Experimental report

13/02/2019

Proposal: 5-31-2575 **Council:** 4/2017

Title: Study of spin reorientation transitions in TmCr1-xFexO3 perovskites (x = 0.6-0.9) by neutron powder diffraction

Research area: Materials

This proposal is a new proposal

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Samples: TmCr0.4Fe0.6O3
TmCr0.3Fe0.7O3
TmCr0.1Fe0.9O3
TmCr0.2Fe0.8O3

Instrument	Requested days	Allocated days	From	To
D1B	0	2	24/03/2018	26/03/2018
D2B	2	2	21/03/2018	23/03/2018
D20	2	0		

Abstract:

Multiferroic and magnetoelectric materials have gained notoriety due to potential technological applications. Recently, a study on weakly ferromagnetic perovskite system YCr1-xMxO3 (M= Fe or Mn) found ferroelectricity induced by disordered cations of non-equivalent spins at B-site. This holds interesting possibilities for the design of new materials. As a first approximation of tuning transition temperatures in this system, we synthesized four novel simple perovskites TmCr1-xFexO3 with x= 0.6-0.9. Structural characterization was performed with XRPD at room temperature using Rietveld refinement. All samples are orthorhombic and belong to Pbnm space group. Magnetic susceptibility versus temperature was measured. Magnetic order begins at TN < Tamb for all samples. As temperature decreases, a complex magnetic behaviour appears. There is a marked susceptibility increase around 120 K, followed by a sharp decrease. This behaviour is usually associated with a spin reorientation transition, which consists in a shift in the easy axis of the magnetic coupling. We aim to closely follow this transition using both high intensity and high resolution neutron powder diffraction.

Introduction

A ferroelectric material exhibits a stable and switchable electrical polarization (P). A ferromagnetic material exhibits a stable and switchable magnetization. Multiferroic materials exhibit both properties, and they have recently gained notoriety due to their possible technological applications. The broader category of magnetoelectric materials, whose properties are coupled whatever the order parameters are, is also of great interest **[1]**. In a study by Rajeswaran et al. on the weakly ferromagnetic perovskite system $YCr_{1-x}M_xO_3$ (M = Fe or Mn) it was found that ferroelectricity can appear by disordered cations of non-equivalent spins at the B-site **[2]**. This type of ferroelectricity has been recently discovered and shows a strong correlation between changes in magnetic ordering and the appearance of the ferroelectric phase **[3]**, which highlights the importance of a detailed knowledge of the magnetic structure. When the A cation is a paramagnetic rare-earth cation a new phenomenon appears, called spin reorientation (SR). This phenomenon consists in a shifting of the easy axis of the magnetic coupling. We synthesized the perovskites with formula $TmCr_{1-x}Fe_xO_3$ with x = 0.6, 0.7, 0.8, and 0.9 to assess the effects of substitution in magnetic properties and its consequent magnetic structure. The perovskite $TmCr_{0.5}Fe_{0.5}O_3$ has already been reported by our group **[4]**, displaying correspondence between the magnetic transitions observed in magnetization measurements and the magnetic structures observed by means of NPD. Our main goal was to probe if this correspondence was maintained along the Fe-rich part of the family, and to properly determine the magnetic structure at each temperature, which is of great importance when assessing potential magnetoelectric couplings.

Experimental

We synthesized the novel series of simple perovskites with formula $TmCr_{1-x}Fe_xO_3$, with x = 0.6, 0.7, 0.8, and 0.9. Preliminary structural characterization was performed with XRPD at room temperature using Rietveld refinement. All samples are orthorhombic and belong to the space group *Pbnm* as expected. The experiments performed under proposal 5-31-2575 were aimed at the proper determination of magnetic structures for all samples. The goal was to use **D2B** to precisely determine the magnetic structures at temperatures far from magnetic transitions, and then follow the transitions with temperature-dependent data obtained in **D1B**. **D2B** measurements were carried out at different temperatures depending on the sample, being RT and 2K the only temperatures measured for all samples. Five patterns were obtained for $TmCr_{0.1}Fe_{0.9}O_3$, four for $TmCr_{0.3}Fe_{0.7}O_3$, and three for both $TmCr_{0.2}Fe_{0.8}O_3$ and $TmCr_{0.4}Fe_{0.6}O_3$. All patterns were collected with λ = 1.594 Å. On the **D1B** instrument, temperature dependent diffraction data was collected for all the samples, within temperature ranges also depending on the magnetic transitions observed in each sample. Patterns were collected both while cooling and warming the samples in order to maximize data output. In this instrument, all patterns were collected with λ = 2.52 Å.

