Importance of local structural distortions in magnetocaloric effect in Mn based antiperovskites

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Abstract. Mn₃GaC and Mn₃SnC are two antiperovskites which exhibit a large magnetocaloric effect associated with a magnetostructural transformation. Although structurally similar, the magnetic transition and the nature of magnetocaloric effect in the two compounds is completely different. While Mn₃GaC transforms from a ferromagnetic to an antiferromagnetic state at Tᵣ = 178K with the antiferromagnetic propagation vector along \( \mathbf{k} = \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \), in Mn₃SnC the transformation occurs at Tᵣ = 280K from a paramagnetic state to an antiferromagnetic state with \( \mathbf{k} = \frac{1}{3}, \frac{1}{3}, 0 \). Mn K EXAFS has been employed to show that these differences in magnetic properties are related to local structural distortions in Mn₆C octahedra which are quite different in the two compounds.

1. Introduction

A class of materials that have attracted attention as candidates for ferroic cooling applications are the Mn based antiperovskite materials. Amongst these Mn₃GaC undergoes a volume discontinuous first order transition from a ferromagnetic (FM) to an antiferromagnetic (AFM) ground state around 160K [1, 2] accompanied by a large inverse table like magnetocaloric effect (MCE) in relatively low fields especially preferred in designing a practical refrigerant unit [3, 4]. On the other hand, isostructural Mn₃SnC exhibits a sharp first order change from a paramagnetic (PM) state to a non-collinear antiferromagnetic state at 279K accompanied by a conventional magnetic entropy change (80.69 mJ/cm³·K under a magnetic field of 2T) [2, 5].

Although both the samples undergo a cubic-cubic phase transformation, neutron diffraction studies have shown that the antiferromagnetic propagation vector \( \mathbf{k} \) in the two compounds is different. In Mn₃GaC, \( \mathbf{k} \) is along \( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \) direction [6] while Mn₃SnC orders with \( \mathbf{k} = \frac{1}{3}, \frac{1}{3}, 0 \) which makes two of the three Mn atoms to order antiferromagnetically while the third one has a small ferromagnetic component along the \( z \) direction [7]. There are however, no signatures of any structural disorder that could explain this difference in magnetic behavior. In order to check for any local structural disorder, Mn K edge EXAFS studies were performed across the first order transition on Mn₃GaC and Mn₃SnC compounds. Our study reveals presence of such
a disorder that could be related to the observed differences in the magnetic properties of the two compounds.

2. Experimental
The compounds used here were prepared by solid state reaction method, details of which are given in Ref. [8] and characterized by x-ray diffraction (XRD) and magnetization as a function of temperature during the zero field cooling (ZFC), field cooled cooling (FCC) and field cooled warming (FCW) cycles. Extended x-ray absorption fine structure (EXAFS) data at the Mn K edge (6539 eV) was collected in transmission mode at 300K (RT) and 80K (LT) in the range from -200 to 1300 eV with respect to the Mn K edge at the XAFS beamline at Elettra, Trieste [9]. The data was processed using Demeter program [10].

3. Results and Conclusions
Rietveld refined XRD patterns recorded in the angular (2θ) range of 20° to 100° in steps of 0.02° using Cu Kα radiation are presented in Figure 1 and show the formation of cubic antiperovskite phase for both the compounds along with minor impurity phases (~1%).

Magnetization (M) of Mn3GaC, recorded as a function of temperature under ZFC, FCC and FCW conditions at an applied field of 0.01T (see inset of Figure 1a) exhibits a PM to FM transition at $T_C = 242K$ followed by a FM to AFM first order transition at $T_t = 178K$ [11]. Mn3SnC on the other hand exhibits a single transition depicted by a sharp increase in magnetization at $T_t = 280 K$ (inset of Figure 1b) which corresponds to a first order transition from a high temperature low volume PM state to a low temperature high volume magnetically ordered phase with competing FM and AFM interactions [7].

k weighted Mn K edge EXAFS data in R space and back transformed k space recorded
Therefore, the structural constraints were relaxed and bond distances and for Mn (shown as a dashed line (cubic model) in Figure 2(a)), satisfactory fits could not be obtained Mn of Mn (c)). Similarly, the cubic model, though fitted well (dashed line in Figure 2(c)) to the LT data at RT and LT for Mn GaC EXAFS data at RT could be well fitted to a model incorporating structural constraints (shown as a dashed line (cubic model) in Figure 2(a)), satisfactory fits could not be obtained for MnSnC EXAFS data recorded at both, RT and LT using this model (Figure 3(a) and (c)). Similarly, the cubic model, though fitted well (dashed line in Figure 2(c)) to the LT data of MnGaC, gave some unphysical parameters (mean square relative displacements, $\sigma^2 < 0$). Therefore, the structural constraints were relaxed and bond distances and $\sigma^2$ for each scattering path were varied independently. The resulting fit is shown as a solid line (distorted octahedra) in Figure 2(c). The fitted values of bond distances are listed in a table alongside the Figure 2. It can be seen that, at LT, the Mn–C and Mn–Ga distances slightly shorten while Mn–Mn bonds elongate. This situation corresponds to a rhombohedral distortion of the cubic unit cell in the transformed phase. The AFM ground state of Mn consists of a distribution of shorter and longer bond distances (distorted octahedra model). While about 2/3 of Mn–C and Mn–Mn bonds shorten and the rest grow longer. In the case of Mn–Sn distances the distribution was exactly reversed. Such a local structural distortion though preserves the overall cubic symmetry, distort the Mn6C octahedra so as to elongate along one direction and compress along other two. The best fits to the data in R space are shown as solid lines in Figure 3(a) and (c) and the back transformed data at RT and LT along with the best fits are shown in Figure 3(b) and (d) respectively. The best values of bond distances obtained are listed in a Table alongside the Figure 3.

These distortions of Mn6C octahedra agree well with the observed propagation vector $k$ and

| Bond | $R_{\text{XRD}}$ | $R_{\text{EXAFS}}$ |
|------|-----------------|-----------------|
| Mn–C | 1.949           | 1.923(4)        |
| Mn–Mn| 2.757           | 2.720(6)        |
| Mn–Ga| 2.757           | 2.720(6)        |
| LT   |                 |                 |
| Mn–C | 1.943           | 1.937(3)        |
| Mn–Mn| 2.748           | 2.779(5)        |
| Mn–Ga| 2.748           | 2.735(2)        |

Figure 2. EXAFS spectra in R space ((a) and (c)) and Fourier filtered k space ((b) and (d)) at RT and LT in Mn3GaC. The dashed lines and the solid lines indicate best fit for cubic and distorted octahedra model respectively. The table gives the best fitted values of bond lengths from XRD and EXAFS.
Figure 3. R space ((a) and (c)) and back transformed k space ((b and (d)) EXAFS spectra recorded at RT and LT for Mn$_3$SnC. The dashed lines and the solid lines indicates best fit with cubic and distorted octahedra model respectively. The table gives the best fitted values of bond lengths from XRD and EXAFS.

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