Experimental report

03/04/2019

Proposal: **5-31-2549** **Council:** 4/2017

Title: COMPETING ANISOTROPIES IN AF CONICAL Mn1-xMxWO4 MULTIFERROICS

Research area: Materials

This proposal is a new proposal

Main proposer: **Jose Luis GARCIA MUNOZ**

Experimental team: XIAODONG ZHANG
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Arnau ROMAGUERA CAMPS

Local contacts: Clemens RITTER
Gabriel Julio CUELLO

Samples: Mn1-xNixWO4 (x=0.125, 0.18, 0.25)
Mn1-xFexWO4 (x=0.125, 0.23, 0.25)

Instrument	Requested days	Allocated days	From	To
D1B	0	0		
D20	3	3	20/04/2018	23/04/2018

Abstract:

MnWO4 is regarded as a reference spin-induced multiferroics, with the antisymmetric Dzyaloshinskii-Moriya (D-M) interaction governing the polar distortions. In Mn1-xCoxWO4, isotropic Mn2+-Mn2+ exchange interactions compete with the uniaxial Co magnetic anisotropy giving rise to a rich variety of magnetic phases that we have studied in detail in recent years. Of special interest is the stabilization of an AFM conical structure composed of a COM plus an ICOM modulations. Interestingly, for Co2+ the strong uniaxial magnetocrystalline anisotropy is almost perfectly perpendicular to the easy plane of Mn moments in Mn1-xCoxWO4 (where spiral ICOM order develops). So, the response of the ferroelectric conical phase to external magnetic fields along the easy and hard spin directions is being thoroughly investigated in different Mn-CoWO4 systems. But this geometry may be very different using other magnetic metals such as Ni2+ and Fe2+ instead of Co2+, for which the expected magnetic anisotropy is not perpendicular to the easy plane orientation of Mn2+ spins.

Experimental Report

Experiment n°:D20-5-31-2549

COMPETING ANISOTROPIES IN AF CONICAL Mn1-xMxWO4 MULTIFERROICS

Title: **COMPETING ANISOTROPIES IN AF CONICAL Mn1-xMxWO4 MULTIFERROICS**			**5-31-2549**
Proposer (to whom correspondence will be addressed)			
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Experimental Report

Proposal No: D20-5-31-2549
Title: COMPETING ANISOTROPIES IN AF CONICAL Mn1-xMxWO4 MULTIFERROICS
Instrument: D20
Local Contact: RITTER Clemens, CUELLO Gabriel Julio
From :20/04/2018 To :23/04/2018
Experimentalists: Xiaodong Zhang, Arnau Romaguera, Jose Luis Garcia-Muñoz

Abstract:
MnWO4 is regarded as a reference spin-induced multiferroics, with the antisymmetric Dzyaloshinskii-Moriya (D-M) interaction governing the polar distortions. In Mn1-xCoxWO4, isotropic Mn2+-Mn2+ exchange interactions compete with the uniaxial Co magnetic anisotropy giving rise to a rich variety of magnetic phases that we have studied in detail in recent years. Of special interest is the stabilization of an AFM conical structure composed of a COM plus an ICOM modulations. Interestingly, for Co2+ the strong uniaxial magnetocrystalline anisotropy is almost perfectly perpendicular to the easy plane of Mn moments in Mn1-xCoxWO4 (where spiral ICOM order develops). So, the response of the ferroelectric conical phase to external magnetic fields along the easy and hard spin directions is being thoroughly investigated in different Mn-CoWO4 systems. But this geometry may be very different using other magnetic metals such as Ni2+ and Fe2+ instead of Co2+, for which the expected magnetic anisotropy is not perpendicular to the easy plane orientation of Mn2+ spins.

Measurements were made on samples Mn1-xMxWO4 mainly at low temperatures using wavelengths 2.41 and 1.54 Å, with emphasis within the temperature range 1.5K - 100 K. In general the samples were measured at different fixed selected temperatures (20 or 40 min patterns for the 2.41 Å configuration), and also in dynamic mode by means of temperature ramps with heating rates of mostly 0.5K/min.

