Neutron Diffraction Studies on Co and Ru based Double Perovskites

[1] P. S. Ramu Murthy [2] K. R. Priolkar [3] A. Das
[1]Dhempe College of Arts and Science, Goa
[2]Goa University, Goa
[3]Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai

Abstract:— **This paper reports the neutron diffraction measurements on LaSrCoRuO6 and La2xSr2-2xCo2xRu2-2xO6. Based on these measurements, in LaSrCoRuO6, it is interpreted to be due disorder in site occupancy of Co and Ru leading to octahedral distortions and formation of the Ru-O-Ru ferromagnetic linkages which are known to align ferromagnetically. Ferromagnetic interactions are clearly seen in the disordered LaSrCoRuO6 which has a larger B-site occupancy disorder of the Co and Ru sites. In La2xSr2-2xCo2xRu2-2xO6, the compounds crystallize in the double perovskite structure. The 20K neutron data shows extra super-lattice reflections due to antiferromagnetic ordering in x = 0.75. These reflections are accounted for by an antiferromagnetic alignment of the Co and Ru spins.**

Index Terms:--**Antiferromagnetism, Double Perovskite, Itinerant ferrimagnetism, negative magnetoresistance.**

I. INTRODUCTION

The interplay of magnetism and electron transport in double perovskite oxides has been of recent interest following the discovery of itinerant ferrimagnetism in Sr2FeMoO6 and Sr2FeReO6 [1,2]. The itinerancy and ferrimagnetism are found to arise from a double exchange type of mechanism in which the ordering and electronic configuration of the transition metal cations plays a critical role [3].

It is found that structurally, the 3d and 4d or 5d transition metal cations are ordered in an alternating (rock salt) manner within a perovskite lattice. Also, electronically, the 3d cation is found to have a large spin whereas the 4d or 5d cations usually have $S \leq \frac{1}{2}$. Equal spins of the 3d and 4d or 5d cations could result in a so-called half-metallic antiferromagnet (HMAF) where completely filled spin-polarized conduction occurs in a zero magnetization material. Prospective candidates for HMAF are double perovskite materials such as (LaA) CoRuO6 where both high-spin Co^{2+} and Ru^{5+} have S = 3/2. However, studies have shown that these materials order antiferromagnetically with two opposed Co and two opposed Ru spin sub lattices. They are variable range hopping semiconductors (VRH) for A = Sr at 85K and show no magnetotransport effects [4]. Excess A-cation substitution (hole doping) is found to result in a rapid reduction of the resistivity while the Neel temperature increases only moderately. Also, structurally, the antisite disorder is found to increase rapidly for hole doping and

Sr_2CoRuO_6 is completely cation disordered. Excess La substitution is found to reduce the cation ordering much less significantly and La_2CoRuO_6 is found to have an ordered arrangement of Co and Ru. In an attempt to investigate the effect of having more equal spin occupancies, on the two cations, Cobalt Ruthenate double perovskites have been investigated.

Many materials illustrate the importance of ordered Ru and 3d transition metal sub-lattices. For example, in $RuSr_2GdCu_2O_8$, antiferromagnetism and superconductivity coexist [5,6]. Other ruthenates that show notable electronic properties are $SrRuO_3$ – high temperature ferromagnetism [7], Sr_2RuO_4 – superconductivity [8]. The only reported transition metal ruthenate double perovskite where a rock salt ordered sub-lattice exists are $LaACoRuO_6$ (A= Sr, Ba) [9] and $LaBaCuRoO_6$ [10]. The cobalt ruthenates are found to be semi-conducting with magnetic ordering temperatures of 157 K (A=Sr) and 40K (A=Ba).

One of the starting members of LaACoRuO6 (A = Sr), the perovskite compound $SrRuO_3$ is a rare example of a ferromagnetic 4d oxide with a sizeable magnetic moment [11]. At room temperature, the structure like many of the ABO_3 perovskite compounds, exhibits orthorhombic Pbnm symmetry and a high-resolution powder neutron diffraction study demonstrates it to be iso-structural with $GdFeO_3$. It is found to be a Stoner ferromagnet despite its relatively low conductivity. This Stoner criterion is found to be satisfied because of the high density of states at the Fermi level that critically enhances the electron magnetic susceptibility.

