Evidence of spin lattice coupling in MnTiO$_3$: An x-ray diffraction study

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Abstract – Here we investigate the temperature evolution of the structural parameters of a potential magnetoelectric material, MnTiO$_3$. The experimental results reveal interesting temperature dependence of the lattice parameters, which can be divided into three regions. In region I (300 K to 200 K), the lattice parameters show linear temperature dependence due to the thermal effect. In the region II (200 K to 95 K), lattice parameters show deviation from the linear behaviour due to the competing intra-layer antiferromagnetic interactions setting in $\sim$ 200 K. The $c/a$ ratio is seen to display a minima around 140 K. Below 140 K, the short Mn-O bonds increase suggesting the onset of inter-layer antiferromagnetic interaction $\sim$ 100 K. In region III (95 K to 23 K), the lattice parameter $c$ shows negative thermal expansion where the antiferromagnetic interaction is fully established. The behaviour of the calculated Mn-O bonds based on first-principle calculations are in line with the experimental results. This study demonstrates the importance of spin lattice coupling in understanding the magnetic properties of the compound which is expected to be helpful in revealing the origin of magnetically induced ferroelectricity.

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The physical properties of a solid are governed by the behaviour of the electrons within it. The properties become more complex and interesting if the motion of electrons is decided by the interplay between charge, spin, lattice and orbital degrees of freedom. Such cross-coupling is the marked feature of strongly correlated electron systems. One of the properties which has gained a significant amount of attention from both the application and the fundamental physics point of view is multiferroicity [1]. In these kinds of compounds, the magnetism can be controlled electrically and polarization can be controlled magnetically. This phenomenon is possible when there are significant couplings among spin, lattice and electrical dipole moment. MnTiO$_3$ is one such system which exhibits magnetically induced ferroelectricity. The thin films of this compound show ferrotoroidicity [2]. For a material to undergoferrotoroidicity, it is necessary to break both the inversion and time-reversal symmetries. In view of this, coupling of spin and lattice degrees of freedom is expected to be present. In this paper, we employ the x-ray diffraction (XRD) technique to study the spin lattice coupling in MnTiO$_3$ which is an important parameter to understand the multiferroic properties of this compound.

MnTiO$_3$, an ilmenite, stabilizes in hexagonal structure with centro-symmetric $R3$ space group [3]. Here, the Mn$^{2+}$ ions are magnetic and the Ti$^{4+}$ ions are non-magnetic. This material undergoes a paramagnetic (PM) to antiferromagnetic (AFM) transition at $\sim$ 64 K with a broad anomaly $\sim$ 100 K. The broad anomaly is attributed to the setting of two-dimensional intra-layer antiferromagnetic interactions [4–9]. Goodenough has worked out both the intra- and inter-layer superexchange interactions and has shown mainly two intra-layer and three inter-layer superexchange interactions [10].

MnTiO$_4$ also reveals linear magnetoelectric coupling similar to that observed in Cr$_2$O$_3$ [11]. At zero magnetic field, the spins are aligned along the $c$-axis and no ferroelectric behaviour is observed. With the application of the field, the material becomes ferroelectric and beyond a critical applied magnetic field of 6.5 T along the $c$-axis, the spins tend to flop along the basal plane. At zero field, no anomaly is observed in the dielectric constant. Based

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on this fact, Mufti et al. [8] have pointed out that this material shows weak spin lattice coupling at the virgin state, i.e. zero applied magnetic field. There are several factors which contribute to changes in the dielectric constant induced by magnetization. These include spin lattice coupling, electronic structure, orbital degrees of freedom, etc. Non-observance of anomalies in the dielectric constant due to spin lattice coupling indicates that the nature of the spin structure is such that no break in spatial symmetry is observed. It has been observed in CoCr$_2$O$_4$ that the spiral spin structure would lead to the break in the inversion symmetry to obtain magnetically induced ferroelectric order [11]. Hence, the non-observance of dielectric anomalies in the case of MnTiO$_3$ does not guaranty that there is insignificant spin lattice coupling. In addition, MnTiO$_3$ exhibits quasi-two-dimensional AFM structure. In such low-dimensional system, the intra- and inter-layer superexchange interactions are expected to depend on the Mn-O, Mn-Mn bond lengths and Mn-O-Mn bond angles. Hence it is expected to show structural response across the region of intra- and inter-layer magnetic interactions.

