1. Introduction

Antiperovskite compounds that have attracted considerable attention due to significant properties like superconductivity [1, 2], giant magnetoresistance [3, 4], magnetostriction effect [5] and giant negative thermal expansion (NTE) [6–10]. Amongst these is Mn$_3$SnC which exhibits a large magnetic entropy change near room temperature with $S_{\text{max}}$ values ($\approx 80.69 \text{ mJ cm}^{-3} \text{K}^{-1}$ and $133 \text{ mJ cm}^{-3} \text{K}$ under a magnetic field of 2 T and of 4.8 T, respectively) comparable to those observed in contemporary magnetic refrigerant materials [11].

In spite of its relatively simple cubic structure (Sp. Gr. Pm$\overline{3}$m) with Mn atoms located at the face centers of a cube, Sn atoms at the corners and a carbon atom positioned at the body center [12], Mn$_3$SnC transforms from a room temperature paramagnetic (PM) state to a high volume magnetically ordered state with a complicated spin arrangement consisting of antiferromagnetic (AFM) and ferromagnetic (FM) components via a spontaneous first order transition at 280 K [11, 13–15]. The non collinearity of Mn spins in the transformed state has been attributed to a novel magnetic structure obtained from neutron diffraction studies. Though equivalent in crystal structure, Mn atoms in the magnetic unit cell ($a\sqrt{2}$, $a\sqrt{2}$, $a$) of Mn$_3$SnC generated using a propagation vector $k = [0 \frac{1}{2} \frac{1}{2} 0]$ are of two types. Firstly, two of the three Mn atoms present themselves in a square configuration in the (0 0 1) plane with a net antiferromagnetic moment of 2.4 $\mu_B$ per Mn along with a small FM moment of $\pm 0.15 \mu_B$ along the [0 0 1] direction. While, the remaining Mn atoms have their spins aligned parallel to each other thus contributing to the FM component with a moment of $0.65 \pm 0.15 \mu_B$ along the 001 direction [14].

In contrast, Mn$_3$GaC, which also undergoes a first order transition at $T \approx 160 \text{ K}$ has a collinear AFM structure described by a propagation vector $k = [\frac{1}{4} \frac{1}{4} \frac{1}{4}]$ resulting in ferromagnetic...
[1 1 1] planes of Mn atoms alternating in their spin direction along the (1 1 1) axis [16].

2. Experimental

To prepare polycrystalline Mn₃SnC, starting materials (Mn, Sn and C powders) were separately weighed and intimately mixed in the stoichiometric molar ratio 3:1:1 with about 15% excess graphite powder added to compensate for possible carbon deficiencies during the reaction [17]. The mixture was then pressed into a pellet and encapsulated in an evacuated quartz tube before sintering at 1073 K for the first 48 h and at 1150 K for the next 120 h [11]. After quenching to room temperature, the product was pulverized, mixed and annealed again under the same conditions to obtain a homogeneous sample. Room temperature x-ray diffraction (XRD) studies were carried out using a Rigaku diffractometer with CuKα radiation to determine the phase formation and purity of the compound formed. Thermal expansion across the first order transition was measured from XRD patterns recorded in the temperature range of 25 – 300 K using BL18B at Photon Factory, Japan. Temperature dependent magnetization measurements in the 5 – 350 K range were performed using a Quantum Design SQUID magnetometer in an applied field of 0.01 T while resistivity measurements in the same temperature range were accomplished using the standard four probe method. Neutron powder diffraction patterns as a function of temperature were recorded on the PD2 diffractometer (λ = 1.2443 Å) at Dhruva reactor, Bhabha Atomic Research Centre, Mumbai, India. Rietveld analysis for all diffraction patterns recorded in the temperature range of 25–300 K using the FullProf Suite refinement program [18]. To understand the local structural changes, if any, in the Mn–C octahedra in Mn₃SnC, Extended x-ray absorption fine structure (EXAFS) data at the Mn K edge (6539 eV) was collected in transmission mode at 300 K (RT) and 80 K (LT) in the range from −200 to 1300 eV with respect to the Mn K edge at the XAFS beamline at Elettra, Trieste [19]. Both incident (I₀) and transmitted (I) intensities were measured simultaneously using an ionization chamber filled with appropriate gases. To restrict the absorption edge jump (Δμ) to an optimum value, the number of layers of Mn₃SnC powder coated scotch tape were appropriately adjusted. The edge energy was calibrated using Mn metal foil as standard. To obtain EXAFS (χ(k)) signal, Mn K edge data was reduced following standard procedures in the Demeter program [20].

