

Local structure and lattice dynamics in multiferroic MnWO_4 and $\text{Mn}_{1-c}\text{Co}_c\text{WO}_4$

A. Kuzmin, A. Anspoks, A. Kalinko, and J. Timoshenko

Institute of Solid State Physics, University of Latvia, Kengaraga street 8, LV-1063 Riga, Latvia

MnWO_4 is recently discovered multiferroic material, which contains formally only one magnetic ion (Mn) [1, 2]. It crystallizes in the wolframite-type structure [3] and is isomorphous to other antiferromagnetic transition-metal tungstates such as CoWO_4 ($T_N=55$ K), NiWO_4 ($T_N=67$ K), and FeWO_4 ($T_N=76$ K). At ambient pressure and in zero magnetic field, MnWO_4 undergoes below 14 K three magnetic phase transitions to antiferromagnetically (AF) ordered states (AF3 at $T_3=13.5$ K, AF2 (multiferroic) at $T_2=12.3$ K, and AF1 at $T_1=8.0$ K) [3]. The magnetic phase transitions in MnWO_4 are responsible for anomalies of the specific heat, the dielectric constant, and the magnetic susceptibility [4]. The appearance of simultaneous ferroelectric polarization in the AF2 phase is explained by the loss of inversion symmetry due to the helical magnetic order and a strong spin-lattice coupling [5].

The magnetic properties of MnWO_4 can be also governed by replacing Mn^{2+} with Fe^{2+} or Co^{2+} ions. The c - T phase diagram of solid solutions $\text{Mn}_{1-c}\text{Co}_c\text{WO}_4$ ($c<0.3$) has been established recently using the temperature-dependent magnetic susceptibility and neutron powder diffraction studies [6]. It was found that Co doping at $c>0.05$ suppresses the commensurate AF1 phase and stabilizes the incommensurate spiral AF2 phase down to the lowest temperature [6]. Above $c\sim 0.12$ a simple collinear antiferromagnetic phase (AF4), as in pure CoWO_4 , appears below T_N , but it coexists with the AF2' phase below ~ 12 K [6]. The lattice parameters as well as the unit-cell volume of $\text{Mn}_{1-c}\text{Co}_c\text{WO}_4$ decrease linearly with cobalt doping, reflecting the smaller radii of Co^{2+} ions. However, the temperature coefficients of the lattice parameters a and b show non-linear behavior with cobalt concentration suggesting that complex magnetism and transitions in $\text{Mn}_{1-c}\text{Co}_c\text{WO}_4$ are closely tied to the temperature-dependent changes in the lattice [6]. Recent, Raman and infra-red spectroscopy studies of $\text{Mn}_{0.85}\text{Co}_{0.15}\text{WO}_4$ revealed an unusual behaviour for some phonon modes below 100-200 K, which were related to the rigidity of zigzag chains of edge-shared MnO_6 octahedra, directly influencing various exchange interactions [7]. Therefore, the information on the local structure in solid solutions $\text{Mn}_{1-c}\text{Co}_c\text{WO}_4$ is the key to the deeper understanding of their properties.

In this work we have performed the first x-ray absorption spectroscopy study of the local dynamics and atomic structure around W, Mn and Co ions in pure MnWO_4 and CoWO_4 as well as in the solid solution $\text{Mn}_{0.7}\text{Co}_{0.3}\text{WO}_4$. The W L_3 -edge and Mn(Co) K-edge EXAFS spectra were recorded in transmission mode at the HASYLAB DESY C1 beamline in the temperature range from 6 to 300 K. Representative Mn(Co) K-edge EXAFS spectra and their Fourier transforms are shown in Fig. 1. The analysis of the first coordination shell around W atoms in pure MnWO_4 and CoWO_4 suggests that the WO_6 octahedra are strongly distorted, but a type of the distortion with four short (2×1.80 Å, 2×1.92 Å) and two long (2×2.14 Å) W–O distances is similar in both tungstates.

The situation with the local environment of Co and Mn atoms is more complicated. While the distortion of the CoO_6 octahedra is close in the solid solution $\text{Mn}_{0.7}\text{Co}_{0.3}\text{WO}_4$ and in pure CoWO_4 , the MnO_6 octahedra are significantly more distorted in pure MnWO_4 but order on Co doping in the solid solution. Note that the mean values of the Co–O and Mn–O distances in the solid solution remain nearly the same as in pure compounds.

