

Experimental report

01/02/2024

Proposal: 5-41-1187

Council: 10/2022

Title: Magnetic structure and phase diagram in giant magnetocaloric TmFeO₃

Research area: Physics

This proposal is a new proposal

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Samples: TmFeO₃

Instrument	Requested days	Allocated days	From	To
ORIENTEXPRESS	1	1	03/04/2023	04/04/2023
D23	8	6	04/04/2023	10/04/2023

Abstract:

The interest on rare-earth orthoferrites RFeO₃ has been regained recently, because of the discovery of their multiferroic properties at high temperatures and the giant magnetocaloric effect in some of them. TmFeO₃ is one of the less studied representatives of RFeO₃ family with a complex and interesting magnetic behaviour. It has strong magnetocaloric anisotropy along a and b axes. It shows Gamma₄->Gamma₂ magnetic phase transition in temperature range 82 - 93 K. Dzyaloshinsky-Moria interaction in it causes presence of ferromagnetic component in addition to main antiferromagnetic contribution. We propose to examine magnetic structure evolution with temperature under different external magnetic fields of TmFeO₃. We expect to map a comprehensive magnetic phase diagram of TmFeO₃ for the first time. We ask for 8 beam days on D23 using a high field magnet.

Magnetic structure and phase diagram in giant magnetocaloric TmFeO₃

Experimental report for proposal no 5-41-1187 (D23 and OrientExpress)

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TmFeO₃ crystallizes in the orthorhombic Pbnm crystal structure with $a = 5.251 \text{ \AA}$, $b = 5.576 \text{ \AA}$, and $c = 7.584 \text{ \AA}$. Below $T_{N,Fe} = 650 \text{ K}$ the magnetic moments of iron are oriented according to the Pb'n'm magnetic space group, i.e. the Γ_4 irrep of the Pbnm space group corresponding to the $\mathbf{G}_x\mathbf{A}_y\mathbf{F}_z$ mode in Bertaut notation. At $T_{SR,Fe} \approx 90 \text{ K}$ a reorientation of the iron spins occurs and Fe³⁺ magnetic moments become oriented according to the Pbn'm' magnetic space group, i.e. the Γ_2 irrep corresponding to $\mathbf{F}_x\mathbf{C}_y\mathbf{G}_z$ mode. The thulium subsystem has no own magnetic order down to 1.6 K [1]. The large maximum of magnetic entropy change of $\Delta S = 12 \text{ J/kg K}$ was observed at a temperature around $T = 17 \text{ K}$ and in a field $B = 0 - 7 \text{ T}$ along the c axis [2]. ΔS for a and b axes are about one order of magnitude smaller than those along the c axis in the whole temperature range which indicates a strong magnetocaloric anisotropy.

We performed neutron diffraction on a TmFeO₃ single crystal on the D23 instrument as a function of temperature and magnetic field using two sample orientations: with magnetic field along a and c axis. Both sample orientations were checked using OrientExpress neutron Laue camera. For both sample orientations we measured all on D23 accessible Bragg reflections at 20 K without magnetic field.

Furthermore, we performed scans at 20 K for selected peaks with increasing and decreasing magnetic field up to 5.8 T. We did not observe a hysteresis with magnetic field applied along the a axis, but observed a hysteresis of some peaks with magnetic field applied along the c axis, i.e. the giant magnetocaloric axis. The biggest hysteresis was observed for G(0,-3,1) peak, see Fig. 1a, and a smaller hysteresis was observed for G(0,1,1), G(0,-1,1), A(0,-4,1), A(0,-2,1), and F(0,-2,2) peaks (not shown here).

Based on our measurements of selected reflections we confirm that the Fe³⁺ $\Gamma_4 \rightarrow \Gamma_2$ spin reorientation takes place between 82 K and 93 K without external magnetic field, see Fig. 1b. The magnetic field couples to the weak Fe³⁺ ferromagnetic component, which results in that applying magnetic field along a or c axis increase or reduce (Fig. 1c) spin reorientation transition temperature, respectively.

Below 40 K and above 3 T we also observed peak shifts in the omega angle from the centre of the scan window determined at 20 K without magnetic field. We interpret this as a magnetostriction effect. The amplitude of this shift strongly depends on the hkl indices and varies between the two magnetic field directions. For the magnetic field along the a axis we observed positive shifts for all investigated reflections with significantly higher shifts for F(1,1,0), A(1,1,3), and C(102) peaks. For the magnetic field along the c axis peaks with positive k and l show positive shift, while peaks with negative k and positive l show negative shift. It may be a manifestation of symmetry lowering, but this should be investigated in the future.

Furthermore, we noticed different evolutions of peak intensities if magnetic fields are applied along the a or c axis. For each measured temperature for $a || H$ with increasing field all measured peaks intensities remain constant or increase/decrease monotonically respectively,

while for $c \parallel H$, some peaks intensities show local minima or maxima around 0.5 – 2 T, see Fig. 1d. For $a \parallel H$ the biggest changes in peak intensities were observed for C(1,0,2), A(0,-2,1). In comparison with $c \parallel H$ the intensity changes of C(1,0,2) and A(0,-2,1) are much smaller and much stronger, respectively. Based on the evolution of intensities of the magnetic peaks we expect to be able to reconstruct the magnetic phase diagram of TmFeO₃ with magnetic fields along a and c axes, respectively.

