Probing the involvement of non-magnetic Sr ion in the ferromagnetic transition of SrRuO$_3$, using XAFS

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Abstract. Recent calculations by Maiti et al. have shown that non-magnetic ions like Sr/Ca in Sr/Ca ruthenates may not be mere spectators in the magnetic transitions but their strong hybridization with O atoms may modify the magnetic ground state by distorting the Ru-O-Ru bond angle. Our XAFS results at Sr and Ru K-edges on SrRuO$_3$ indeed demonstrate that the Debye Waller factor for the Sr-coupled bonds viz. Sr-Sr evolve most significantly across the ferromagnetic transition, almost replicating the magnetization curve while the Ru-octahedra evolves only gradually. This clearly establishes the definite role of Sr disorder in the ferromagnetic transition.

1. Introduction
Ruthenium based perovskite oxides have attracted a great deal of attention due to possibilities in significant technological applications in addition to various interesting fundamental issues [1-3]. In particular, SrRuO$_3$, the only itinerant ferromagnet among the 4$d$ transition metal oxides ($T_c = 165$ K) [4], is a promising candidate for several technological applications due to its metallic character, high magnetic moment (1.4 $\mu_B$/Ru, high chemical stability, etc. [3-5]. Strangely, iso-structural CaRuO$_3$ though exhibiting similar high temperature magnetic moment, does not show long range ferromagnetic order [3-5]. This is very interesting since magnetism has been conventionally attributed only to the magnetic moment of the Ru ions. The Sr or Ca ions, on the contrary, have been considered to be mere spectators in the magnetization process for their negligible contribution to the electronic density of states near the Fermi level. The anomalous experimental observation, thus, questions the conventional theory and calls for a fresh approach by accommodating the participation of Ca, Sr. Recent calculations [6] indicate significant covalency between Sr, Ca and O that distorts the Ru-O-Ru angle and results in angle-dependent magnetic ground state. While the covalency induced effects appear in the Sr and Ca core level spectra [8], the derived correlation between Ru-O-Ru angle and ferromagnetism contradicts the prediction from Hund’s rule [6]. Under the circumstances, an important consideration could be structural disorder. Local disorder is known to significantly modify system properties [7], by inducing localization effects in band structure. The thermal evolution of the Ca and Sr core electronic levels [8] and magneto-volume effect in SrRuO$_3$ [9] testify to the role of structure. However, none of these reports could conclusively clarify the mechanism by which the so-called non-magnetic ions modify magnetic properties. In this report, we address this issue in SrRuO$_3$ using x-ray absorption fine structure (XAFS) technique. XAFS is best-suited to this problem since, by virtue of its element specificity, it can directly probe the short range structure around...
different atoms viz. magnetic Ru and non-magnetic Sr. The temperature dependence of the structure can then establish their distinct roles in the magnetic transition. Moreover, XAFS is the only structural tool to probe disorder.

2. Experimental

High quality sample of SrRuO$_3$ was prepared in the polycrystalline form following solid-state reaction route [8]. Good crystalline quality was confirmed by x-ray diffraction. Magnetic susceptibility measurements exhibit a ferromagnetic transition at 165 K. The magnetic moment of 2.7 $\mu_B$ in the paramagnetic phase is close to their spin only value of 2.83 $\mu_B$ corresponding to $t_{2g}^{3}$ electronic configurations at Ru sites. The polycrystalline samples were further ground to ~5 $\mu$m particle size and pasted on scotch tape. XAFS data at Sr K-edge (16.105 keV) and Ru K-edge (22.117 keV) were collected at the undulator beamline of MRCAT (Materials Research Collaborative Access Team) [10], Advanced Photon Source, USA. The temperature-dependent measurements (10-300K) were performed using a Displex cryostat. The data were processed using ATHENA [11] and the structural parameters (bond-length, coordination and DWF) were fit using the programs FEFF8 and FEFFIT [11]. The persistence of XAFS oscillations up to $k = 15$ Å$^{-1}$ re-confirms good data quality (Figures 1a and 1b). The $k^2$-weighted Fourier Transform spectra [$\chi(r)$] for all the temperatures at Sr and Ru K-edges are shown in Figures 2a and 2b respectively. By comparing figures 2a and 2b, it is clear that the structure around Sr is more sensitive to temperature than around Ru. The atoms corresponding to each peak are marked in the figures. The location of the peaks is consistent with the crystallographic structure of SrRuO$_3$.

