbF_6$ was also investigated by means of high resolution powder neutron diffraction to benefit from the most accurate description of its anionic framework.

The magnetic behaviour in these $M$$TbF_6$ (M=Cd, Ca, Sr, Ba) compounds will be discussed with respect to crystal-chemical considerations, with a particular focus on the α and β polymorphs of $BaTbF_6$. The nature of the magnetic interactions involved in these fluoroterbates will be investigated.

2. Material and methods

Polycrystalline samples of the title compounds were obtained by heating overnight stoichiometric mixtures of MF_2 (Strem chemicals) (M=Cd, Ca, Sr, Ba) and TbF_4 (prepared by fluorination of Tb_4O_7, (Merck)), under pure fluorine gas, at 500 °C. The samples were then annealed for 12 h at temperatures ranging from 540 to 720 °C.

Neutron powder diffraction patterns were recorded at the Leon Brillouin Laboratory (LLB, Saclay, France) on the two-axis G4.1 diffractometer (λ=2.4266 Å) down to 1.4 K, without any magnetic field, for the determination of the magnetic structure [10], and on the 3T2 high resolution diffractometer (λ=1.2251 Å) at 300 K for the refinement of the crystal structure of α-$BaTbF_6$. It is worth mentioning that all the structural refinements performed were fully consistent with the previously reported crystallographic data [2,4,7,8], and thus confirmed the tetravalent oxidation state of terbium ions in the title compounds. NDP under magnetic field for the β-$BaTbF_6$ fluororterbate were recorded on the super-D2B instrument at the Institut Laue Langevin (ILL, Grenoble). The data were analysed with the FULLPROF program [11], using the magnetic form factor of Gd^{3+} for the magnetic refinements, as this ion is isoelectronic to Tb^{4+} for which no magnetic form factors are available. The dipolar magnetostatic energy of β-$BaTbF_6$ has been obtained using the concept of non-overlapping charges developed by Bertaut [12] to account for the long range character of the dipolar interactions. The results in Section 3.1.3 are for Tb^{4+} magnetic moments equal to 7 μ_B (theoretical value).

3. Results and discussion

3.1. α and β-$BaTbF_6$ fluorides

3.1.1. Nuclear structure

3.1.1.1. ***α–β****–$BaTbF_6$:*. Neutron Powder Diffraction (NPD) patterns were recorded on the G4-1 diffractometer in the temperature range 1.4–5 K. The nuclear structure of β-$BaTbF_6$ at 5 K was refined on the basis of the model determined from single-crystal X-ray diffraction [8], leading to conventional R_{Bragg}=3.0% (Table 1). Refined atomic coordinates, in good agreement with those obtained from single-crystal X-ray data, are presented in Table 2. The crystal structure of β-$BaTbF_6$ is built of infinite $[TbF_6]^{2-}$ linear chains arising from $[TbF_8]^{4-}$ polyhedra sharing opposite and almost orthogonal edges. These chains adopt a