It is worth noticing an issue that was encountered during measurements in the **D2B** instrument. During the night of March 21st 2018, the readings in the instrument computers appeared to show a complete stop in data storage, which led us to modify the experiment being carried out in order to compensate the possible losses. We were later informed that there was a general issue with the *serdon* system which did not avoid information storage. The issue was resolved without data loss, resulting in approximately an hour of measurement reprogrammed. The assistance of the local contacts was fundamental for the reprogramming and solution of the problem.

Results and discussion

To exemplify the obtained results, we will focus on one of the samples ($TmCr_{0.1}Fe_{0.9}O_3$) and the observations made possible by the combination of data from both instruments. For reference, the magnetic behaviour of this sample is represented in its magnetization as a function of temperature, shown in **Figure 1** for both its ZFC and FC modes. We were able to obtain similarly corresponding results for the remaining samples in the proposal.

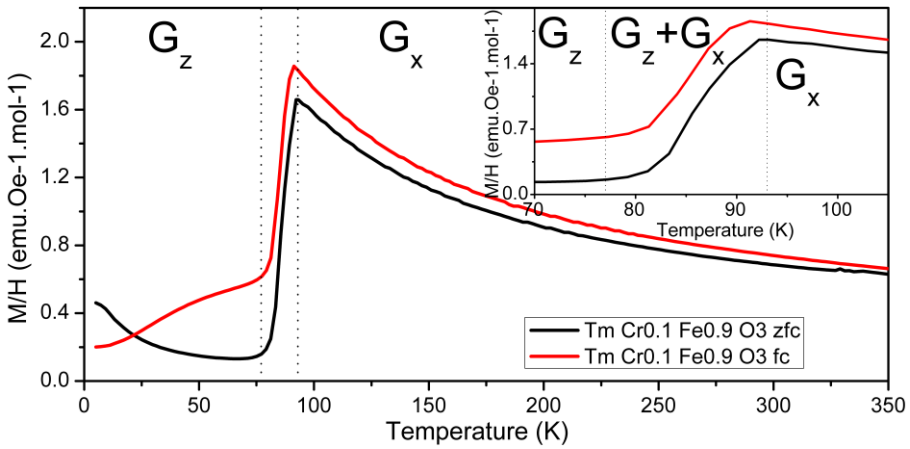

Figure 1) ZFC and FC magnetization as a function of temperature for $TmCr_{0.1}Fe_{0.9}O_3$. Dashed lines indicate the beginning and end of SR transition. Inset shows a smaller temperature range focused on the SR transition. Each region is characterized with capital letters indicating the type of magnetic structure observed.

As mentioned before, all NPD data confirmed that the space group *Pbnm* is suitable for the description of the structure. Within this space group, the interpretation of magnetic structures with propagation vector $\boldsymbol{k}$ = (0, 0, 0) can be performed using the formalism enunciated by Bertaut **[6]**. Essentially, all the magnetic structures observed can be defined solely by using different G-type arrangements within the transition metal (Cr^{3+}/Fe^{3+}) sublattice. **Figures 2a** and **2b** show NPD patterns from D2B for $TmCr_{0.1}Fe_{0.9}O_3$ at two different temperatures, above (98 K) and below (60 K) the transition temperatures indicated in the magnetization in **Figure 1**. In **Figures 2a** and **2b** we also show the Rietveld refinement results. The magnetic structures refined belong to the Gx and Gz antiferromagnetic arrangements respectively. In Figure 2c we show a comparison between NPD at 60 K and 2 K, together with a plot of the difference between them. Since the patterns are almost superimposable in the whole 2θ range, we assume there are no further changes in the long-range magnetic order below the first SR reorientation transition. This shows some differences with respect to previous reports in the related $TmCr_{0.5}Fe_{0.5}O_3$ perovskite, which does show long range ordering of the lanthanide sublattice **[4]**.