3. Results and discussion

Room temperature XRD pattern recorded in the angular (2θ) range of 20° to 100° in steps of 0.02° using Cu Kα radiation is presented in figure 1. Rietveld refinement of the pattern shows the formation of cubic Mn₃SnC with a lattice constant, a = 3.996 72(4) Å [13] along with minor impurities of C, Sn and SnO. Existence of thermal hysteresis between the cooling and warming process in both magnetic and transport measurements implies the first order character of the transition at $T_C$. 
X-ray diffraction intensities in the 25–300 K temperature range were collected over a 2θ range between 8°–45° with a step size of 0.005° using an x-ray wavelength λ ~ 0.619 Å. Abrupt structural changes that occur around the ordering temperature are highlighted in figure 3 via the temperature evolution of the (1 1 1), (3 1 1) and (4 2 0) reflections. One can notice a sudden shift in the position of these reflections to higher values of inter planar distance ‘d’ between 285 K and 250 K. This fact coupled with the absence of any additional peak indicates that Mn₃SnC undergoes a cubic–cubic volume discontinuous transition at about 279 K along with a change in its magnetic state. The calculated change in the lattice constant value at the transition is of the order of 0.1% which is in agreement with previously reported values [15].

As mentioned before the non collinearity of Mn spins observed in Mn₃SnC below TC is attributed to a complicated arrangement of FM and AFM spins. To reconfirm magnetic structure below its Curie temperature and to study the thermal evolution of Mn magnetic moments, neutron diffraction patterns were recorded at selected temperatures between 6 K and 300 K, in the angular range 3°–135°. The patterns were Rietveld refined to obtain the crystal and magnetic structure. At 300 K,
Bragg reflections corresponding only to the nuclear structure (in the space group Pm\(\bar{3}m\)) and impurity phase C are present as can be seen in figure 4(a). The refined value of lattice constant obtained from this fitting \(a = 3.9961(1) \text{\AA}\) is in good agreement with that obtained from x-ray diffraction. Temperature dependence of lattice constant values obtained from synchrotron x-ray diffraction and neutron diffraction are shown in figure 4(b). Both the results, obtained from synchrotron x-ray and neutron diffraction, are in fair agreement with each other.

On cooling below \(T_C\) in addition to the nuclear scattering peaks defined by the Pm\(\bar{3}m\) space group superlattice reflections with significant magnetic contribution appear as shown in the diffraction data recorded at 6 K in figure 6(a). These magnetic reflections cannot be indexed on the basis of the obtained chemical structure. They can only be indexed by defining a propagation vector as \(k = \left[ \frac{1}{2}, \frac{1}{2}, 0 \right]\) and adopting a larger magnetic unit cell of type \((a\sqrt{2}, a\sqrt{2}, a)\) giving rise to a spin alignment shown in figure 5. This magnetic structure envisages two magnetic Mn atoms. One, Mn1, has only a FM \(= 0.7 \pm 0.4 \mu_B\) along the 001 axis and the other (Mn2) with only an antiferromagnetic component are arranged in a ‘square configuration’ in the \(a-b\) plane with a net moment \(= 2.3 \pm 0.1 \mu_B\). Thermal evolution of the magnetic moments of the two species of Mn atoms present in the magnetic structure of Mn\(_3\)SnC is shown in figure 6(b). With the lowering of temperature below transition temperature one can see a sharp increase in the magnetic moment of Mn2 species which is as expected for a first order transformation. While the moment of Mn1 which contributes purely to the FM component exhibits a comparatively gradual increase. Furthermore, with lowering of temperature, while the magnetic moment of Mn2 continuously increases, that of Mn1 shows a slight decrease. The behaviour of Mn magnetic moments near transition temperature, gives an impression that only Mn2 atoms contribute to the first order transformation in Mn\(_3\)SnC. Even though, magnetic structure has a tetragonal symmetry, no structural distortions were visible either in neutron diffraction or in synchrotron XRD measurements at lower temperatures.

