Neutron diffraction studies of magnetic phase transition in mixed $(Mn_{1-x}Fe_x)WO_4$

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Abstract. Энэ ажилд Вольфрамитын кристалл болон соронзон бүтцийг рентген туяа, дулааны нейтроны сарнилын тусламжтайгаар судлав. Мөн $(Mn_{1-x}Fe_x)WO_4$-ийн бага температурт үүсэх соронзон фазын шилжилтийг ажиглаж, соронзон бүтцийг илэрхийлэх параметрүүдийг x=0; 6 утгуудад фаз бүрт тодорхойлон харьцуулав.

I. Introduction

A. The crystal structure of the mixed crystal $(Mn_{1-x}Fe_x)WO_4$

Ferberite $FeWO_4$ and huebnerite $MnWO_4$ are both members of family of divalent transition metal tungstates with small cations and they are isostructural, crystallize in the monoclinic space group P2/c and possess only small differences in lattice constants of about 1% [1-2]. Despite their very similar chemical structure the magnetic structures are quite different.

This family of AWO4 compounds (A=Mg, Mn, Fe, Co, Ni, Zn, Cd, Cu) adopts the wolframite structure, which may be thought of in terms of a distorted hexagonal close packed array of the oxygen ions (Fig.1).

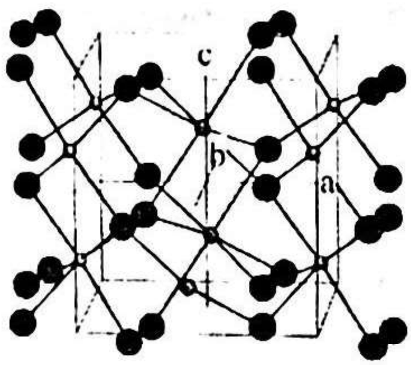


Fig.1. Structure of (Mn,Fe)WO_4, $(Mn/Fe)^{2+}$ions (small hatched circles) and the W^{6+} ioms (small circles) are surrounded by distorted oxygen (large circles) octahedra.

B. Magnetic structures of the mixed system $(Mn_{1-x}Fe_x)WO_4$

The $FeWO_4$ have a doubled magnetic unit cell (2a, b, c), whereas the magnetic unit cell of $MnWO_4$ at 4.2 K is 16 times that of the crystallographic structure with magnetic lattice constants 4a, 2b, 2c. The magnetic structure of ferberite and the huebnerite is displayed in Fig. 2 and Fig.3, respectively[3-4]. The collinear antiferromagnetic (AF) ground state of $FeWO_4$ below T_N =76 K is described by propagation vector k= (0.5, 0, 0) and the magnetic moments are inclined by about 26^0 to the *a*-axes in *ac*-plane (Fig. 2).
Recently the different magnetic phases of $MnWO_4$ were determined by neutron diffraction [5]. $MnWO_4$ has three antiferromagnetic phases AF1, AF2, and AF3 below 13.5K. These measurements confirmed that the collinear AF magnetic ground state AF1 of $MnWO_4$ occurring below 8 K can be described by a propagation vector k=(0.25, 0.5, 0.5). Similar to $FeWO_4$ the magnetic moments are again in the in *ac*-plane and they are inclined by about 37^0 to the *a*-axes. In addition two incommensurate (IC) phases with a propagation vector k=(-0.214, 0.5, 0.457) and with different orientation of the moments were observed between 8 K and 13.5 K

In the mixed system $(Mn_{1-x}Fe_x)WO_4$ two antiferromagnetic phases were observed simultaneously over the miscibility range 0.12<x<0.32 [6-7]. The magnetic Bragg intensities measured by neutron diffraction were related to the low temperature magnetic structure of $MnWO_4$ and to the magnetic structure $FeWO_4$ The occurrence of different magnetic phases in $MnWO_4$ and the coexistence of different magnetic structures in the mixed system $(Mn_{1-x}Fe_x)WO_4$ with low iron concentration motivated us to look in more detail at the magnetic phase transition by neutron diffraction.
Here we report on neutron diffraction studies at a $Mn_{0.94}Fe_{0.06}WO_4$ and natural sample of and natural $MnWO_4$ with very small concentration Fe.