Three different types of magnetic phases were detected at low temperatures in the samples, (i) the collinear AF4 order inherent to the pure wolframites MWO_4 (M:Ni, Fe, Co), characterized by the translational symmetry **k4**= (1/2, 0, 0); (ii) the incommensurate AF2 cycloidal order associated to the generation of electrical polarization and ferroelectricity in these improper Fes, and characterized by the magnetic propagation vector **k**2=(ε, 1/2, -2ε) (ε incommensurate); (iii) the third observed phase is the non-FE and commensurate collinear order AF1, with characteristic propagation vector **k**1=(1/4, 1/2, -1/2).

Interestingly, the magnetic and FE properties strongly differ when Mn^{2+} is substituted by the isovalent cations Ni^{2+} , Fe^{2+} or Co^{2+}, but in spite of this, conical FE phases (initially described in $Mn_{1-x}Co_xWO_4$ for x≥0.15 in ref. 8) have been observed in a variety of compositions.

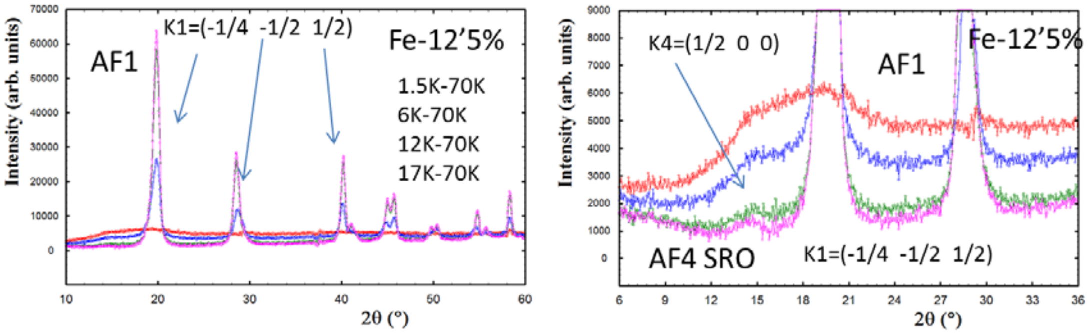

Fig. 1. *(L) Magnetic intensities plotted as "difference plots" as indicated in the inset for* $Mn_{0.875}Fe_{0.125}WO_4$. *(R) Detail showing the presence of SRO magnetic order of AF4 type coexisting with the AF1 phase in* $Mn_{0.875}Fe_{0.125}WO_4$.

In $Mn_{1-x}Fe_xWO_4$ with x=0.125 and 0.25 we did not observe conical order. On cooling the sample $Mn_{0.75}Fe_{0.25}WO_4$ (Fe-0.25) the AF4 collinear phase appears first (at 17K), and then, below 8 K there is coexistence of AF4 and AF1. Decreasing the Fe content the AF1 phase dominates over the AF4, whose presence only occurs in short-range-order (SRO) form in $Mn_{0.875}Fe_{0.125}WO_4$. In the latter, strong magnetic reflections with **k**1=(1/4, 1/2, -1/2) develop below 15 K.

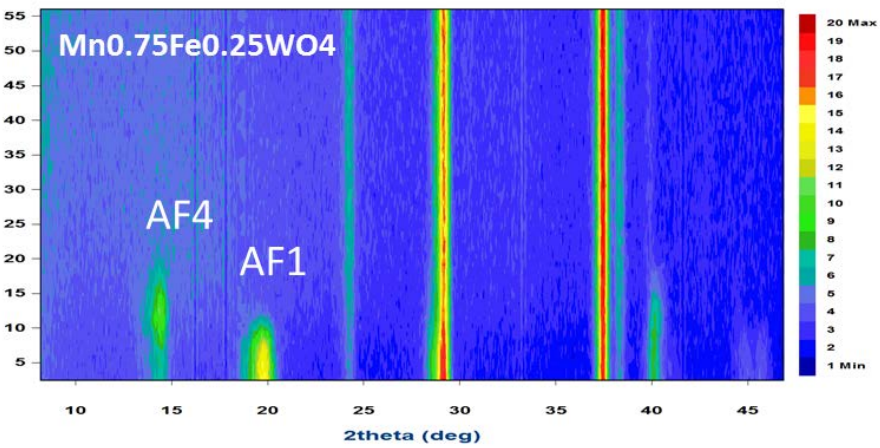

Fig. 2. *(a) Intensity evolution in* Mn0.75Fe0.25WO4 *showing the emergence of commensurate AF4 (k4=(1/2 0 0)) reflections that coexist with AF1 collinear order below 8K. Both commensurate spin orders are collinear.*