To check the possibility of existence of any local structural distortions around Mn in Mn\(_3\)SnC which could be responsible for the above behaviour of Mn spins, EXAFS data recorded at the Mn K edge at RT and LT was analyzed. For this \(\chi(k)\) signal in the range 2 \(\text{Å}^{-1}\) to 13 \(\text{Å}^{-1}\) was Fourier transformed (FT) to \(R\) space. The magnitude of FT of EXAFS data at the two temperatures in the \(R\) range of 0 \(\text{Å}\) to 6 \(\text{Å}\) are presented in figure 7. The plot shows two distinct peaks between 1 \(\text{Å}\) to 3 \(\text{Å}\) corresponding to Mn–C and equidistant Mn–Mn and Mn–Sn correlations. The scattering contributions from each

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**Figure 4.** (a) Rietveld refined neutron diffraction patterns of Mn\(_3\)SnC recorded above the magnetic ordering temperature \((T = 300 \text{K})\). (b) Variation of refined lattice parameters obtained from neutron diffraction (open circles) and synchrotron x-ray diffraction (open squares) as a function of temperature.

**Figure 5.** Magnetic spin alignment of Mn atoms in the nuclear unit cell of Mn\(_3\)SnC at low temperature as obtained from neutron diffraction.
of these correlations were obtained using FEFF6.01 [21] and were used in fitting the experimental data in \( R \) space in the range 1 Å–3 Å. Since the observed crystal structure at RT is cubic, the data was initially fitted using the structural restrictions imposed by the \( Pm\bar{3}m \) space group. These restrictions implied that the nearest neighbour Mn–C correlation had a bond distance equal to \( \frac{a}{2} = 1.998 \) Å and both eight neighboured Mn–Mn and four neighboured Mn–Sn correlations had a bond distance equal to \( \frac{a}{\sqrt{2}} = 2.826 \) Å. The resulting fit in the \( R \) space and the back transformed \( k \) space is shown in figure 7(a). As can be seen, the fit was not quite good enough (\( R \)-factor = 0.047 20). An attempt to fit the data by relaxing the above restrictions resulted in a very good fit. However, Mn–Mn bond length was obtained to be slightly shorter than Mn–Sn bond distance. This hints towards the presence of local structural distortions. Taking into account the crystal and magnetic structure obtained from x-ray and neutron diffraction a model was designed consisting of a fraction \( \chi \) of shorter and longer bond distances of Mn with its near neighbours while still preserving the structural restrictions imposed by the crystal structure. Such a model resulted in a very good fit (\( R \)-factor = 0.013 99), (see figure 7(c)) wherein about two
third of the nearest neighbour Mn–C distances are shorter while the remaining one third are longer. Likewise around two third Mn–Mn distances and about one third of Mn–Sn distances were found to be shorter and the remaining fraction longer. Such a fitting indicates that Mn6C octahedra distort from their cubic symmetry by elongating along one direction and shrinking along the other two. The structural parameters obtained from the fitting are tabulated in Table 1. The same model can also be used to fit the LT data equally well but with shorter bonds showing a small increase in their bond lengths and the longer bond distances reducing in their lengths.

