Experimental report

17/02/2020

Proposal: 5-31-2689 **Council:** 4/2019

Title: Study of spin reorientation transitions in TmCr1-xFexO3 perovskites (x = 0.1-0.4) by neutron powder diffraction

Research area: Chemistry

This proposal is a continuation of 5-31-2575

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

Instrument	Requested days	Allocated days	From	To
D1B	2	2	13/01/2020	15/01/2020
D2B	2	2	15/01/2020	17/01/2020

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. We have previosly studied related perovskites with formula TmCr1-xFexO3 with x= 0.5-0.9. We now aim to complete the characterization of the compositional range by studying perovskites TmCr1-xFexO3 with x= 0.1-0.4. Structural characterizationwas 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. Samples with x = 0.1 and 0.2 behave differently than samples with x = 0.3 and 0.4, which might suggest a difference in the observed magnetic structures. We aim to closely follow the observed magnetic transitions using both high intensity and high resolution neutron powder diffraction.

Preliminary experimental report on proposal 5-31-2689

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 possible technological applications. The broader category of magnetoelectric materials, where are coupled whatever the order parameters are, is also of great interest **[1]**. In a recent study 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 shows a strong correlation between changes in magnetic ordering and appearance of the ferroelectric phase **[3]**, which highlights the importance of a detailed knowledge of the magnetic structure. In this type of perovskites, when the A cation is a magnetic rare-earth cation, a phenomenon called spin reorientation appears, which consists in a shift of the easy axis of the magnetic ordering. These transitions change the magnetic symmetry of the material, which may be relevant to different magnetoelectric phenomena.

With this problematic in mind, we have previously explored some related perovskites with formula $TmCr_{1-x}Fe_xO_3$ (x = 0.5, 0.6, 0.7, 0.8, and 0.9) in different ILL experiments, at instruments D1B and D2B (Proposal 5-31-2575 **[4]**). In that experiment, we found different magnetic structures at different temperatures, in strong accordance to what was observed in magnetization data. In addition, results for $TmCr_{0.5}Fe_{0.5}O_3$ have already been published by our groups too **[5]**. In turn, these findings prompted us to present a second proposal (Proposal 5-31-2689 **[6]**), covering the Cr-rich region of this compositional space. Namely, the studied compounds in this second proposal were $TmCr_{1-x}Fe_xO_3$ (x = 0.1, 0.2, 0.3, 0.4, and 0.5), and this preliminary experimental report will provide some initial findings. This set of NPD experiments is very recent (Jan-2020) and the data analysis is far from complete. The information hereby provided may be subject to later revision.

Experimental

We synthesized the novel series of simple perovskites with formula $TmCr_{1-x}Fe_xO_3$, with x = 0.1, 0.2, 0.3, and 0.4. 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 5-31-2689 were aimed at the determination of magnetic structures for all samples at different temperatures. In the **D2B** instrument, between three and five NPD patterns were obtained for each sample, including one measurement at room temperature for each sample. 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 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. For some samples, "static" measurements at constant temperatures were also performed to take advantage of the very high flux available in D1B. As it will be seen later, this proved to be of utmost importance for magnetic structure determination. In this instrument, most NPD patterns were collected with λ = 2.52 Å. There was some extra data collected at λ = 1.28 Å, but the lower intensity and shorter wavelength were both detrimental to magnetic structure refinement.

As stated in the "User Satisfaction Form", an issue that was encountered during measurements in the **D1B** instrument. In the night of January 13th, 2020, during a wavelength change assisted by one of the local contacts, there was a "filter position" error that resulted in noisy background-type data. Control room personnel was made aware of the situation, but their revision found either no problem with the shutter nor a solution for the error.

Posterior tests with the controlling software allowed to reset the position of the "filter". All these tests, examinations and changes took around 2 hours of measuring data from the allocated time of 48 hours in D1B.

Results and discussion

As a preliminary insight on the results of these experiments, the data for samples $TmCr_{0.9}Fe_{0.1}O_3$ and $TmCr_{0.6}Fe_{0.4}O_3$ will be discussed.