The temperature dependence of the mean square relative displacements (MSRDs) for the Co–O and Mn–O bonds is shown in Fig. 2 and consists of the dynamic, i.e. temperature dependent, and static, caused by the octahedra distortion, parts. The dynamic part of the MSRDs is close in the three compounds and is well approximated by the Einstein model. The difference in the MSRDs,

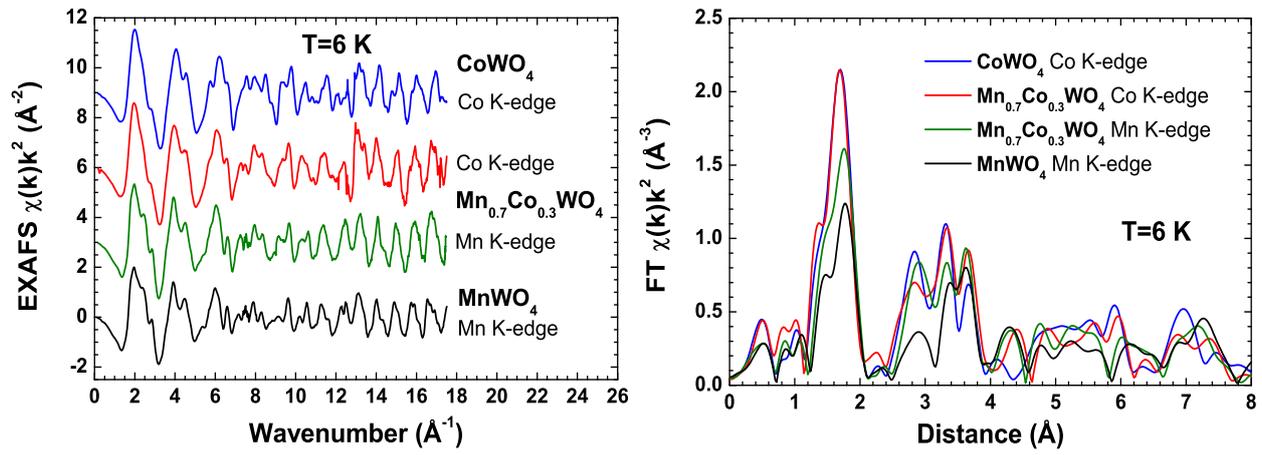


Figure 1: Experimental Mn(Co) K-edge EXAFS $\chi(k)k^2$ spectra and their Fourier transforms (FT) in Mn(Co)WO₄ and Mn_{0.7}Co_{0.3}WO₄ at $T=6$ K.

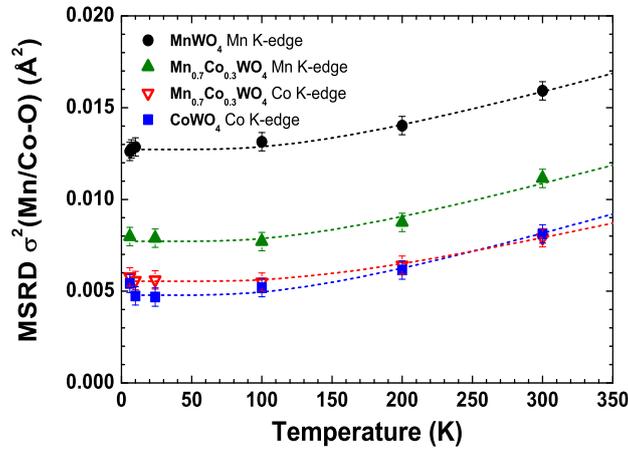


Figure 2: Temperature dependence of the first coordination shell MSD σ^2 for Mn–O and Co–O atom pairs in Mn(Co)WO₄ and Mn_{0.7}Co_{0.3}WO₄. Dashed lines show the Einstein model approximation.

being due to the static part, gives direct evidence of that cobalt doping influences significantly the distortion of the MnO₆ octahedra. This original result confirms the stabilizing role of cobalt doping in solid solutions Mn_{1-c}Co_cWO₄, suggested in [6, 7].

This work was supported by ESF Project 2009/0202/1DP/1.1.1.2.0/09/APIA/VIAA/141 and Latvian Government Research Grant No. 09.1518. Access to synchrotron radiation facilities of HASYLAB (project I-20100098 EC) is acknowledged. We would like to thank Dr. R. Chernikov for assistance during the experiment at the beamline.

References

- [1] O. Heyer et al., J. Phys.: Condens. Matter **18**, L471 (2006).
- [2] K. Taniguchi, et al., Phys. Rev. Lett. **97**, 0972003 (2006).
- [3] G. Lautenschlager, et al., Phys. Rev. B **48**, 6087 (1993).
- [4] A.H. Arkenbout, T.T.M. Palstra, T. Siegrist, T. Kimura, Phys. Rev. B **74**, 184431 (2006).
- [5] M. Mostovoy, Phys. Rev. Lett. **96**, 067601 (2006).
- [6] Y.-S. Song, J.-H. Chung, J.M.S. Park, Y.-N. Choi, Phys. Rev. B **79**, 224415 (2009).
- [7] M. Maczka, et al., Phys. Rev. B **83**, 174439 (2011).