In this paper, we report the temperature evolution of the various structural parameters of MnTiO$_3$ across the magnetic phase transition of the compound by using the XRD technique. Based on the behaviour of thermal expansion coefficients, the temperature-dependent structural parameters are divided into 3 regions. In the region I, the structural parameters show linear decrements due to a simple thermal effect. As the material enters into the region II, the decrements in the lattice parameters are drastically reduced and are also reflected in the Mn-O and Mn-Mn bonds. A minimum is also observed in the c/a ratio. In region III, the lattice parameter c shows negative thermal expansion. The experimental results were corroborated with the first-principle calculations. These behaviours have been interpreted to the setting up of short-range intra-layer and inter-layer AFM interactions ~ 200 and ~ 100 K, respectively. Apart from this, we also observed unusual behaviour in the Ti-O bonds across the region of magnetic phase transitions which still needs to be understood.

The sample was prepared by conventional solid-state route. The starting materials, MnCO$_3$ and TiO$_2$, were ground using mortar and pestle and sintered at 1200°C for 24 hours in air. The sample was characterized by using powder XRD and dc magnetization techniques. The results show complete solid solubility. The temperature-dependent powder XRD experiments were performed using Smart lab 9kW rotating anode x-ray diffractometer. The diffraction patterns were collected for 18 different temperatures to understand the temperature evolution of the structural parameters. The dc magnetization measurements were carried out using PPMS set up in the temperature range (300 K to 4 K) at applied field of 0.7 T.

The structures corresponding to the PM and AFM phases of MnTiO$_3$ have been relaxed by using the state-of-the-art full potential linearized augmented plane-wave (FP-LAPW) method [12]. In the calculations for the PM and AFM phases, the lattice parameters were fixed to the experimentally obtained values corresponding to 300 K and 23 K, respectively. The Muffin-Tin sphere radii were chosen to be 2.05, 1.76, and 1.59 a.u. for Mn, Ti, and O atoms, respectively. The recently developed PBESol [13] exchange-correlation functional has been used in the calculations. The convergence was achieved by considering $512 \times 512 \times 512$ $k$-points within the first Brillouin zone. The error bar for the energy convergence was set to be smaller than $10^{-6}$ Ry/atom. The structure was considered to be relaxed when the total force became less than 1 mRy/atom.

In fig. 1, we show the Rietveld refinement of the XRD patterns of MnTiO$_3$ collected at (a) room temperature (300 K) and (b) 23 K. The open circle and solid line correspond to the observed and calculated patterns, respectively. The Bragg reflections are represented by ticks. $R_p$, $R_w$, $R_e$, and $S$ correspond to the profile, weighted profile, expected weighted profile factors, and the goodness of fit, respectively.

Fig. 1: (Colour on-line) Rietveld refinement of the XRD patterns of MnTiO$_3$ collected at (a) room temperature (300 K) and (b) 23 K. The open circle and solid line correspond to the observed and calculated patterns, respectively. The Bragg reflections are represented by ticks. $R_p$, $R_w$, $R_e$, and $S$ correspond to the profile, weighted profile, expected weighted profile factors, and the goodness of fit, respectively.
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Fig. 2: (Colour on-line) Temperature evolution of (a) the DC magnetic susceptibility carried out at the applied magnetic field of 0.7 T, (a’) the first derivative of susceptibility, (b) the lattice parameters. The solid line shows the linear thermal contribution. The inset shows a closer view of the c-parameter in the temperature range from 20 to 200 K. The green line is a guide to the eye.

Above $T_N$ which will be explained later in the manuscript. Here, $T_N$ marks the transition from PM to a 3-dimensional AFM phase. The value of $T_N$ is obtained by taking the first derivative of the susceptibility as a function of temperature which is $\sim 62.9 \pm 1$ K as shown in fig. 2(a’). This value is in line with the reported value [8].

To obtain the structural parameters across the region of magnetic phase transitions, a Rietveld profile refinement [14] was carried out at all the temperatures. In figs. 1(a) and (b), we show a typical Rietveld refinement of the XRD patterns. The goodness of fit (S) obtained at all the temperatures is close to 1.5. The temperature evolution of the lattice parameters $a$ and $c$ is shown in fig. 2(b). The careful analysis of the data shows that the lattice parameters decrease with the decrease in temperature in a wide temperature range. However, this decrement is not uniform throughout the temperature range studied here. We observe the linear decrement of the lattice parameters up to 200 K and later on the deviation from the linear decrement is observed up to $\sim$ 95 K. On further reducing the temperature, the lattice parameter $a$ decreases marginally up to 50 K and later on it remains almost the same while $c$ shows an increase below 95 K. Figure 2(b) clearly shows the existence of three regions. In region I (300 K to 200 K), both the lattice parameters decrease by 0.07% and show linear thermal behaviour. In region II (200 K to 95 K), lattice parameters decrease by 0.04% and there occurs a deviation from linear thermal behaviour. In region III (below 95 K), the $a$-parameter shows a marginal decrease up to 50 K and later on it remains almost the same while the $c$-parameter increases by 0.014%, inset of fig. 2(b).