Even though no structural disorder is seen in room temperature x-ray or neutron diffraction patterns of Mn3SnC, EXAFS analysis indicate a presence of local structural disorder around Mn atoms in the paramagnetic phase. The presence of such a distortion at RT in Mn3SnC could be either due to the proximity to the magnetostructural transition temperature or due to the presence of larger atoms like Sn. It may be mentioned here that such local structural distortions have not been hitherto reported in other antiperovskite compounds above their transformation temperature. Larger atoms like Sn could induce local strains which may be alleviated by a structural distortions while maintaining the cubic symmetry of the overall crystal structure. EXAFS studies also show that though distortions persist even in the magnetically ordered phase the shorter bond distances tend to elongate while the longer bond distances shrink.

The presence of such disorder in the corner sharing Mn6C octahedra could also be the reason behind the change in magnetic propagation vector from $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in Mn3GaC to $(\frac{0}{2}, 0, \frac{1}{2})$ in Mn3SnC. The competition between the direct Mn–Mn ($J_1$) and indirect Mn–C–Mn ($J_2$) interaction strengths that controls the nature of magnetic ordering in antiperovskite compounds depends critically on the distance between Mn atoms [15, 22]. Therefore the observed local structural distortions which occur in shorter and longer Mn–Mn bond distances affect the magnetic interactions and thereby the long range magnetic order in Mn3SnC. Even in the case of Mn3GaC the magnetostructural transition is driven from a point where the weaker FM Mn–Mn interactions are overcome by a discontinuous volume expansion (~0.5%) to the AFM state wherein the stronger Mn–C–Mn interactions dominate [23]. The present study indicates that when larger Sn atoms replace Ga at the A-site resulting in Mn3SnC, along with an increase in the unit cell volume, Sn atoms also introduce an anisotropic tensile strain in the Mn6C octahedra which in turn causes the stretching and shortening of Mn–Mn bond distances. These local structural distortions allow the existence of a complex AFM structure with a weak FM component that influences the magnetic ground state.

4. Conclusions

A systematic exploration of the Mn3SnC crystal structure using a combination of x-ray and neutron diffraction and x-ray absorption fine structure (XAFS) spectroscopy was carried out to understand the nature of the first order magnetic transformation in the compound. Although x-ray and neutron diffraction patterns show no structural distortions in the compound at low temperatures, they indicate a cubic–cubic volume discontinuous transition accompanying the magnetic transition ($T \sim 279$ K). However EXAFS results suggest a structural distortion of the Mn6C octahedra from their cubic symmetry due to the presence of larger atoms of Sn. These distortions critically affect the magnetic order of Mn3SnC ground state consisting of antiferromagnetic and ferromagnetic Mn atoms.

Acknowledgments

This work is supported by Board of Research in Nuclear Sciences (BRNS) under the project 2011/37P/06. Further financial support and experimental facilitation granted by Department of Science and Technology, India and Saha Institute of Nuclear Physics, India at the Indian Beamline, Photon Factory, KEK, Japan is gratefully acknowledged. M/s Devendra D Buddhikot, G Jangam and Dr V Srihari are acknowledged for the experimental assistance.

References

[1] He T et al 2001 Nature 411 54–6
[2] Uehara M, Yamazaki T, Kri T, Kashida T, Kimishima Y and Hase I 2007 J. Phys. Soc. Japan 76 034714

Table 1. Interatomic bond distance $R$ and mean-square displacement of the path lengths due to thermal or static disorder ($\sigma^2$) obtained for Mn3SnC compound by fitting Mn K-edge EXAFS to a model representing distorted octahedra.

