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Local structural effects in $\text{Sr}_3\text{NiRhO}_6$ across magnetic transition

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We investigate the temperature dependence of the structural parameters of quasi-one-dimensional $\text{Sr}_3\text{NiRhO}_6$ across the region of magnetic phase transitions using Ni-K edge and Sr K-edge extended x-ray absorption fine structure (EXAFS) spectroscopy. The setting of the intra chain super exchange interaction starts ~ 200 K which is well above the Neel temperature. The onset of the inter chain super-super exchange interaction appears to be ~ 125 K and below 55 K, the system undergoes three dimensional magnetic ordering. Interestingly, the role played by direct exchange interaction between the Ni 3d and Rh 4d states in stabilising the magnetic interaction is less significant. The present results shed light on the generic features exhibited by isostructural compounds and may help in identifying the magnetic exchange pathways useful to understand the unusual properties exhibited by them.

In the mid eighties, the interest in low dimensional materials has been revived since the discovery of high temperature superconductivity owing to its intimate connection with the strong magnetic fluctuations. Quasi-one-dimensional magnetic systems are interesting from the point of view of basic physics and technological applications etc¹ like multiferroic devices, thermoelectric devices, possible quantum computational devices. From basic physics point of view they provide unique platform to study the interplay between spin chain phenomena and geometrical frustration in a single compound.

Among all the quasi-one-dimensional magnetic systems that stabilises with $\text{A}_3\text{MM}'\text{O}_6$ formula (M and M' are transition metal), $\text{Ca}_3\text{Co}_2\text{O}_6$ (CCO) compound has been widely investigated. These compounds stabilize in $\text{R}\bar{3}\text{C}$ space group. It has been reported that this material exhibits similar magnetic behaviour²⁻⁷ as $\text{Sr}_3\text{NiRhO}_6$ (SNRO), $\text{Sr}_3\text{NiIrO}_6$ (SNIO), $\text{Ca}_3\text{CoRhO}_6$, $\text{Ca}_3\text{CoIrO}_6$ and $\text{Sr}_3\text{Co}_2\text{O}_6$ in many respects. To understand the origin of the common behaviours exhibited by such isostructural compounds, we have chosen SNRO for further investigation. Each of the chain contains face shared NiO_6 trigonal prism (TP) and RhO_6 octahedra along the c-axis coupled ferrimagnetically, arranged in a triangular antiferromagnetic lattice giving rise to partially disordered antiferromagnetic (PDA) structure. The valence states of Ni and Rh are 2+ and 4+, respectively with the Ni in the high spin state (HS) and Rh in the low spin state (LS). The magnetic susceptibility exhibits two transitions around 45 K (T1) and in the range 10-15 K (T2). This material exhibits PDA structure between 45 and 15 K. Apart from T1 and T2, a broad shoulder region (50 to 70 K) is reported and has been attributed to short range magnetic fluctuations⁸. Band structure calculations have shown that electron correlation effects in the Ni and Rh sites are sufficient to open a gap in the electronic spectrum⁹. The localisation of the electrons at the Ni and Rh sites are dependent on the extent of hybridisation of the 3d and 4d orbitals with neighbouring oxygen ions and hence on the local bond lengths surrounding the Ni and Rh sites. Also the intra and in-

FIG. 1: The first column shows the temperature dependent Fourier transform of $k^2\chi(k)$ for the (a) Ni K-edge of $\text{Sr}_3\text{NiRhO}_6$. Representative fits at 15 K for the (b) first and (c) higher coordination shells. The second column shows the temperature dependent Fourier transform of $k^2\chi(k)$ for the (d) Sr K-edge of $\text{Sr}_3\text{NiRhO}_6$. Representative fits at 15 K for the (e) first and (f) higher coordination shells. The open circle and solid line represent the experimental and fitted patterns.

ter chain magnetism exhibited by these kinds of systems strongly depend on orbital occupancy and hence on the local bond lengths. Therefore, we have employed Ni K-edge and Sr K-edge EXAFS spectroscopy to study the evolution of local structure around the Ni and Sr ions. We observe signatures of intra and inter chain interactions at temperatures much above the magnetic transition. The role played by direct $d-d$ hybridisation is less significant in deciding the magnetic interactions. These behaviours appear to be similar to CCO¹⁰, SNIO¹¹.