Metals that possess high-density of states at the Fermi levels form giant localized magnetic moments around magnetic impurities that polarize the neighboring itinerant electrons. The first evidence of this phenomenon in oxides has been found in studies on $SrRuO_3$ substituted with $LaFeO_3$. Alignment of the spin polarized electron atmospheres around Fe^{3+} under a field is found to give rise to the emergence of a large magneto resistance at low temperatures in $(Sr_{1-x}La_x)(Ru_{1-x}Fe_x)O_3$ systems [12, 13].

The other starting member $LaCoO_3$ is known to have a perovskite-type structure and is reported to show a unique nonmetal-metal crossover with change in temperature. The ground state of $LaCoO_3$ is a nonmagnetic insulator with a predominant electron configuration of $3d^6$ of Co^{3+} fully occupying the t_{2g} level as reported in [14, 15]. At room temperature, the powder x-ray diffraction pattern shows the crystal to be a slightly distorted perovskite with rhombohedral structure (R $\bar{3}$c) [16]. Like Fe^{3+}, Co^{3+} also provides electron energy levels that are in the vicinity of the Fermi level of $SrRuO_3$. This is an important prerequisite for forming a localized moment according to Anderson, Wolff and Clogston, who have treated localized moments as virtual bound states that arise by resonance. Therefore, if the concept of electron polarization is correct, then very similar behavior, including enhanced saturation magnetization and a large negative MR, should also be observed in Co-substituted $SrRuO_3$. However, in the case of $LaSrCoRuO_6$ no such behavior is observed [4]. This could be attributed to the somewhat lower energy levels of Co^{3+} as compared to Fe^{3+} as well as transitions between the various electronic states of Co including high spin Co^{2+}, Co^{3+} and Co^{4+}, and low spin Co^{3+} and Co^{4+}.

Therefore, $(Sr_{1-x}La_x)(Ru_{1-x}Co_x)O_3$ system should not behave like $(Sr_{1-x}La_x)(Ru_{1-x}Fe_x)O_3$. Previous investigations of $SrRu_{0.9}Co_{0.1}O_3$ suggest an enhanced saturation magnetization and negative MR in the vicinity of Curie temperature [17]. A negative MR is also reported to be observed in $La_{0.5}Sr_{0.5}Co_{0.9}Ru_{0.1}O_3$[18]. Studies on $(Sr_{1-x}La_x)(Ru_{1-x}Co_x)O_3$ by Mamchik et al [19] suggest that Co, like Fe, spin polarizes the itinerant electrons in $SrRuO_3$ to form large local magnetic moment. In the spin glass regime, where Anderson localization dominates, a large negative MR emerges as a result of spin polarization of mobile carriers which occupy states beyond the mobility edge. It must be noted here that ordered $La_{0.5}Sr_{0.5}Co_{0.5}Ru_{0.5}O_3$ is reported to be magnetically frustrated with a spin freezingtemperature of about 50K. The large difference in the size and valence between Ru^{5+} and Co^{2+} leads to ordering of the B sub-lattice. However,

the studies by Bos et al have shown $LaSrCoRuO_6$ is an antiferromagnet with $T_N = 87K$ or a spin glass and the transition at 157K could be due to $SrRuO_3$ impurity.