D1B data allowed us to follow the SR closely. Two graphs are included in **Figure 3**, with two different plots of the temperature dependent diffraction data. The change in the intensity of the first two peaks is indicative of the spin reorientation transition. By refining these individual patterns separately, we could generate **Figure 4**, that indicates the component of the magnetic moments in the transition metal sublattice as a function of temperature.

Conclusions

The preliminary analysis of the data is very promising, as we have achieved our goal of obtaining both high resolution and high intensity NPD data. This allowed us to fully characterize the magnetic structure before, after and during a complex magnetic transition.

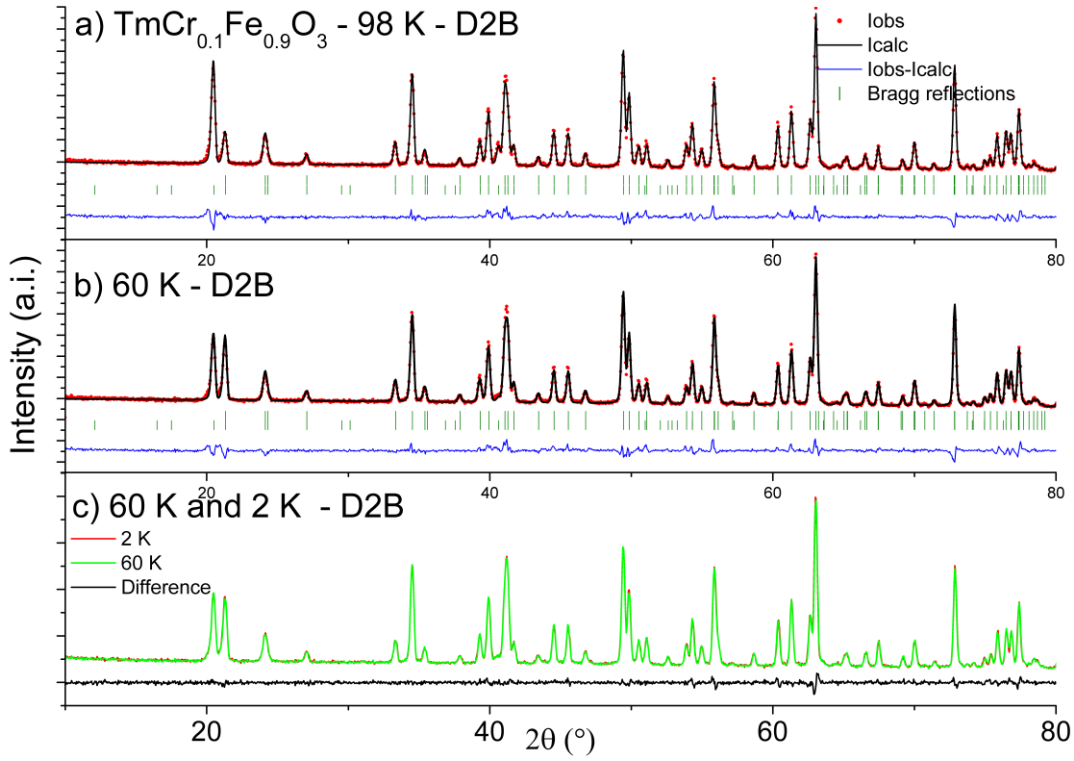

Figure 2) D2B NPD patterns for $TmCr_{0.1}Fe_{0.9}O_3$ at 98 K **(a)**, 60 K **(b)**, and a comparison between 2 K and 60 K **(c)**.