The powder sample of SNRO was prepared by solid state reaction route. The details of the sample preparation and characterisation are given in the reference⁸. Temperature dependent Ni K-edge and Sr K-edge EXAFS experiments were carried out in X-18B beamline

at National Synchrotron Light source, Brookhaven National Laboratory. The storage ring was operated at 2.8 GeV, 300 mA. The beamline used a Si(111) channel cut monochromator with an energy resolution 0.8 eV at the Ni K-edge andeV at Sr K-edge. The Ni and Sr K-edge EXAFS analysis were carried out using the DEMETER¹² data analysis package following the standard procedure. The Fourier transform to the r -space was taken in the range 3.1 to 12.5 $\text{\AA}^{-1}$ for Ni K-edge and 3 to 13.6 $\text{\AA}^{-1}$ for Sr K-edge by Fourier transforming $k^2\chi(k)$ with a Kaiser-Bessel window function.

The Fourier transform (FT) amplitudes for both the Ni and Sr K-edges are uncorrected for the central and back scattering phase shifts. For clarity, FT of only few temperatures are displayed in Figs. 1(a and d). The FT of the $k^2\chi(k)$ of the Ni K-edge show 3 dominant peaks A, B and C situated around 1.6 $\text{\AA}$, 2.6 $\text{\AA}$ and 3.4 $\text{\AA}$, respectively, Fig. 1(a). The features observed ~ 1.28 and 1.97 $\text{\AA}$ correspond to spectral leakage due to the limited k -range. Peak A corresponds to Ni-O bond lengths near 2.181 $\text{\AA}$. Peaks B and C correspond to Ni-Rh (~ 2.766 $\text{\AA}$) and Ni-Sr1 (~ 3.505 $\text{\AA}$), Ni-Sr2 (~ 3.57 $\text{\AA}$) single scattering paths, respectively with a weak contribution from Ni-O-Rh and Ni-O-O multiple scattering paths. From the figure, we find the intensity of all the peaks increases until 75 K and below 75 K it remains unchanged down to 15 K. The changes observed in Fig.1a suggest significant modification in the local structure around the Ni ions. To obtain the structural parameters across the region of magnetic phase transitions, we have carried out EXAFS fitting for the first three coordination shells. In the EXAFS fitting, the error bars in the bond lengths are due to the uncertainty in the absolute value. Large part of uncertainty is mainly due to the correlation with other variables. During the fitting process, care was taken to reduce the number of correlated parameters. In some temperature range, the changes in the bond lengths are smaller than the error bars. Owing to the above reasons, one cannot ignore the small systematic changes observed in the bond lengths in terms of slope change around the region of phase transitions^{10,13}.

The first shell fitting was done in the r -range 1.41 to 1.93 $\text{\AA}$ for all the temperatures. Based on the x-ray diffraction results¹⁴, we have modelled the first coordination shell with six Ni-O bonds. The higher shell fitting was carried out to obtain the information about the Ni-Rh, Ni-Sr1 and Ni-Sr2 bond lengths. During this fitting, the Ni-O bond lengths obtained from the first coordination shell was kept fixed. To reduce the uncertainty of the variables, we have used average bond lengths and single scattering paths. We have fitted the higher coordination shells with two Ni-Rh bonds, three Ni-Sr1 and six Ni-Sr2 bonds in the Fourier filtered k -space in the range 1.93 to 3.6 $\text{\AA}$ for all the temperatures. During the fitting, the coordination number was kept fixed and only bond lengths and corresponding Debye-Waller factors (DWF) were varied to reduce the number of correlated parameters. The representative fits for the first and higher coor-

FIG. 2: Temperature dependence of (a) Ni-O, (b) Ni-Rh and (c) av.Ni-Sr bond lengths. Temperature dependent Debye Waller factors corresponding to (d) Ni-O, (e) Ni-Rh, (f) av. Ni-Sr, (g) Local crystal field energy diagram of Ni^{2+} (h) TP environment of Ni^{2+} . The Ni ion (yellow) and the oxygen ions (brown) occupy the centre and corners of the TP, respectively. The arrows indicate the expansion of the NiO_6 TP due to the occupation of $d_{\pm 1}$ states.

dination shells are shown in Figs 1.(b and c). The typical R-factors for the first and higher coordination shells are ~ 0.002 .