3. Results and Discussions

The Sr-O bond parameters were best fit for $k^1$ --weighted Fourier transform of the data, over the range 3.2-12.5 Å$^{-1}$. $k^2$-weighted transform resulted in the O peaks lying along the shoulder of the Ru peaks. For $k^1$-transform, the Sr-O bond distribution is reflected as two peaks (named O1 and O2) in real space in the range 1.2-2.8 Å, over which fitting was performed. The datasets corresponding to different temperatures were fit simultaneously; while the coordination was constrained to be common between the various datasets, rest of the parameters viz. bond-length and DWF were fit variables for each temperature. The Sr-O1 and Sr-O2 bond-lengths remain constant (within uncertainties) at 2.45 Å and 3.1 Å respectively, over the entire temperature range. The thermal variation of the DWF, for Sr-O1 and Sr-O2, are shown in figure 3. Sr-O1 DWF is small and varies only slightly (0.0035-0.0045 Å$^2$) with temperature, which is signature of strong binding, possibly resulting from covalency. The DWF for Sr-O2, on the other hand, is much higher than for Sr-O1, since the O atoms of the Ru-O octahedra are not equidistant from Sr atom. Moreover, Sr-O2 DWF evolves anomalously across the ferromagnetic transition.
temperature: the saturation of the disorder beyond 200K almost resembles an inverse of the magnetization curve [3].

Ru and Sr neighbors are reflected as two peaks over the range 2.8-4 Å. Fitting over this range was performed for \( k^3 \) weight in order to de-emphasize the contribution / leakage of the Sr-O bonds into the Sr / Ru peaks. Simultaneous fitting, as before, yielded Sr-Ru bond-length constant (within uncertainties) at 3.425 Å and Sr-Sr bond-length varying slightly between 3.930-3.945 Å with temperature. Sr-Sr DWF (like Sr-O2) shows a significant evolution with temperature, replicating ferromagnetic transition in figure 3. On the other hand, Sr-Ru DWF evolution is gradual (typical of conventional phonon models), consistent with the poor coupling between Sr and Ru atoms. Note that the possibility of hidden segregating Sr nano-cluster (beyond the detection limit of XRD) was ruled out by fitting. Thus the observed anomalous DWF evolution of Sr-O2 and Sr-Sr bonds is real and not a fitting artifact, resulting from such hidden phases. All of our fits showed excellent fit quality (R-factor ≤ 0.005) [11]. A typical fit (higher shell at 20 K) of Sr K-edge data is shown in Figure 4a.

Ru-O bond parameters were best fit for \( k^1 \) –weighted Fourier transform of the data, over the range 2.5-13 Å\(^{-1}\). Ru-O DWF is found to be very low (0.0007-0.0012 Å\(^2\)) and evolves gradually with temperature. Ru-O bond-length remains constant (within uncertainties), at 1.945 Å. Both of these convey the rigidity of Ru-O octahedra. Therefore, the significant and anomalous evolution of the Sr-O2 DWF (that we observed at Sr K-edge) must happen due to Sr-O covalency. The Ru-Ru bond parameters were best fit for \( k^2 \)-weighted Fourier transform of the data over the range 2.5-13 Å\(^{-1}\). Ru-Ru bond-length is found to be constant at 4.02 Å and the thermal evolution of Ru-Ru DWF to be gradual (figure3). These fits were of excellent quality (R-factor < 0.005). A typical fit (at 20 K) of Ru K-edge data is shown in Figure 4b.
4. Conclusion
In summary, we have studied the evolution of Ru-O bond-lengths, Sr-O bond-lengths and their Debye Waller factors with temperature. Ru-O bond-length and corresponding DWF are found to be similar at all the temperatures studied. Sr-O bond-lengths are also found to remain unchanged with temperature. On the other hand, DWF of Sr-O bonds representing the disorder/distribution of Sr-O bond-lengths exhibit significant change with temperature. Interestingly, this modification starts much before the transition temperature is reached.

Significant evolution of disorder across ferromagnetic transition is well reported [12]. But SrRuO$_3$ is unique in that the most significant evolution of disorder lies with a non-magnetic ion (viz Sr). Thus, (1) the ferromagnetic transition appears to be sensed by the DWF of Sr bonds, which are conventionally considered spectators in these materials. Their thermal evolution shows signature of precursor effect; (2) disorder presumably plays significant role in the ferromagnetic transition. Calculation of the electronic structure is underway to determine the mechanism and extent of this participation.

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6. References
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