Very different is the magnetic competition in $Mn_{1-x}Ni_xWO_4$ samples. In contrast to the Fe substitution the presence of FE conical phases were detected in different compositions. In particular there are conical FE phases with compositions x≥0.12 (such as x=0.125, 0.18, 0.25, .). The AF4 collinear phase (**k4**= (1/2, 0, 0)) appears at ~45K in $Mn_{0.75}Ni_{0.25}WO_4$ and below ~15K a multi-k structure with coexistence of COM (AF4) and ICOM order (AF2, **k**2=(ε, 1/2, -2ε)) generates conical AFM order. In $Mn_{0.875}Ni_{0.125}WO_4$ the conical phase was detected below 13 K.

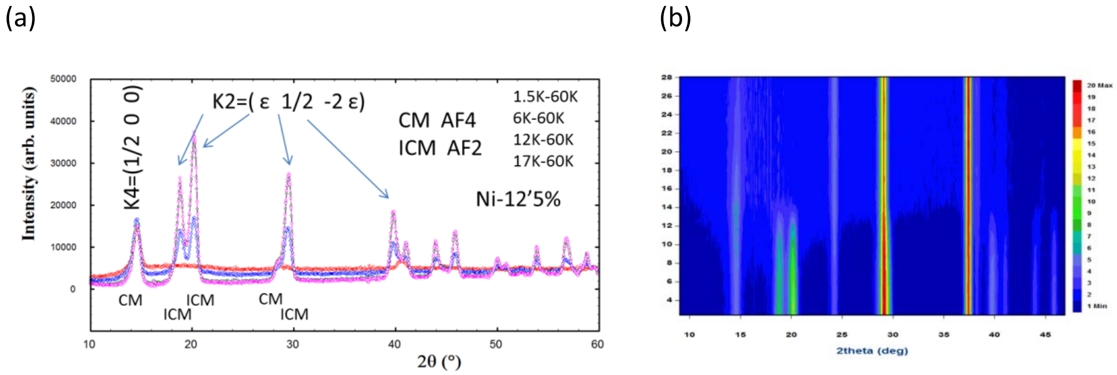

Fig. 3. *(a) Magnetic intensities plotted as "difference plots" as indicated in the inset for* $Mn_{0.875}Ni_{0.125}WO_4$*. (b) Intensity evolution in* $Mn_{0.875}Ni_{0.125}WO_4$ *showing the occurrence of conical order bellow 13 K.*

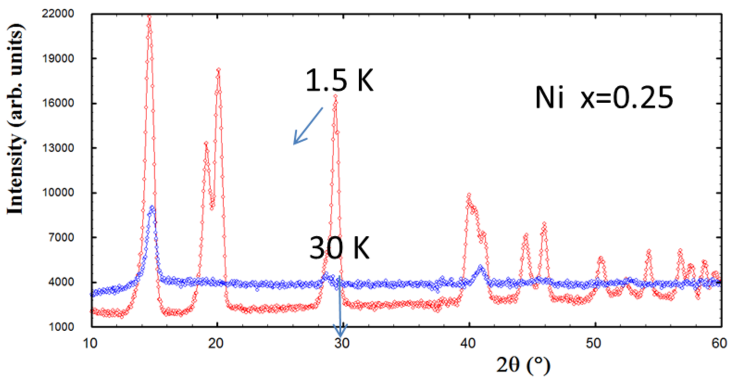

Fig. 4. *Coexistence of commensurate AF4 and incommensurate AF2 orders in* $Mn_{0.75}Ni_{0.25}WO_4$ *at low temperatures* (difference plots*).*

Additional details about the direction of the uniaxial magnetic anisotropy in the samples containing Ni2+ and Fe2+ cations respect to the easy plane orientation of Mn2+ spins, and its comparison with the practically perfect *transverse conical* ferroelectric orders in $Mn_{1-x}Co_xWO_4$ will be published elsewhere from the full analysis of the neutron data collected in this experiment.