The above discussion clearly suggests the unusual temperature dependence of the $a$ and $c$ parameters in three different temperature regions. In order to shed more light on this, we have plotted the $c/a$ ratio vs. temperature in fig. 3(a). It is evident from the figure that the $c/a$ ratio shows a monotonic decrease in the region I. In region II, it shows non-monotonic behaviour where it reaches a minimum at around 140 K. In region III, an increase is observed in the $c/a$ ratio. In order to understand the temperature-dependent behaviour of the lattice parameters in a better way we have extracted the thermal contribution of lattice parameters from the raw data. The values of the $a’$ and $c’$ parameters thus obtained are plotted in fig. 3(b). Below 200 K, the values of both the parameters increase with the decrease in temperature as is evident from the figure. The $c’$-parameter shows a sharp increment with decreasing temperature. The thermal expansion coefficient $\alpha$ of the $a$ and $c$ parameters obtained by fitting the linear part of the graph (from 200 K to 300 K) is found to be $\sim 6.7 \times 10^{-6}$ K$^{-1}$ and $8.3 \times 10^{-6}$ K$^{-1}$, respectively, which are closer to the values of other ilmenite compounds [15]. The above behaviour of the lattice parameters clearly suggests the setting up of the magnetic interaction below 200 K, which is much higher than $T_N$.

Normally in the strongly correlated electron systems, the magnetic interactions are decided by the local structural parameters like neighbouring bond lengths and bond angles. Thus, in order to understand the magnetic interaction it is also important to look into the Mn-O, Ti-O, etc. bond distances. In the region I, the short Mn-O bonds (Mn-O(S)) decrease with the decrease in temperature, fig. 4(a). In the region II, it is found to increase below 140 K, then decreases in the region III and later on remains almost the same. The long Mn-O bond (Mn-O(L)) lengths, fig. 4(b), are found to decrease up to region II and in the region III, it increases from 75 K and below 50 K, it decreases. The Mn-Mn bonds are found to decrease in region I and a marginal increase is observed in the region II and in the region III, it remains almost the same.

In regions I and II, the short and long Ti-O bonds, fig. 5(a) and (b), are found to increase and decrease,
respectively with the decrease in temperature. On further reducing the temperature, both the bonds reveal opposite behaviours. A reduction in the Mn-Ti bond length, fig. 4(c), is observed in the region I and in the regions II and III, it remains almost the same.

The above results show an interesting temperature evolution of various structural parameters across the magnetic phase transitions. However, the changes in bond lengths are small and in some temperature range these changes are within the error bar. At this stage it is important to note that the x-ray diffraction technique provides extremely accurate values for lattice parameters. The presence of error bars in the fourth decimal place, as mentioned above, is an indication of this fact. However, this technique is not very accurate for determining the atomic positions of lighter elements, especially the oxygen ions. This is because the x-rays interact with the electron cloud, so the contribution of the diffracted intensity for the heavier element is greater as compared to the lighter elements. However, in the light of this fact, one cannot outrightly reject the small systematic changes observed in the bond lengths (within the error bars) in terms of change of slope across the region of the transition temperatures [16]. In order to confirm the reliability of the experimental results across the magnetic phase transition, we have performed the DFT-based first-principles calculations by using Wien2k code [12] where the structure of the compound is relaxed in both PM and AFM phases. The computational details are given above. The structural parameters corresponding to both the phases obtained after relaxations are shown in table 1. One can clearly see that the Mn-O(S) bonds increase by \(+0.271\) Å and the Mn-O(L) bonds decrease by \(0.0863\) Å as the compound enters from PM to the AFM phase. The Mn-Mn (intra) bond lengths are seen to increase by \(0.0772\) Å. The changes in the calculated Mn-O and Mn-Mn bond lengths across the magnetic phase transition are in line with the experimental data. However, the changes observed in the calculated bond lengths are more numerous as compared to the experimental results. This is due to the fact that the thermal contribution to the structural parameters is absent in the calculation which is competing with the magnetic contribution. Hence the experimentally observed changes in structural parameters are expected to be less than those observed in the calculations. To further emphasize this fact, a clear increase in the lattice parameters is observed in the region II only after the subtraction of the linear thermal background, figs. 2(b) and 3(b). This essentially means that there occurs strong competition between the thermal and the antiferromagnetic interactions.

The above results clearly show the discernible changes in the structural parameters in the temperature range where various magnetic interactions set in. Thus, the electronic and magnetic properties of this compound are expected to be closely related to the Mn-O and Mn-Mn bonds. This expectation appears to be a reality in the light of the fact

| Bond Lengths | Paramagnetic | Antiferromagnetic |
|--------------|--------------|-------------------|
| Mn-O(S) (Å)  | 1.9801       | 2.2511            |
| Mn-O(L) (Å)  | 2.1743       | 2.0880            |
| Mn-Mn (intra) (Å) | 2.9663 | 3.0435 |

Fig. 4: (Colour on-line) Temperature evolution of (a) Mn-O(S), (b) Mn-O(L) and (c) Mn-Mn intra bond lengths. The dashed lines are a guide to the eye.