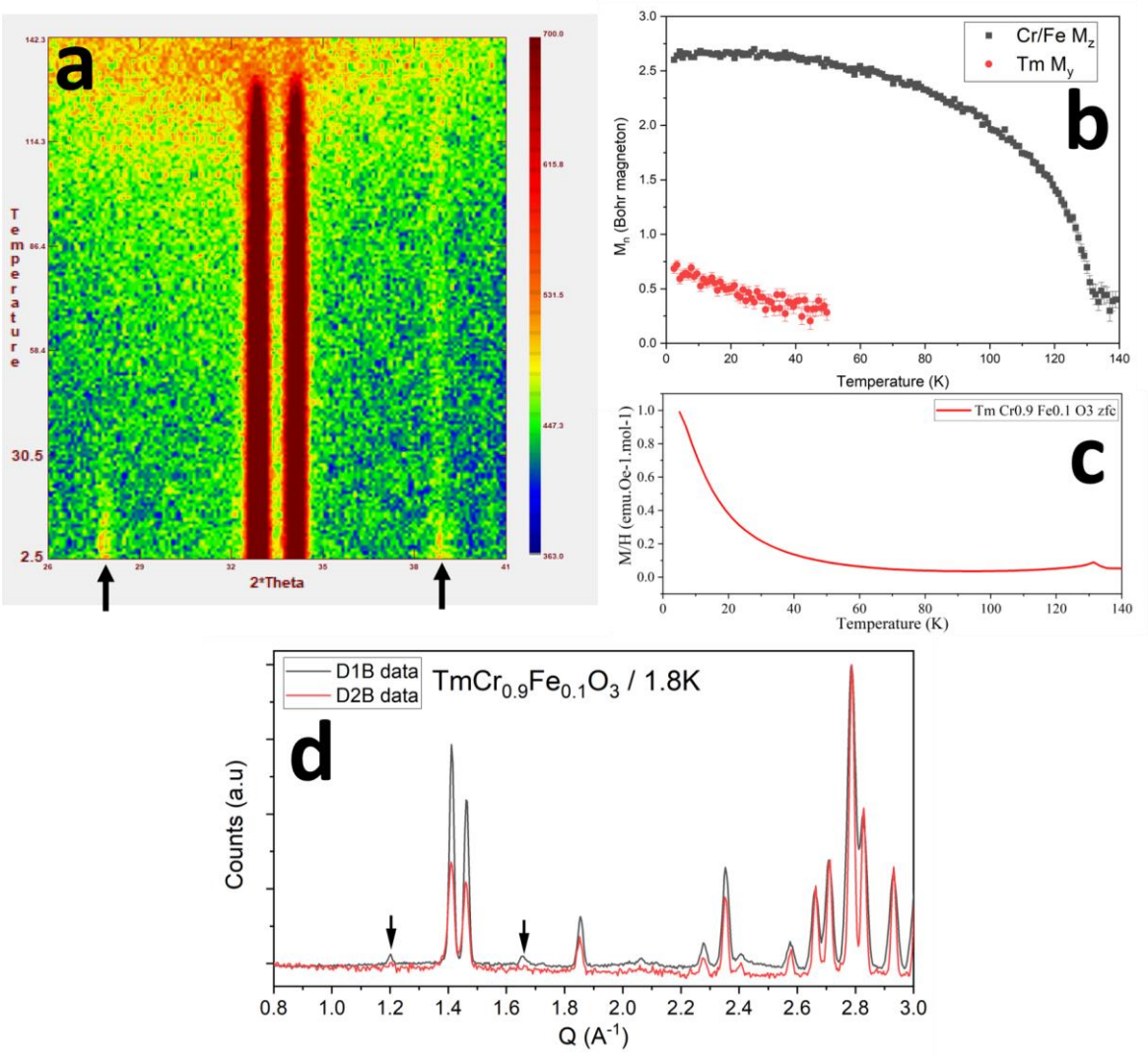

Figure 1.a) Low angle region of thermodiffraction from D1B for $TmCr_{0.9}Fe_{0.1}O_3$. **b)** Refined magnetic moments for Cr^{3+}/Fe^{3+} and Tm^{3+} as a function of temperature. **c)** Zero Field Cooling magnetization as a function of temperature. **d)** Comparison between D1B (45 minutes) and D2B (3 hours) data at 1.8 K.