Therefore, the magnetic ground state of the ordered compound itself is not clear. The importance of different magnetic interactions between $Co^{2+/3+}$ and $Ru^{4+/5+}$ that govern the magnetic ground state have been highlighted in the studies conducted on $LaSrCoRuO_6$ by varying the composition ratio of A-site cations (La and Sr). Another possible was of modifying the magnetic and transport properties are by forming solid solutions of antiferromagnetic $LaCoO_3$ and ferromagnetic $SrRuO_3$. These perovskite solid solutions of the form $Sr_{1-x}La_xRu_{1-x}Co_xO_3$ will have a strong interplay of cationic order, charge balance and complex magnetic interactions between the two B-site cations [20]. In $SrRuO_3$, the 4d electrons of the low spin Ru^{4+} ions occupy the narrow π^* band near the Fermi level [21]. The lower 3d energy levels of Co^{3+} causes a charge transfer from $4dRu^{4+}$ to $3dCo^{3+}$ [19].However, Co can have various electronic states including high spin (HS) Co^{2+}, Co^{3+} and Co^{4+}, intermediate spin (IS) Co^{3+} and Co^{4+} and low spin (LS) Co^{3+} and Co^{4+} [22-26]. This complicates the situation giving rise to properties like localized magnetic moment of Co [27], negative magnetoresistance [28]. In case of $Sr_{1-x}La_xRu_{1-x}Co_xO_3$, a complete charge transfer occurs at x = 0.5. At this composition, the CoO_6 and RuO_6 octahedra align themselves in a pseudocubic array in the rocksalt arrangement forming the archtype "double perovskite" structure. Besides, the charge transfer between Ru and Co in $LaSrCoRuO_6$ is very sensitive to local atomic structure such as cation order [29-31]. Any disturbance in this cation order leads to compensation of antiferromagnetic interactions by the ferromagnetic interactions most likely associated with Ru-O-Ru interactions. The LaCoO3 substituted SrRuO3 has been known to exhibit large local magnetic moment arising due to Co spin polarizing the itinerant electrons of $SrRuO_3$ [19]. The delicate charge transfer achieved in solid solutions by conversion of Co^{3+} to Co^{2+} and oxidation of Ru^{4+} to Ru^{5+} due to formation of double perovskite structure has not been addressed. Hence to gain an insight into the effect of thermally induced site-occupancy disorder in $LaSrCoRuO_6$ on its structural and magnetic properties as well as $(La_{2x}Sr_{2-2x})(Co_{2x}Ru_{2-2x})O_6$, neutron powder diffraction (NPD) measurements in the temperature range 20-300K have been conducted. The temperature dependencies of the structural parameters can then be obtained by later performing Rietveld fitting of the NPD data.

II.   EXPERIMENTAL

LaSrCoRuO$_6$:

Two polycrystalline samples of LaSrCoRuO$_6$ were synthesized by solid state reaction method taking stoichiometric amounts of La$_2$O$_3$, SrCO$_3$, Co (No$_3$)$_2$ and RuO$_3$. These starting powders were ground thoroughly, pressed into pellets and heated for a total of 48hrs, one at 1200°C and the other at 1300°C with three intermediate regrinding steps. The sample annealed at 1200°C was quenched to room temperature while the other was furnace cooled. Both samples were deemed to be phase pure, as the X-ray diffraction data collected on a Rigaku X-ray diffractometer in the range of 18° ≤ 2θ ≤ 80° using CuKα radiation showed no impurity reflections. The diffraction patterns were Rietveld refined using FULLPROF suite and structural parameters were obtained. DC magnetization was measured, both as a function of temperature and magnetic field using the Quantum Design SQUID magnetometer (MPMS-5S). M(T) was measured in an applied field of 50 and 1000Oe in the temperature range of 5-300°K with the sample being initially cooled from 300° to 5°K in zero applied field and the data recorded while warming up to 300°K in the applied magnetic field (ZFC curve) and subsequent cooling (FC curve) back to 5°K. Magnetization as a function of field was measured under sweep magnetic fields up to ±5T at various temperatures. Neutron diffraction measurements were performed at room temperature (RT) and 20K and a wavelength of 1.24A° using powder diffractometer at Dhruva, Trombay.

(La$_{2x}$Sr$_{2-2x}$)(Co$_{2x}$Ru$_{2-2x}$)O$_6$:

Polycrystalline samples of La$_{2x}$Sr$_{2-2x}$Co$_{2x}$Ru$_{2-2x}$O$_6$, 0.25≤ x ≤ 0.75 were synthesized by solid state reaction method by taking pre-dried stoichiometric amounts of La$_2$O$_3$, SrCo$_3$, Co(NO$_3$)$_2$.6H$_2$O and RuO$_2$. These starting powders are ground thoroughly, pressed into pellets and heated for a total of 48hrs, at 1300°C with three intermediate regrinding steps. All samples were deemed to be phase pure, as X-ray diffraction (XRD) data collected on a Rigaku X-ray diffractometer in the range of 18° ≤ θ ≤ 80° using CuKα radiation showed no impurity reflections. The diffraction patterns were Rietveld using FULLPROF suite and structural parameters were obtained. Neutron diffraction (ND) measurements were performed at room temperature (RT) and 20K and at a wavelength of 1.24 A° using powder diffractometer at Dhruva, Trombay for the end members of the series, x = 0.25 and x = 0.75.