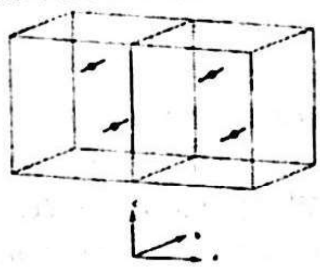


Fig.2 Magnetic unit cell $FeWO_4$

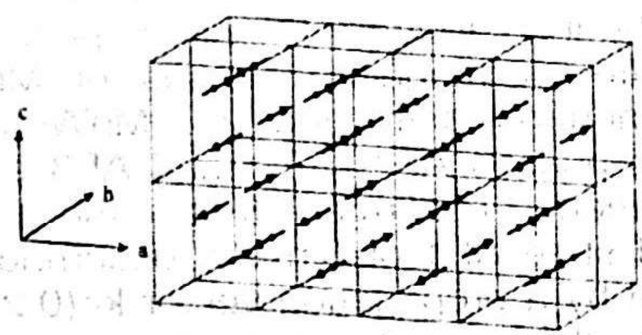


Fig.3 Magnetic unit cell of $MnWO_4$

II. Preparation and sample characterization

Two different powder samples of mixed $(Mn_{1-x}Fe_x)WO_4$ were used for our X-ray and neutron diffraction measurements. First was selected from $(Mn_{1-x}Fe_x)WO_4$ natural samples from Mongolia and was characterized by electron probe microanalysis (EPM). The EPM measurements were performed at 45 different positions on the sample. The average concentration of Mn and Fe was determined to be 99.980±0.001 and 0.020±0.001, respectively. The lattice parameters and occupation consent of Mn and Fe were determined by Rietveld analysis [8] from X-ray diffraction data which was collected out using powder diffractometer Siemens D500. X-ray diffractometer D500 can be controlled by computer, and is thus suited for fully automatic operation. Focusing is accomplished according to Bragg-Brentano. (Fig.4) The focus, the specimen, and the detector diaphragm are located on the focusing circle F; the focus and the detector diaphragm are also located on the measuring circle M.

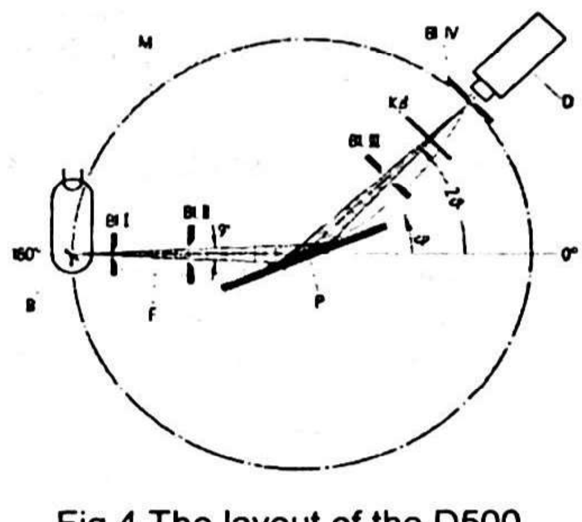


Fig.4 The layout of the D500

B	Focus of the x-ray tube	θ	Glancing angle
Bl.I,II,III	Aperture diaphragm	2θ	Diffraction angle
Bl.IV	Detector diaphragm	φ	Aperture angle
D	Detector	M	Measuring circle
Kβ	Kβ filter	F	Focusing circle
P	*Specimen*		

The X-ray powder diffraction data on $MnWO_4$ was studied at room temperature (RT). Refinement and structural parameters are displayed in Fig.5 and Table 1.

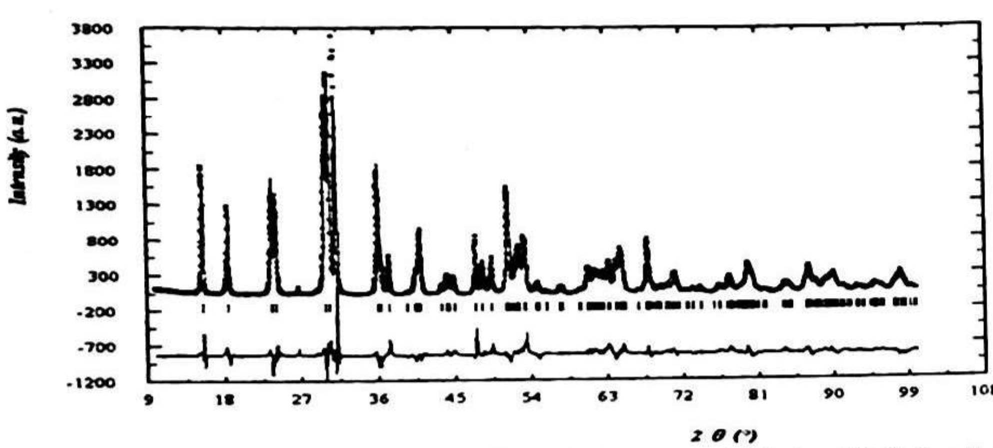


Fig.5 Powder X-Ray diffraction pattern (dots) and Rietveld fit (solid line) for natural $MnWO_4$ at RT together with difference plot