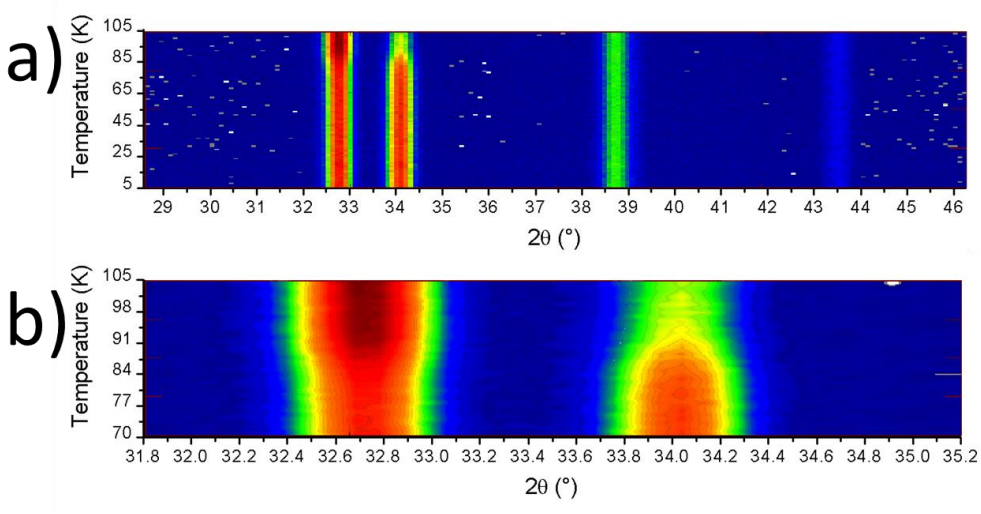

Figure 3) D1B temperature dependent NPD patterns for $TmCr_{0.1}Fe_{0.9}O_3$.

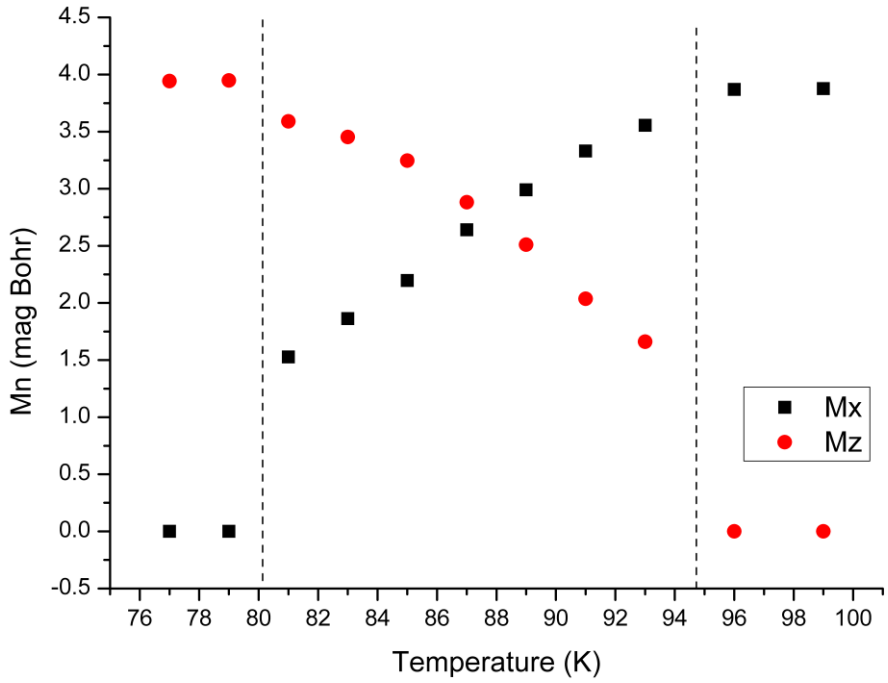

Figure 4) Refined magnetic moments for the Cr^{3+}/Fe^{3+} sublattice during the SR transition.

[1] Eerenstein, W. Multiferroic and magnetoelectric materials. *Nature* **442**, 759-765 (2006).
[2] Rajeswaran, B. et al. Ferroelectricity induced by cations of non-equivalent spins disordered in the weakly ferromagnetic perovskites, $YCr_{1-x}M_xO_3$ (M = Fe or Mn). *Chem. Mater.* **24**, 3591-3595 (2012).
[3] Bousquet, E. et al. Non-collinear magnetism in multiferroic perovskites. *J. Phys.: Condens. Matter* **28**, 123001 (2016).
[4] Pomiro, F. et al. Spin reorientation, magnetization reversal, and negative thermal expansion observed in $RFe_{0.5}Cr_{0.5}O_3$ perovskites (R=Lu,Yb,Tm). *Phys. Rev. B: Condens. Matter* **94**, 134402 (2016).