III.   RESULTS AND DISCUSSION

LaSrCoRuO6

The Rietveld refined XRD patterns for the two samples of LaSrCoRuO$_6$, LSCR13 and LSCR12 prepared at 1300° and 1200°C are presented in Fig.1. The sample has a monoclinic structure with the B-site cations, Co and Ru ordered in the NaCl pattern in the space group P$_{21/n}$. ND patterns recorded at 300K (Fig.2) show evidence for higher degree of B-site order in LSCR13 as compared to LSCR12. A presence of sharper (1/2, 1/2, 1/2) super-lattice reflections in the ND pattern in LSCR13 (inset of Fig. 2) indicates a higher degree of ordering in LSCR13. The scale factor, background parameters, cell parameters, Co and Ru site occupancies along with instrumental broadening, totaling 17 parameters were refined to obtain a good fit. The crystallographic parameters obtained from the refinement of ND patters along with Curie-Weiss parameters calculated from magnetization measurements are shown in Table 1.
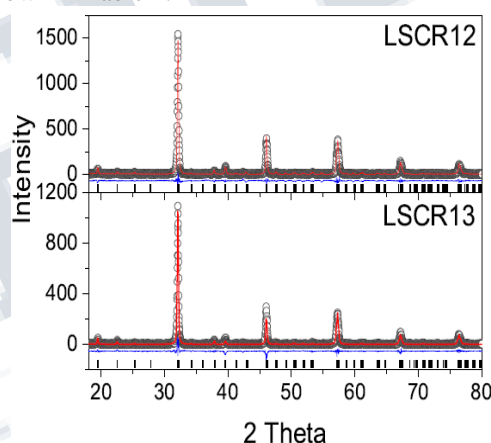

Fig.1. *Rietveld refined XRD patterns for LSCR13 and LSCR12. The open circles show the observed counts and the continuous line passing through these counts is the calculated profile. The difference between the observed and calculated patterns is shown as a continuous line at the bottom of the two profiles. The calculated positions of the reflections are shown as vertical bars.*

The refinement shows that there is only about 4% disorder in the case of LSCR13 while in the case of LSCR12; about 20% of Co occupies the Ru site (2d site) and vice versa thereby resulting in a larger disorder in the occupation of the B-site as compared to LSCR13. Hence, LSCR13 is referred to as an ordered compound while LSCR12 is referred to as a disordered compound.

To confirm the nature of the magnetic order in the present sample, ND patterns were recorded at 20K and are presented in Fig.2. Weak extra reflections due to

antiferromagnetic ordering are seen at the positions described by the propagation vector along the k = ½ 0 ½ with respect to the crystallographic $P_{21/n}$ cell. This magnetic arrangement is the same as that recorded by Bos and Attfield [29]. The ND pattern recorded at 20K also does not show any evidence of long range magnetic order within detectable limits. This could be implied to a magnetically frustrated ground state due to the presence of competing ferro and antiferromagnetic interactions.

$(La_{2x}Sr_{2-2x})(Co_{2x}Ru_{2-2x})O_6$:

The Rietveld refined XRD patterns for all the compounds studied here are presented in Fig. 3. The samples crystallize in the $P2_{1/n}$ monoclinic structure with an initial increase followed by a decrease beyond x = 0.5 of cell volume as LaCoO3 is added to SrRuO3 to form a solid solution. It may be mentioned here that the compounds with values of x < 0.25 and x > 0.75 have Pbnm and R 3^-c structures respectively and hence were not studied as they cannot be classified as double perovskites.