Table 1. Structural parameters of $MnWO_4$ obtained by Rietveld refinement

Lattice constants			
a	B	c	β
4.8253(2)	5.7524(3)	4.9967(1)	91.1231(5)
Positional parameters			
	X	y	Z
Mn	0.5000	0.6907(2)	0.2500
W	0.0000	0.1831(5)	0.2500
O_1	0.2321(3)	0.1458(1)	0.9136(4)
O_2	0.2412(4)	0.3711(8)	0.3998(3)
R factors: R_B=4.57, R_F=4.95			

Second sample was prepared by solid state reaction: appropriate portions of $MnWO_4$ and $FeWO_4$ were mixed and preheated at 1000C in inert gas for one hour. Then the preheated sample was ground and preheated two times at 1000 C for six hours. The powdered product was sintered at 1000 C for one week and finally quenched to room temperature. The composition was found to be $Mn_{0.94}Fe_{0.06})WO_4$ for the prepared sample.

III. Neutron diffraction experiments

All diffraction measurements were performed on the E6 diffractometer using a in double focusing pyrolytic graphite monochromator at wavelength λ_n =2.4 E in the temperature range between 1.5 and 17 K. The neutron diffractometer E6 at the Hahn-Meitner Institute, Berlin is a focusing single crystal diffractometer which cam is also applied for powder diffraction data. The banana-type BF_3 detector with 200 channels covers 20^0 in 2θ-range. The layout of E6 is displayed in Fig.5

