Effect of cobalt doping on the local structure and dynamics of multiferroic $MnWO_4$ and $Mn_{0.7}Co_{0.3}WO_4$

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Abstract. The local atomic structure and dynamics in multiferroic $MnWO_4$ and $Mn_{0.7}Co_{0.3}WO_4$ have been studied by X-ray absorption spectroscopy at the Co(Mn) K-edge and W L_3-edge. The analysis of the first coordination shell of metal ions using single-shell Gaussian approximation and regularization-like method allowed us to determine a distortion of $Mn(Co)O_6$ and WO_6 octahedra. It was found that the local environment of Co^{2+} ions in $Mn_{0.7}Co_{0.3}WO_4$ is close to that in $CoWO_4$, whereas the presence of cobalt ions reduces the distortion of MnO_6 octahedra in comparison with pure $MnWO_4$.

1. Introduction

Pure manganese tungstate $MnWO_4$ is multiferroic material with spiral long-range magnetic order [1, 2]. It crystallizes in the wolframite-type structure [3] and is isomorphous to other antiferromagnetic transition-metal tungstates [4] such as $CoWO_4$ (T_N=55 K), $NiWO_4$ (T_N=67 K) and $FeWO_4$ (T_N=76 K). $MnWO_4$ contains only one kind of magnetic ion (Mn^{2+}) and undergoes three successive magnetic phase transitions to antiferromagnetically (AF) ordered states at ~13.5 K (T_N), ~12.7 K (T_2) and ~7.6 K (T_1) [3]. The magnetic phase transitions in $MnWO_4$ are responsible for anomalies of the specific heat, the dielectric constant and the magnetic susceptibility [5]. The appearance of simultaneous ferroelectric polarization in the AF2 phase between ~7.6 K and ~12.7 K is explained by the loss of inversion symmetry due to the spiral magnetic order and a strong spin-lattice coupling [1, 6].

The magnetic properties of $MnWO_4$ can be influenced by replacing Mn^{2+} with other magnetic Co^{2+} [7, 8, 9, 10, 11], Fe^{2+} [12], Ni^{2+} [13] and non-magnetic Mg^{2+}, Zn^{2+} [14, 15] ions as well as by substitution of W^{6+} with Mo^{6+} [16] ions. The c-T phase diagram of $Mn_{1-c}Co_cWO_4$ ($c<0.3$) has been established recently using the temperature-dependent magnetic susceptibility and neutron powder diffraction studies [7]. Upon Co doping the lattice parameters and the unit-cell volume decrease linearly, reflecting smaller radii of Co^{2+} ions. At the same time, the temperature coefficients of the lattice parameters a and b show non-linear behavior [7]. Recent, Raman and infra-red spectroscopy studies of $Mn_{0.85}Co_{0.15}WO_4$ 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 [10, 17]. Therefore, the information on the local structure in solid solutions $Mn_{1-c}Co_cWO_4$ is one of the key factors for deeper understanding of their properties.

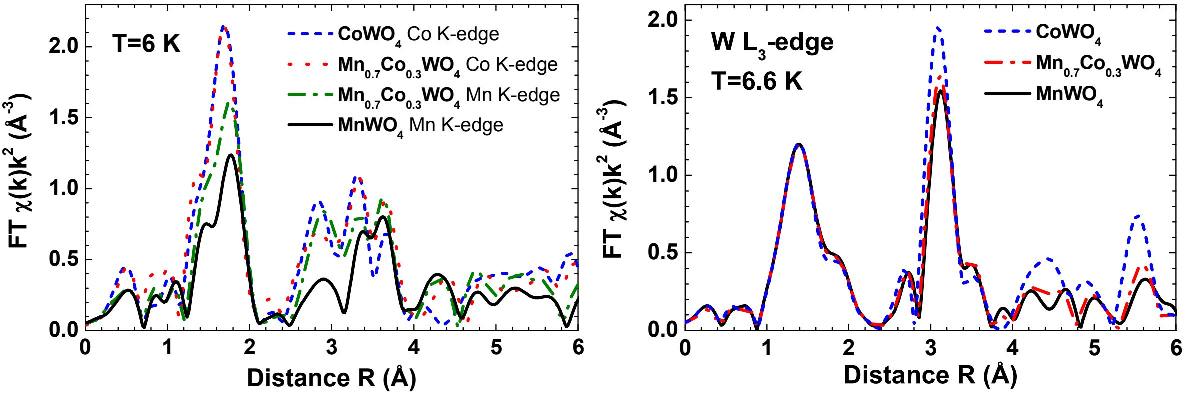

Figure 1. Fourier transforms (FT) of the experimental low-temperature Mn(Co) K-edge and W L$_3$-edge EXAFS spectra $\chi(k)k^2$ in Mn(Co)WO$_4$ and Mn$_{0.7}$Co$_{0.3}$WO$_4$.