Sample	LSCR13	LSCR12
a (Å)	5.5847(4)	5.5891(3)
b (Å)	5.5592(6)	5.5540(5)
c (Å)	7.8674(9)	7.8787(5)
β	90.05(2)	90.10(1)
Volume (Å³)	244.25(4)	244.57(3)
Co ($\frac{1}{2}$,0,$\frac{1}{2}$)	0.98(1)	0.87(1)
Ru ($\frac{1}{2}$,0,$\frac{1}{2}$)	0.02(1)	0.13(1)
Ru ($\frac{1}{2}$,0,0)	0.98(1)	0.87(1)
Co ($\frac{1}{2}$,0,0)	0.02(1)	0.13(1)
μ_{eff} (μ_B/fu)	5.47(2)	5.43(1)
Θ_{CW} (K)	-49(2)	-2.5(4)

Table1. Unit cell parameters, Co and Ru site occupancies from Rietveld refinement and Curie-Weiss parameters calculated from magnetization measurements at 1000 Oe for the two samples of $LaSrCoRuO_6$.
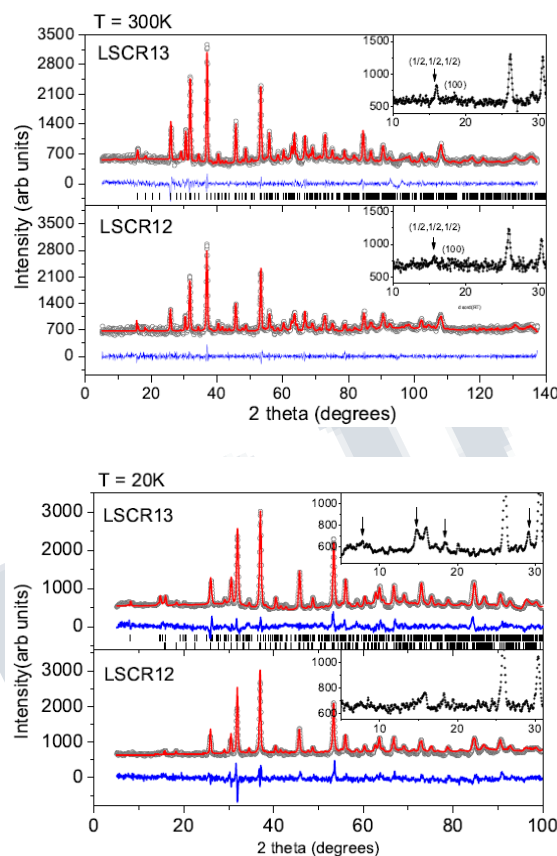

Fig.2. *Observed (circles), calculated (line) and difference ND patterns recorded at 300°K (upper panel) for LSCR13 and LSCR12. The inset presents data in limited range with the super lattice reflections seen clearly in LSCR13 indicating higher degree of order. The lower panel shows neutron data taken at 20K for the same samples with the inset presenting data in a limited range with the arrows indicating magnetic reflections present in LSCR13.*

Rietveld refinement of the XRD patterns were carried out with the $P2_{1/n}$ space group wherein the La/Sr occupy the 4e site with the fractional coordinates (0.00125, 0.00774, 0.2463), Co is at 2c (0.5, 0.5), Ru is at 2d (0.5, 0.0) and the oxygen atoms occupy three sites, viz. (0.2491, 0.2566, 0.0295), (0.2207, -0.2233, 0.0295) and (-0.06418, 0.4995, 0.2507).
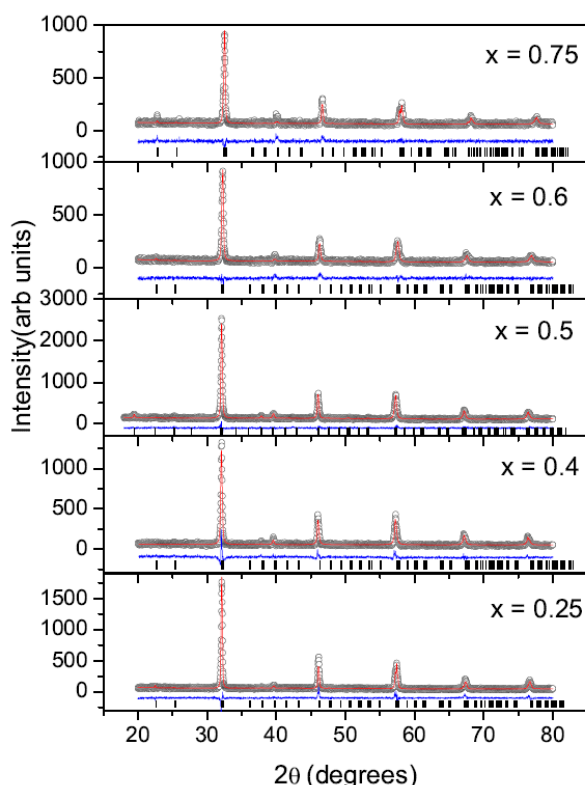
Fig.3. *Rietveld refined XRD patterns of La$_{2x}$Sr$_{2-2x}$Co$_{2x}$Ru$_{2-2x}$O$_6$ The Open circles show the observed counts and the continuous line passing through these counts is the calculated profile. The difference between the observed and the calculated patterns is shown as a continuous line at the bottom of the two profiles. The calculated positions of the reflections are shown as vertical bars.*