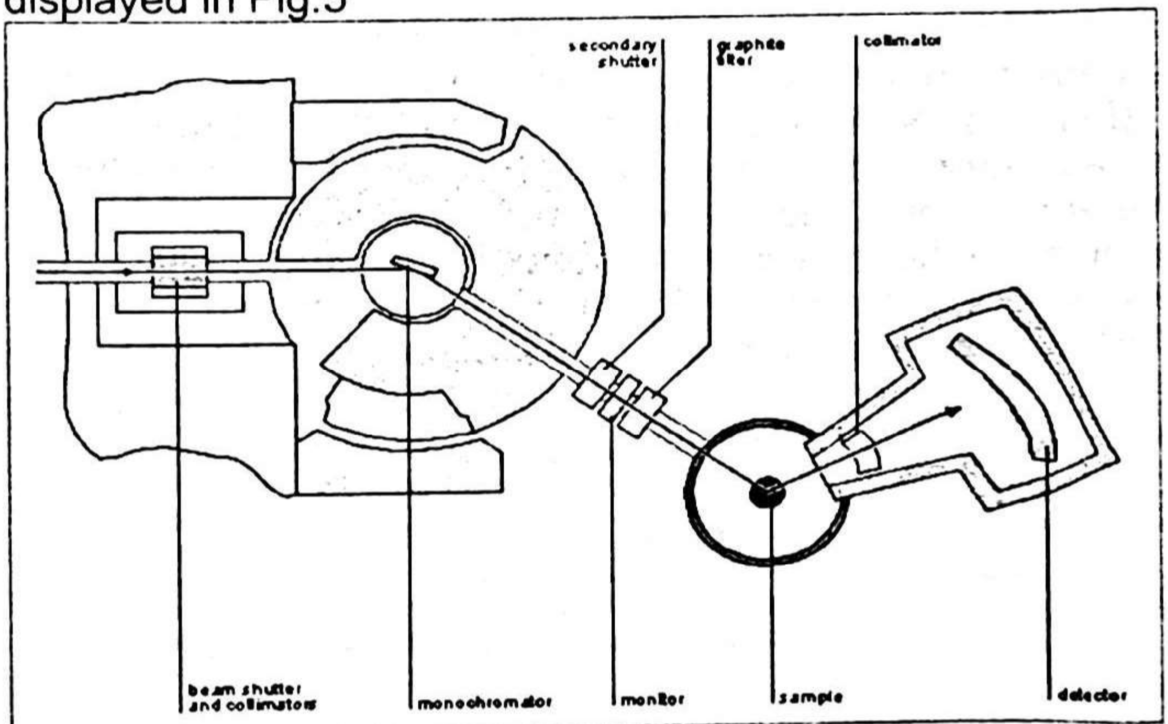


Fig.5. The layout of the E6

The diffraction pattern was collected in the 2θ range 10^0 and 90^0. Rietveld analyses of the magnetic and nuclear structures were then carried out with the Fullprof program [8]. The Rietveld analysis was done by a simultaneous refinement for the nuclear and magnetic structure. The magnetic structure of huebnerite was used as the initial model [2] for the refinement of $MnWO_4$ and $Mn_{1-x}Fe_xWO_4$. The magnetic structure was introduced into the refinements using the concept of the propagation vector. The real magnetic moments were then calculated the refined Fourier components.

During all refinements the magnetic moments were confined to the ac-plane and the angle α was used to specify the inclination of the moment direction with respect to the a- axis.