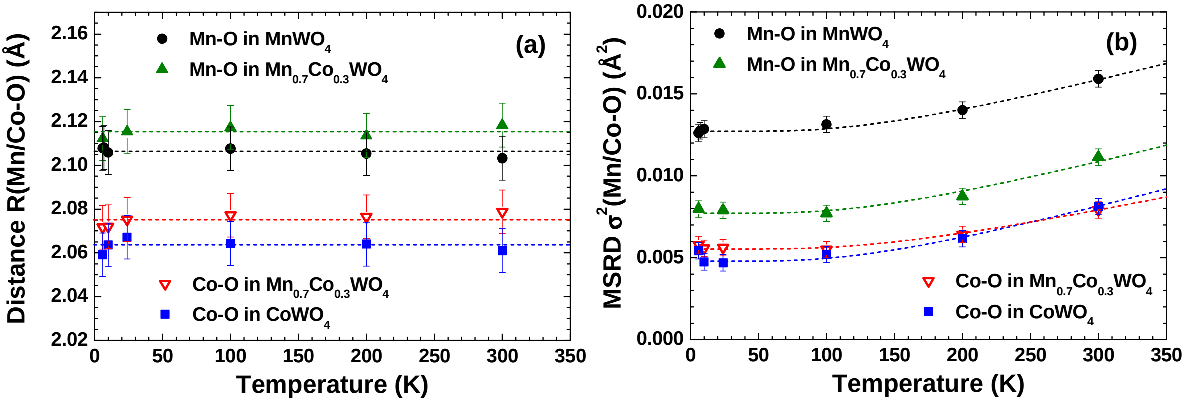

Figure 2. Temperature dependence of (a) the mean interatomic distances R(Mn/Co–O) and (b) the MSRD σ^2 obtained within the single-shell Gaussian approximation for Mn–O and Co–O atom pairs in Mn(Co)WO$_4$ and Mn$_{0.7}$Co$_{0.3}$WO$_4$. Dashed lines in (b) are the Einstein models.

In this work we have performed for the first time temperature dependent (6–300 K) x-ray absorption spectroscopy study of the local structure and dynamics around Mn, Co and W ions in MnWO$_4$, Mn$_{0.7}$Co$_{0.3}$WO$_4$ and CoWO$_4$.

2. Experimental and calculation details

MnWO$_4$, Mn$_{0.7}$Co$_{0.3}$WO$_4$ and CoWO$_4$ powders were synthesized using co-precipitation technique by a reaction of proper amounts of aqueous solutions of Co(NO$_3$)$_2$·6H$_2$O and/or MnCl$_2$·4H$_2$O salts with that of Na$_2$WO$_4$·2H$_2$O at 20°C. The obtained precipitates were washed, dried and finally annealed in air for 8 hours at 800°C. The W L$_3$-edge and Mn(Co) K-edge extended X-ray absorption fine structure (EXAFS) spectra were measured in transmission mode at the HASYLAB/DESY C1 bending-magnet beamline in the temperature range from 6 to 300 K. The x-ray radiation was monochromatized by a detuned Si(111) double-crystal monochromator, and the beam intensity was measured using two ionization chambers filled with argon and krypton gases. EXAFS oscillations $\chi(k)k^2$ were extracted in k-space range up to 18 Å^{-1} following the conventional procedure [18] using the EDA package [19]. Fourier transforms (FTs) of representative low-temperature EXAFS spectra are shown in Fig. 1. The

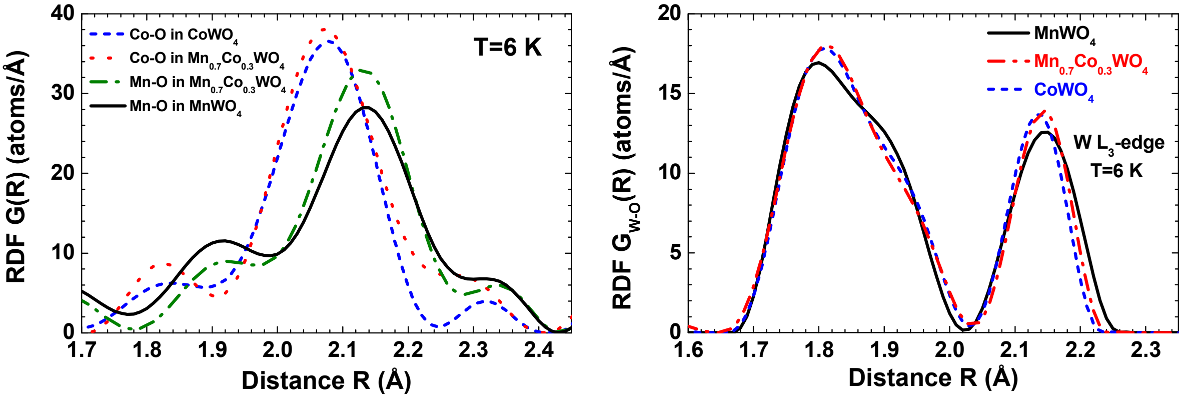

Figure 3. Radial distribution functions (RDFs) for Co–O, Mn–O and W–O atom pairs within the first coordination shell in Mn(Co)WO_4 and $Mn_{0.7}Co_{0.3}WO_4$ reconstructed by regularization-like technique [20].