In the low angle region of the thermodiffraction for $TmCr_{0.9}Fe_{0.1}O_3$ two very strong peaks due to the magnetic structure appear around 2θ 32-35º. The main contribution to these peaks is a G-type ordering along the z-axis of the magnetic moments of the transition metals (**1.b**). The appearance of this magnetic moment matches the transition temperature observed in the ZFC magnetization data at approximately 130 K (**1.c**). At low temperatures, there are two much smaller peaks that have clear magnetic contributions due to their increased

intensities at low temperatures. From a first refinement of these peaks, a magnetic component of the lanthanide sublattice can be inferred, which is also shown in Figure **1.b**. These magnetic moments arrange in a C-type ordering along the y-axis, defined in the same magnetic space group as the ordering of the transition metal sublattice. However, the value of this magnetic moments are small, decrease swiftly with the increase in temperature and also have a high associated error due to the low relative intensity of the characteristic peaks. As shown in Figure 1.d, these peaks can only be seen under a high neutron flux, as they do not appear in high resolution D2B data, even with a much longer counting time. No spin reorientation transitions were detected in this sample. These observations are similar to previous reports on the related $TmCrO_3$ **[7]**.

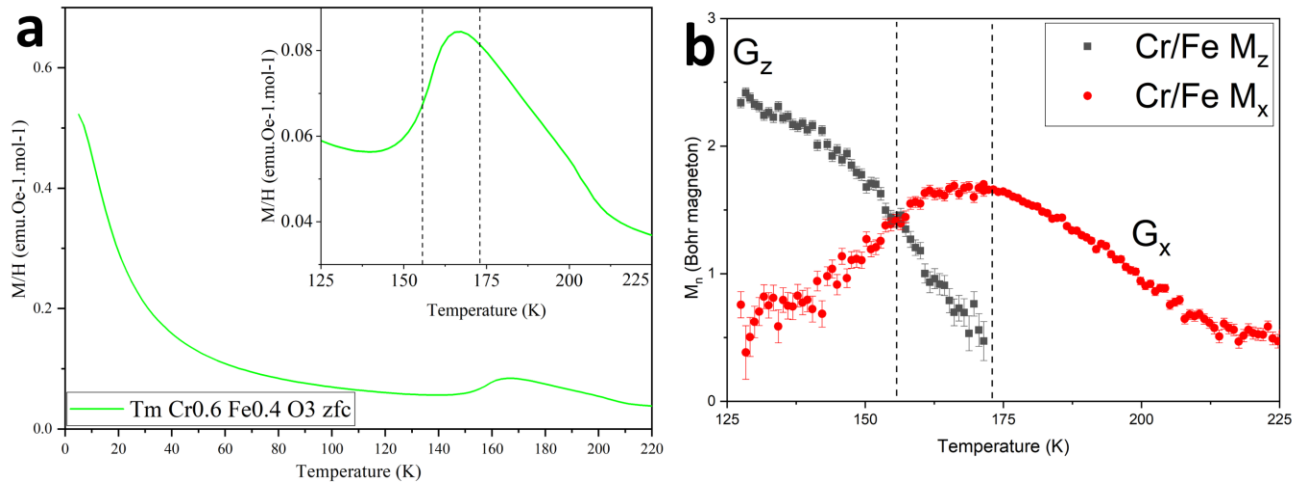

Figure 2.a) Zero Field Cooling magnetization as a function of temperature for $TmCr_{0.6}Fe_{0.4}O_3$. **b)** Refined magnetic moment components for Cr^{3+}/Fe^{3+} as a function of temperature for $TmCr_{0.6}Fe_{0.4}O_3$.

$TmCr_{0.6}Fe_{0.4}O_3$ presents a different case. By refining the D1B NPD data, the magnetic moment components of the transition metal sublattices could be extracted, and are shown in Figure 2 along the magnetization data. As it can be seen, the magnetic transition temperatures match the change in the relation of intensity of the components of magnetic moment, which is typical of a spin reorientation transition. N this particular case, a G-type ordering is kept along the transition, but it shifts from the x-axis to the z-axis as the temperature is lowered. This material also presented the two very small peaks observed in $TmCr_{0.9}Fe_{0.1}O_3$ but with a lower intensity and disappearing at lower temperatures. Clearly the introduction of Fe produces strong changes in the magnetic behaviour.

As a first preliminary conclusion, the two "extreme" compositions in the Cr-rich region of the $TmCr_{1-x}Fe_xO_3$ system display radically different behaviours. We are confident that further analysis of the obtained data will reveal the intricacies of the magnetic structures of these materials.

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[4] Carbonio, R.E. et al, Proposal 5-31-2575: Study of spin reorientation transitions in $TmCr_{1-x}Fe_xO_3$ perovskites (x = 0.6-0.9) by neutron powder diffraction (2018), *Institut Laue-Langevin (ILL)*, 10.5291/ILL-DATA.5-31-2575.
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