1. Measurements on $MnWO_4$-natural sample

The temperature behaviuor of the diffraction pattern of $MnWO_4$-natural sample from Mongolia at 1.5K<T<17.0K range was shown in Fig.6. The high temperature magnetic phase transition in this sample was found between 11 K and 14 K .(Fig. 7). No indication was found for a third magnetic phase as observed in $MnWO_4$[5]. Magnetic structural parameters of the low and high temperature antiferromagnetic phases of the natural sample were listed in Table 2. In Fig.6a and Fig 6b shown temperature behaviuor of $MnWO_4$ powder pattern and magnetic satellite at 1.5K<T<17.0K range.

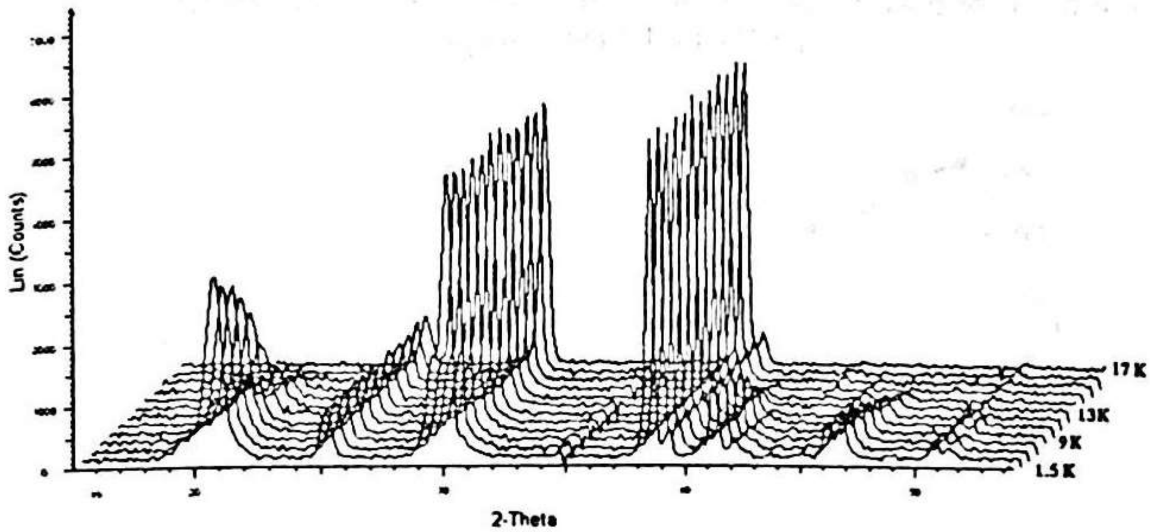
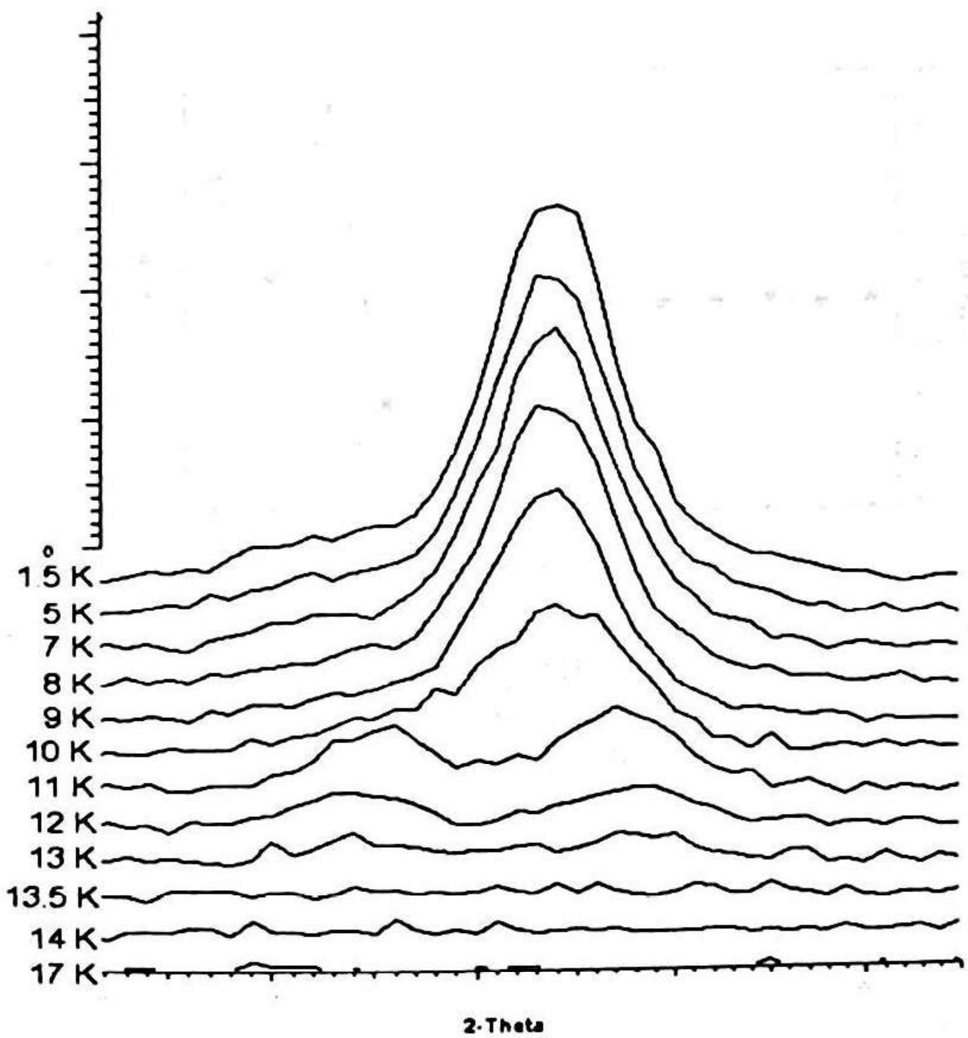