Fig. 5: (Colour on-line) Temperature evolution of (a) Ti-O(S), (b)Ti-O (L) and (c) Mn-Ti bond lengths. The dashed lines are a guide to the eye.
that the magnetoelectric effect in this material arises due to Mn ions and the superexchange interaction depends strongly on the bond distances and bond angles. In the region I, the structural parameters, namely the lattice parameters, Mn-O and Mn-Mn bonds show simple thermal contraction as the values of α are in line with the general ilmenite structures [15]. As the material enters region II, the change in the slope of the lattice parameters vs. temperature graph (fig. 2(b)) suggests the evolution of the short-range intra-layer AFM interaction. To observe any effect on the diffraction pattern due to the onset of intra-layer AFM ordering, the coherence length should be at least some hundreds of ångströms. So the signature of layer AFM ordering, the coherence length should be at least some hundreds of ångströms. So the signature of the short-range magnetic cluster in the diffraction pattern suggests that the spatial extent of the magnetic phase is sufficient to be reflected in the structural parameters.

In MnTiO$_3$, Goodenough et al. [10] have shown that there are five superexchange interactions in this material. Out of these two are intra-layer interactions and the rest are inter-layer ones. The sign of the exchange interaction depends on the number of electrons in the orbitals which are interacting. For half-filled interacting orbitals the superexchange interaction is antiferromagnetic. When there is more than one electron per interacting orbital, the interaction is ferromagnetic. Following the Goodenough-Kanamori rules [17], the intra-layer AFM interaction occurs through the overlap of half-filled orbitals at the Mn sites. Hence in the region II, ~ 200 K, there occurs the onset of the magnetic interaction within the layer and is depicted as a decrease in the Mn-O (L) and Mn-Mn (intra) bond lengths above 140 K. It is interesting to note that the increase in the c/a ratio below 140 K and also the increase in the Mn-O(S) bonds suggest the onset of the weak interlayer superexchange interaction between the cations through the oxygen-oxygen ions. The increase in the Mn-O(S) bond length leads to the decrease in the separation between the O-O bonds lying along the c-axis and hence the enhancement in the super exchange interactions between the layers. So the critical temperature for setting up the intra- and inter-layer AFM interactions occurs in the region II, i.e. around 200 K and 100 K, respectively. This essentially means that the system prepares itself at temperatures much higher than the transition temperatures. In the context of this result, the broad peak and non-appearance of a sharp anomaly in the susceptibility data may be attributed to the short-range ordering above the respective transition temperatures. So far there are no reports on MnTiO$_3$ regarding this aspect.

In the region III, for temperatures below 50 K, the contributions due to the thermal effect and the AFM interaction to the c-parameter are almost the same. Hence almost no change in the value of α is observed, while for the c-parameter the magnetic interaction dominates thereby leading to its increment. The behaviour of the lattice parameters is more evident in the c/a ratio plot shown in fig. 3(a). It is also observed that the Mn-O(S) bonds initially decrease and remain almost the same until the lowest collected temperatures while the Mn-O(L) bonds show an increase at around 50 K and later on remain almost the same.

Apart from the Mn-O bonds, the Ti-O bonds also reveal significant changes across the region of intra- and inter-layer AFM interactions. However, it is still not clear about the role of Ti in magnetism of this compound and also the phenomena of magnetically induced ferroelectricity exhibited by this material. We hope that the careful observation of the local structural studies will provide clues for answering this question.

In summary, we have studied the temperature evolution of the structural parameters of MnTiO$_3$ using the x-ray diffraction technique. The temperature behaviour of the structural parameters can be divided into three regions; i) from 300 to 200 K, ii) from 200 K to 95 K and iii) from 95 K to 23 K. In region I, the linear decrement in the lattice parameters with the decrease in temperature is attributed to the thermal effect. In region II, below 200 K, lattice parameters further decrease non-linearly. This occurs as a result of the competition between the intra-layer AFM interaction and the thermal effect. Around 140 K, a minima is observed in the c/a ratio. The short Mn-O bonds show an increase below this temperature suggesting the onset of inter-layer AFM interaction. In the region III, the c-parameter increases signifying the fact that the antiferromagnetic interaction in 3 dimensions is completely stabilised. The Mn-O bond lengths obtained using first-principle calculations are in agreement with the experimental results. From the present results, it appears that spin lattice coupling plays significant role in stabilising magnetically induced ferroelectricity in this system. X-ray diffraction studies in the presence of magnetic field are expected to be helpful in addressing the origin of magnetically induced ferroelectricity in this compound.

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