first shell EXAFS contributions (Fig. 2(a)) were singled out in the R-space range 1.2–2.1 Å and best fitted using single shell Gaussian model to obtain the mean interatomic distances $\langle R\rangle$ and effective mean-square relative displacements (MSRDs) σ^2 for Co–O and Mn–O bonds (Fig. 2(b)). The radial distribution functions (RDFs) within the first coordination shell of metal ions were reconstructed by the regularization-like method [20] (Fig. 3). Theoretical scattering amplitude and phase shift functions, calculated by the *ab initio* FEFF8 code [21, 22], were used in all simulations.

3. Results and discussion

In wolframite-type structure tungsten and $3d$(Mn/Co) ions have distorted octahedral coordination by oxygen atoms, which can be characterized by a distortion parameter $\Delta = (1/6)\sum_{i=1}^{6}|R_i - \langle R\rangle|$. The WO_6 octahedra are strongly distorted with Δ=0.124 Å in $MnWO_4$ and 0.118 Å in $CoWO_4$, so that six oxygens can be divided into two groups of 4 nearest and 2 distant atoms located at 1.8–1.9 Å and 2.1–2.2 Å, respectively [3, 4]. A distortion of the MnO_6 octahedra Δ=0.064 Å is twice smaller, and that of the CoO_6 octahedra Δ=0.048 Å decreases even more. The octahedra distortion is well observed in the RDFs reconstructed from EXAFS spectra (Fig. 3). While RDFs for Co–O and Mn–O pairs are single-peak shaped, the ones for W–O pairs have two maxima in agreement with diffraction data [3, 4]. Note that the W–O RDFs are very close in all three compounds, and the different position of the RDF maxima for Co–O and Mn–O pairs is due to the size difference of Co^{2+} (0.75 Å) and Mn^{2+} (0.83 Å) ions being in the high-spin state [11].

Rather small distortion of the Mn(Co)O_6 octahedra allows one to perform the analysis of the first shell within the single-shell Gaussian approximation. As a result, the mean interatomic distances R(Mn/Co–O) and the MSRDs σ^2 for Co–O and Mn–O bonds were determined (Fig. 2). The Mn(Co)–O distances remain constant upon increasing temperature within ±0.01 Å, and their values in $Mn_{0.7}Co_{0.3}WO_4$ are close to that in pure tungstates.

The analysis of the Mn(Co)–O MSRDs suggests that they contain dynamic, i.e. temperature dependent, and static, caused by octahedra distortion, contributions. The MSRDs temperature dependent part is close in three tungstates and is well approximated by the Einstein model with the characteristic temperature $\theta_E \approx 415$ K.

The main difference in the MSRDs is due to the static octahedra distortion, being the largest in $MnWO_4$ and the smallest in $CoWO_4$. In $Mn_{0.7}Co_{0.3}WO_4$ the MSRD values for Co–O bonds are close to that in $CoWO_4$, suggesting that Co^{2+} ions adopt similar local environment. On the contrary, the MSRD values for Mn–O bonds in $Mn_{0.7}Co_{0.3}WO_4$ are significantly smaller by about 0.005 Å^2 than in $MnWO_4$, but slightly larger by about 0.002 Å^2 than for Co–O bonds. This means that cobalt doping leads to a decrease of the MnO_6 octahedra distortion. Comparison of the Mn(Co) K-edge FTs in Fig. 1 indicates that the behaviour of the outer shells at 2.5–4.0 Å in $Mn_{0.7}Co_{0.3}WO_4$ is also closer to that in $CoWO_4$. These original results confirm the stabilizing role of Co doping in solid solutions $Mn_{1-c}Co_cWO_4$ suggested in [7, 10].

4. Conclusions

Temperature dependent x-ray absorption spectroscopy study of the local structure and dynamics around Mn, Co and W ions in multiferroic $MnWO_4$ and $Mn_{0.7}Co_{0.3}WO_4$ has been performed in comparison with antiferromagnetic $CoWO_4$. The obtained results provide direct evidence of the stabilizing role of cobalt in $Mn_{0.7}Co_{0.3}WO_4$. We have proved that the local environment of Co^{2+} ions in the solid solution is close to that in $CoWO_4$. At the same time, the presence of cobalt ions influences strongly the local environment around Mn ions, which becomes less distorted compared to pure $MnWO_4$. The strongly distorted octahedral environment of tungsten atoms was found to be close in three tungstates.

Acknowledgments

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