Fig. 6a.Temperature behaviuor of $MnWO_4$ powder pattern at 1.5K<T<17.0K range.



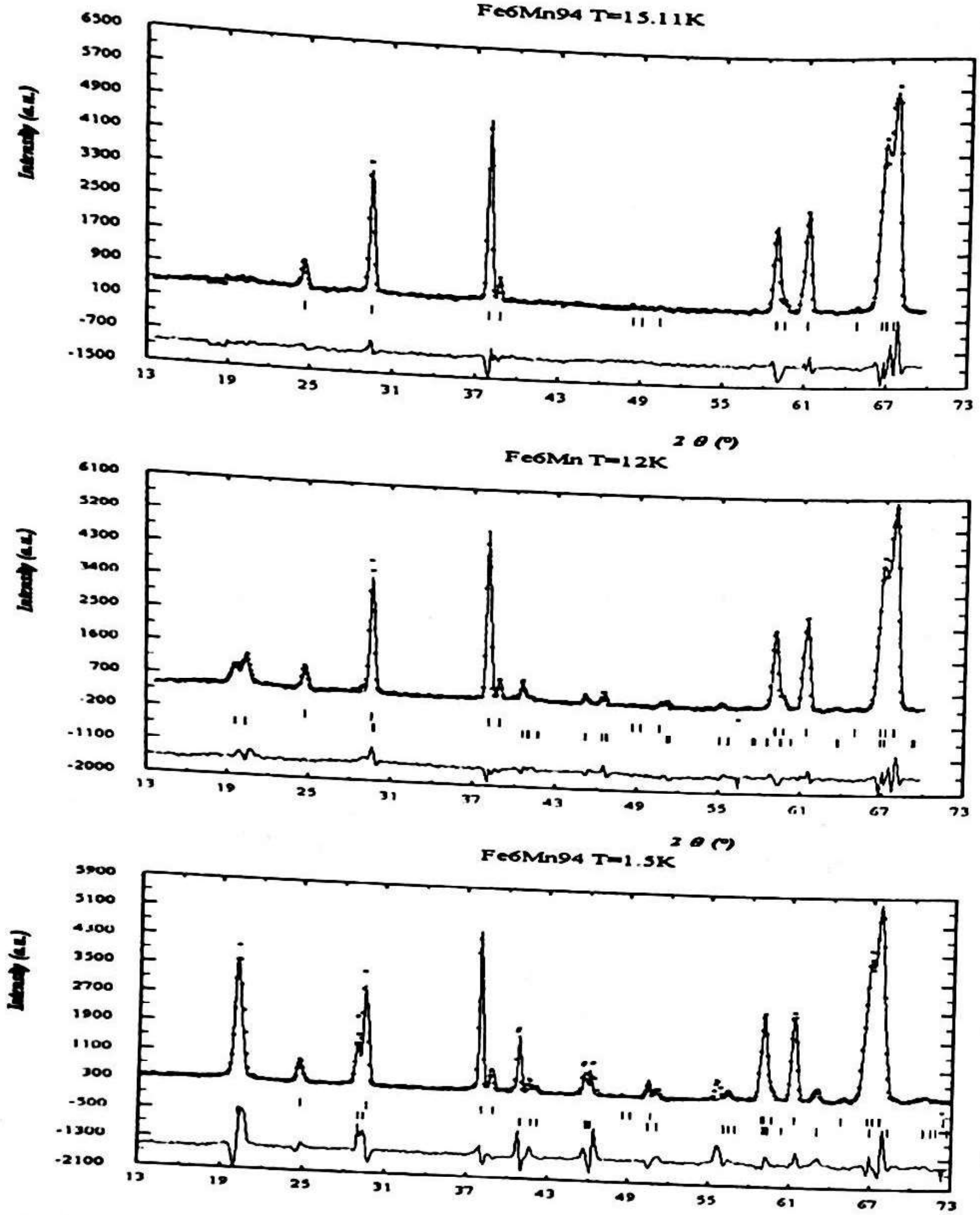


Fig. 9. Crystal and magnetic refinement of $Mn_{0.94}Fe_{0.06}WO_4$ at 1.5K, 12K, 15K

The incommensurate magnetic AFII structure was studied in temperature region 12 K.

The structural and magnetic parameters were determined from powder neutron diffraction data using FullProf program . Three parameters, the Fourier amplitude "m", the moment direction φ and the fractional coordinate "y" were varied and listed in Table 3.

Table 3. Refined magnetic incommensurate structurel parameters of $Mn_{0.94}Fe_{0.06}WO_4$ at 12K using a sinusoidal modulation model.

a=4.7825(2)	b=5.7024(6)	c=4.9621(5)	β=91.0704(3)
Atom	x	y	z
Mn, Fe	0.5000(0)	0.6867(3)	0.2500(0)
Propagation vector k	(-0.220, 0.500, 0.480)		
φ [°]	18.1		
$\lvert m \rvert$ (μ_B)	3.50(3)		
R factors: R_B=5.6, R_F=7.06, R_{mag}=10.5			

Summary and conclusion

1. We have studied the crystal and magnetic structures of different magnetic phases of natural sample $MnWO_4$ (with very small concentration Fe) and $Mn_{0.94}Fe_{0.06}WO_4$ in the temperature range in 1.5 to 17 K by neutron diffraction.
2. Diffraction patterns showed out that in $MnWO_4$ two incommensurate magnetic phases, AF3 phase between 8K and 13.5 K and commensurate magnetic phase T<8 K .
3. The absence of an AF2-like phase in $Mn_{0.94}Fe_{0.06}WO_4$ is probably related to the influence of the Fe^{2+} ions anisotropy, which may be suppress a magnetization component along the b-axes.
4. From our experimental investigations we can consider that a 6 % substitution of Fe on the Mn position leads to an interesting competition between and a coexistence of interpenetrating magnetic structures related to the pure systems $MnWO_4$ and $FeWO_4$.
5. The influence of the presence Fe^{2+} ions to crystal structure parameters and magnetic properties and the propagation vectors was looked. The calculated values of the propagation vectors of $MnWO_4$ and $Mn_{0.94}Fe_{0.06}WO_4$ at one phase showed that the Fe^{2+} ions influences to the propagation vectors and mainly increases the shift of k.

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