The scale factor, back ground parameters, cell parameters, Co and Ru site occupancies along with instrumental broadening, totaling 17 parameters were refined in that order to obtain a good fit. As can be seen from Table. 2.1 and 2.2, the B-site disorder was found to be least for x = 0.5 which also happens to be the stoichiometric double perovskite LaSrCoRuO$_6$. Interestingly, the disorder or the deviation from expected occupancy is highest for x = 0.4 and x = 0.6. The crystallographic parameters obtained from the above refinements along with the Curie-Weiss parameters calculated from magnetization measurements not shown here are all summarized in Table. 2.1 and 2.2.

$x \to$		0.25		0.4		0.5		0.6		0.75	
sites	atoms	E	R	E	R	E	R	E	R	E	R
$(\frac{1}{2}, 0, \frac{1}{2})$	Co	0.25	0.19	0.4	0.26	0.5	0.49	0.5	0.36	0.5	0.45
	Ru	0.25	0.31	0.1	0.24	–	0.01	–	0.14	–	0.05
$(\frac{1}{2}, 0, 0)$	Ru	0.5	0.44	0.5	0.36	0.5	0.49	0.4	0.26	0.25	0.20
	Co	–	0.06	–	0.14	–	0.01	0.1	0.24	0.25	0.30

Table2.1. *Expected (E) and refined (R) occupancies of Co and Ru for different values of La$_{2x}$Sr$_{2-2x}$Co$_{2x}$Ru$_{2-2x}$O$_6$.*

x	a(Å)	b(Å)	c(Å)	$\beta°$	V (Å^3)
0.25	5.5577(4)	5.5715(6)	7.8409(9)	90.05(2)	242.80(4)
0.40	5.5750(3)	5.5733(3)	7.8683(9)	90.25(2)	244.47(4)
0.50	5.5847(3)	5.5591(3)	7.8674(9)	90.05(2)	244.25(4)
0.60	5.5626(3)	5.5287(3)	7.8245(9)	90.08(2)	240.63(4)
0.75	5.4824(3)	5.5310(5)	7.7697(5)	89.93(3)	235.60(3)

Table2.2. *Unit Cell parameters obtained from Rietveld refinement for La$_{2x}$Sr$_{2-2x}$Co$_{2x}$Ru$_{2-2x}$O$_6$.*

To establish the nature of magnetic order, Neutron diffraction (ND) measurements were recorded at low temperature (20K) and 300K for the two end members x = 0.75 and x = 0.25. The Rietveld refined ND patterns at 300K for both these compounds are presented in Fig. 4. The parameters obtained from Rietveld refinement agree well with those obtained from XRD studies. The low temperature (20K) data shown in the limited range in Fig. 4 indicates extra super-lattice reflections due to antiferromagnetic ordering in x = 0.75. These reflections can be accounted for by an antiferromagnetic alignment of Co and Ru spins with a propagation vector along the k = ½ 0 ½ with respect to crystallographic axis. The magnetic arrangement is the same as determined for x = 0.5 in Ref [29]. As per this model, the antiferromagnetic alignment is of type II which means that antiparallel spins are related by (½, ½, ½) translation operation.