Fig.2(a) shows the temperature evolution of Ni-O bond distance and its DWF. Careful analysis of the data shows the Ni-O bonds increase with decrease in temperature and its DWF decreases with decrease in temperature. Interestingly, we observe increment in the Ni-O bond lengths from 300 K and down to 15 K. In the temperature range 300 to 200 K, a 0.05% increment is observed in the Ni-O bond lengths. The increment is $\sim 0.4\%$ in the temperature range 200 K to 55 K and below 55 K, the changes are insignificant. So here it appears that the behaviour of the Ni-O bonds does not follow simple thermal effect from 300 K. In the below discussions, we focus on temperatures at and below 200 K only, as there is a dramatic change in this bond length below this temperature only. At this juncture, it is tempting to compare our earlier EXAFS studies¹⁰ done on isostructural, CCO. At room temperature, the value of the Co-O bonds at the TP site is ~ 2.04 $\text{\AA}$ and for SNRO, the Ni-O bond length is ~ 2.13 $\text{\AA}$. It is interesting to note, in the case of CCO, the changes observed in the Co-O bonds as a function of temperature are very less in comparison to SNRO. This could be due to stronger bonds of Co-O in comparison to the Ni-O bonds. Apart from this, the observation of magnetic anomalies at low temperature in CCO as compared

FIG. 3: Temperature dependence of (a) Sr-O, (b) Sr-Rh and (c) av. Sr-Ni bond lengths. The DWF corresponding to (d) Sr-O, (e) Sr-Rh and (f) av. Sr-Ni with temperature.

to SNRO is possibly due to the larger distance between the magnetic Co^{3+} ions as compared to the Ni^{2+} - Rh^{4+} bonds. At room temperature, the DWF of Ni-O bonds in SNRO is $\sim 0.008 \text{ \AA}^2$ and for Co-O in $\text{Ca}_3\text{Co}_2\text{O}_6$ is $\sim 0.004 \text{ \AA}^2$. The larger value of DWF for Ni-O compared to Co-O suggests structural disorder of Ni-O bonds in SNRO is greater in comparison to Co-O bonds in CCO.

The temperature dependent behaviour of the higher coordination shells are shown in Figs. 2 (b and c). In the temperature range 200 to 125 K, changes in the Ni-Rh and av. Ni-Sr bonds are insignificant. For the range 125 to 55 K, the Ni-Rh bonds show a marginal increase while the av. Ni-Sr bonds decrease with decrease in temperature and below 55 K, the variation in the bond lengths remain unaffected. The DWF corresponding to the Ni-Rh bonds decreases while for av. Ni-Sr bonds, the variations are not significant.

The Fourier transform (FT) of the $k^2\chi(k)$ of the Sr K-edge show 3 dominant peaks D, E and F at $\sim 1.9 \text{ \AA}$, $2.8 \text{ \AA}$ and $3.7 \text{ \AA}$ respectively, Fig. 1(d). Peak D corresponds to the average Sr-O bond lengths. Peaks E and F corresponds to Sr-Rh, Sr-Ni1 and Sr-Ni2 single scattering paths and Sr-Sr single scattering path, with contribution from Sr-O-Rh multiple scattering paths, respectively. From the figure, we find the intensity of all the peaks increases significantly until 150 K and later on there is only marginal increase until 15 K.

The first shell fitting was done in the Fourier filtered k -space in the range 1.43 to $2.53 \text{ \AA}$ for all the temperatures. We have modelled the first coordination shell with eight Sr-O bonds. The higher shell fitting was carried out to obtain the information about the Sr-O, Sr-Rh and av. Sr-Ni bond lengths. During this fitting, the Sr-O bond lengths obtained from the first coordination shell was kept fixed. To reduce the uncertainty of the variables, we have used average bond lengths and single scattering paths. We have fitted the higher coordination shells with two Sr-Rh bonds, one Sr-Ni1 and two Sr-Ni2 in the Fourier filtered k -space in the range 2.55 to $3.44 \text{ \AA}$ for all the tempera-

tures. During the fitting, the coordination number was kept fixed and only bond lengths and its corresponding DWF were varied to reduce the number of correlated parameters. The representative fits of the first and higher coordination shells are shown in Figs. 1(e and f). The typical R factor obtained for the first and higher coordination shells is ~ 0.005 .

Fig. 3 shows the temperature evolution of Sr-O, Sr-Rh, av. Sr-Ni bonds and its DWF. It is interesting to note that the variations in all the three bond lengths in the temperature range 200 to 125 K are $\leq 0.05\%$. In the temperature range 200 K to 125 K, the decrement in the Sr-O and Sr-Ni bonds are $\sim 0.2\%$ while for av. Sr-Rh it is $\sim 0.1\%$. Below 55 K, the changes are marginal.