| Bond   | C.N. | $R_{90K}$ ($\text{Å}$) | $x$  | $\sigma^2$ ($\text{Å}^2$) | $R_{90K}$ ($\text{Å}$) | $x$  | $\sigma^2$ ($\text{Å}^2$) |
|--------|------|------------------------|------|--------------------------|------------------------|------|--------------------------|
| Mn–C   | 2    | 1.998                  | 0.37(3) | 0.006(3)                  | 1.997                  | 0.32(4) | 0.009(5)                |
|        | 0.63(3) | 2.032(2)                 |      |                          | 1.958(2)               | 0.68(4) |                          |
| Mn–Mn  | 8    | 2.826                  | 0.37(3) | 0.006(1)                  | 2.824                  | 0.32(4) | 0.005(1)                |
|        | 0.63(3) | 2.874(2)                 |      |                          | 2.769(2)               | 0.68(4) |                          |
| Mn–Sn  | 4    | 2.826                  | 0.37(3) | 0.008(1)                  | 2.824                  | 0.32(4) | 0.006(1)                |
|        | 0.63(3) | 2.874(2)                 |      |                          | 2.769(2)               | 0.68(4) |                          |

C.N. corresponds to the coordination number, $R_{90K}$ and $R_{90K}$ are interatomic distances calculated from the neutron diffraction pattern at 300 K and 100 K respectively, $\sigma^2$ denotes the fraction of elongated/shortened bond lengths.
[3] Kamishima K, Goto T, Nakagawa H, Miura N, Ohashi M, Mori N, Sasaki T and Kanomata T 2000 Phys. Rev. B 63 024426
[4] Zhang X H, Yin Y, Yuan Q, Han J C, Zhang Z H, Jian J K, Zhao J G and Song B 2014 J. Appl. Phys. 115 123905
[5] Asano K, Koyama K and Takenaka K 2008 Appl. Phys. Lett. 92 161909
[6] Takenaka K and Takagi H 2005 Appl. Phys. Lett. 87 261902
[7] Takenaka K, Asano K, Misawa M and Takagi H 2008 Appl. Phys. Lett. 92 011927
[8] Ikubo S, Kodama K, Takenaka K, Takagi H, Takigawa M and Shamoto S 2008 Phys. Rev. Lett. 101 205901
[9] Huang R, Li L, Cai F, Xu X and Qian L 2008 Appl. Phys. Lett. 93 081902
[10] Takenaka K and Takagi H 2009 Appl. Phys. Lett. 94 131904
[11] Wang B S et al 2009 Europhys. Lett. 85 47004
[12] Howe L and Myers H P 1957 Phil. Mag. 2 554–60
[13] Lorthioir G, Fruchart M E, Nardin M, l’Heritier P and Fruchart R 1973 Mater. Res. Bull. 8 1027–34
[14] l’Heritier P, Senator J F, Fruchart R, Fruchart D and Bertaut E F 1977 Mater. Res. Bull. 12 533–41
[15] Li Y B, Li W F, Feng W J, Zhang Y Q and Zhang Z D 2005 Phys. Rev. B 72 024411
[16] Fruchart D, Bertaut E, Sayetat F, Eddine M N, Fruchart R and Snateur J 1970 Solid State Commun. 8 91–9
[17] Yu M H, Lewis L H and Moodenbaugh A R 2003 J. Appl. Phys. 93 10128–30
[18] Rodriguez-Carvajal J 1993 Physica B 192 55–69
[19] Cicco A D, Aquilanti G, Minicucci M, Principi E, Novello N, Cognigni A and Olivi L 2009 J. Phys. Conf. Ser. 190 012043
[20] Ravel B and Newville M 2005 J. Synchrotron Radiat. 12 537–41
[21] Zabinsky S I, Rehr J J, Ankudinov A, Albers R C and Eller M J 1995 Phys. Rev. B 52 2995
[22] Takenaka K, Ichigo M, Hamada T, Ozawa A, Shibayama T, Inagaki T and Asano K 2014 Sci. Technol. Adv. Mater. 15 015009
[23] Lewis L H, Yoder D, Moodenbaugh A R, Fischer D A and Yu M H 2006 J. Phys.: Condens. Matter 18 1677