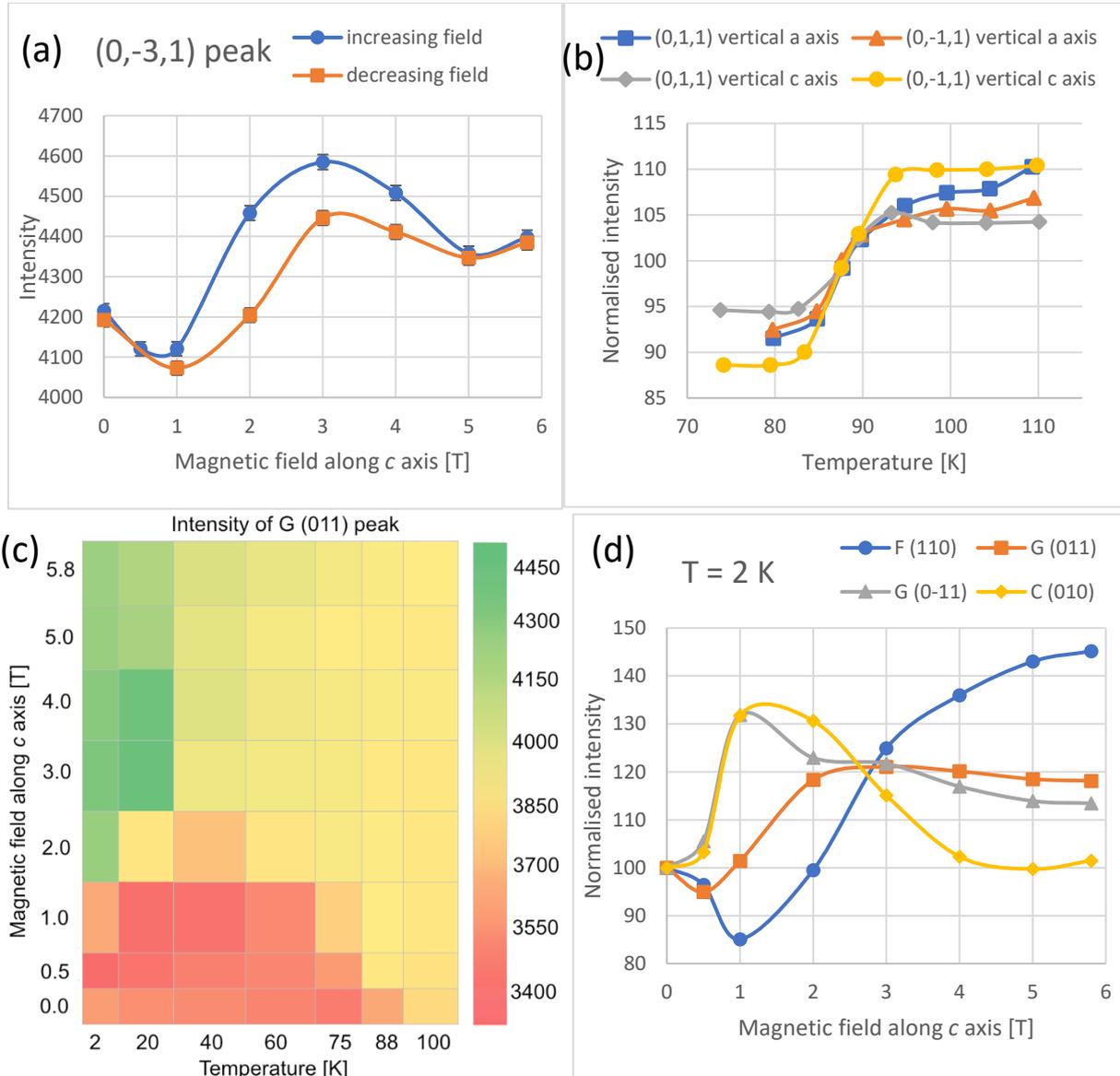


Fig. 1: (a) Hysteresis of G type (0,-3,1) peak intensity in magnetic fields along the c axis at 20 K. Error bars are of the size of the symbols. (b) Normalised intensities of G type (0,1,1) and (0,-1,1) peaks measured with two sample orientations showing a $G_x \rightarrow G_z$ spin reorientation of the Fe³⁺ magnetic moment. Error bars are smaller than symbols. (c) Heatmap of the G(0,1,1) peak intensities as a function of temperature and magnetic field along c axis. (d) Intensities of selected peaks at 2 K as a function of applied magnetic field along the c axis. Error bars are of the size of or smaller than the symbols themselves.

References:

- [1] J. A. Leake, G. Shirane, and J.P. Remeika; *Solid State Commun.* **6** (1968) 15
- [2] Y.-J. Ke, et al.; *Sci. Rep.* **6** (2016) 19775
- [3] E. F. Bertaut, *Acta Cryst. A* **24** (1968) 217