The above discussions clearly suggest that in the temperature range 200 to 125 K, all the bonds except Ni-O bonds do not show significant variations, Figs. 2(a) and 3. In the temperature range 125 to 55 K, the Sr related bonds decrease with decrease in temperature. Below 55 K, the variations are not substantial.

The schematic $3d$ energy level diagram of Ni^{2+} is given in Fig. 2(g) based on the *ab-initio* band structure calculations⁹. Due to TP environment, the $3d$ states split into d_0 (d_{z^2}) in lowest energy level, $d_{\pm 2}$ ($d_{x^2-y^2}$ and d_{xy}) in the intermediate energy levels and $d_{\pm 1}$ (d_{xz} and d_{yz}) in the highest energy levels. Ni^{2+} ion being in HS state with $3d^8$ electronic configuration and considering the Hund's rule, five electrons will occupy the up spin band of d_0 , $d_{\pm 2}$ and $d_{\pm 1}$ and three electrons will occupy the down spin band of d_0 and $d_{\pm 2}$ leaving the up spin band of $d_{\pm 1}$ partially filled. Partial filling of $d_{\pm 1}$ bands will lead to extension of all the bond lengths at the TP site, Fig. 2(h). So when the intra chain super exchange interaction sets in, an increase in the Ni-O bonds are expected. In these kinds of compounds, the inter chain super super exchange interactions occur through the intervening oxygen-oxygen ions. So when such inter chain interaction sets in, an increase in the Ni-O bond lengths are also expected and this is what we observe in the present situation. Over all, we know that as the Ni-Ni bond distance is about twice of Ni-O bonds, the intra chain interaction is expected to set in at higher temperature as compared to the inter chain interactions. So one can demarcate both the interactions based on the local bond lengths that are sensitive to intra and inter layer interactions separately. It is expected Ni-O and Sr-O bonds to be sensitive to both intra chain and inter chain interactions while av. Sr-Ni and Sr-Rh bonds to inter chain interactions predominantly. So the increment observed in the Ni-O bonds $\sim 200 \text{ K}$ marks the onset of intra chain super exchange interaction which is well above T_N . It is interesting to note, based on inelastic neutron scattering experiments¹¹, signature of magnetic excitations have been observed in SNIO compound (which falls in the regime of spin-orbit coupling) until 200 K which is well above T_N . From Figs. 3(b and c), we observe temperature variation of Sr-Rh bond is less sensitive as compared to Sr-Ni bond length. In the ionic model, owing to

columbic interactions, Ni^{2+} - Sr^{2+} separation is expected to be more than Rh^{4+} - Sr^{2+} . So Sr-Rh bonds are stronger than Sr-Ni and hence the response of Sr-Rh bonds to temperature will be less as compared to Sr-Ni bonds. For temperatures below 125 K, the decrement in the Sr related bonds is possibly due to the onset of inter chain super-super exchange interactions. With regard to the Ni-Rh bond lengths, it is interesting to note that these bond lengths are less sensitive down to low temperatures despite the highly extended nature of the $4d$ orbitals of Rh ions. In the CCO compound also we found¹⁰ the Co-Co bonds do not play significant role in stabilising the magnetic interactions despite the face sharing nature of the CoO_6 TP and CoO_6 octahedra. These behaviours show the common features exhibited by SNRO, CCO and SNIO compounds.

In summary, the temperature evolution of Ni and Sr K-edge EXAFS studies have been carried out on Sr based spin chain system, $\text{Sr}_3\text{NiRhO}_6$. The increment observed in the Ni-O bonds from 200 K marks the onset of intra-

chain super exchange interaction. The decrement in the Sr related bond lengths from 125 K is possibly related to the onset of inter chain super-super exchange interactions. Below 55 K, the three dimensional magnetism is completely set in. The low sensitivity of the Ni-Rh bonds to the temperature implies less role played by the direct hybridisation of Ni- $3d$ and Rh- $4d$ orbitals to the stabilisation of magnetic interaction. The above observations are common to CCO and SNIO compounds. The present results clearly show how one can discern the onset of the magnetic interaction existing between the chains well above the transition temperatures. These results will provide an impetus in unravelling the generic features exhibited by similar kinds of compounds and thereby providing clue in understanding the unusual magnetic properties exhibited by them.

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