No long range magnetic order is visible in case of Ru rich composition (x = 0.25) indicating that the sharp rise in magnetization at about 160K is due to short range ferromagnetic correlations [20]. The short range ferromagnetic correlations could be due to Ru-O-Ru linkages intervened by Co ions. These ferromagnetic correlations are present along with antiferromagnetic interactions as evidenced by the wide separation between ZFC and FC curves for this sample [20].
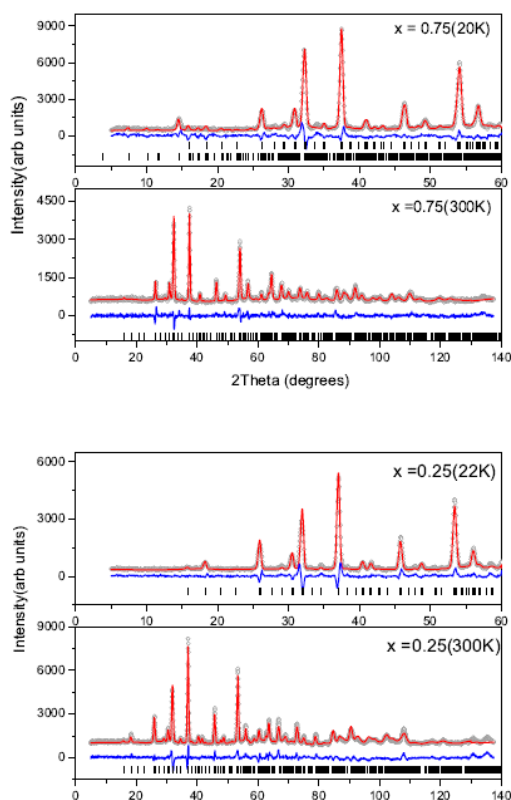
Fig.4. Observed (circles), calculated (lines) ND patterns recorded at 300K and 20K in the case ofLa$_{2x}$Sr$_{2-2x}$Co$_{2x}$Ru$_{2-2x}$O$_6$. The data at 20K is shown in limited range for clarity. The continuous line at the bottom is the difference line between the observed and calculated data.

IV. CONCLUSION

LaSrCoRuO6 is an AA'BB'O6 type of double perovskite that crystallizes in a monoclinic structure that allows for ordering of the B-site cations in a NaCl fashion. This ordering is favored due to the charge difference ($\Delta q \geq 3$) between Co and Ru. In an ordered LaSrCoRuO6, Co2+ and Ru5+ magnetic ions couple antiferromagnetically leading to an antiferromagnetic ground state as can be seen from the neutron diffraction measurements. A disorder in the Co and Ru site occupancy will result in Ru-O-Ru type linkages which are known to align ferromagnetically. The presence of ferromagnetic interactions is clearly seen in LSCR12 which has a larger B-site occupancy disorder. Due to such a disorder in occupancy of the Co and Ru sites, octahedral distortions set in, as the immediate neighbor of a Ru octahedral could be either a Ru octahedral or a Co octahedral. InLa$_{2x}$Sr$_{2-2x}$Co$_{2x}$Ru$_{2-2x}$O$_6$. present studies indicate that with the addition of LaCoO$_3$ to

SrRuO$_3$ leads to stabilization of double perovskite phase as seen in a broad concentration region of $0.25 \leq x \leq 0.75$. The double perovskite structure with space group P$_{21/n}$ is stabilized over the wide composition range from x = 0.25 to x = 0.75. With an increase in Co content, ferromagnetic interactions are found to weaken and at x = 0.75, the compound orders antiferromagnetically at T$_N$ = 34K. This interplay of ferromagnetic and antiferromagnetic interactions can be attributed to the presence of Ru^{4+}/Ru^{5+} and Co^{2+}/Co^{3+} redox couple in all the compounds. The only exception to this is the ordered compound x = 0.5 wherein Co and Ru exist in divalent and pentavalent states respectively representing an archtype double perovskite.

REFERENCES

[1] K.L. Kobayashi, T. Kimura, H. Sawada, K. Terakura and Y. Tokura, Nature **395**, 677 (1998).

[2] J.Gopalkrishnan, A. Chattopadhyay, S.B. Ogale, T. Venkatesan, R.L. Greene, A. J. Mills, K. Ramesha, B. Hannoyer and G. Marest, Phys. Rev. B **62**, 9538 (2000).

[3] D.D. Sarma, Curr. Opin. Solid State Mater. Sci, **5**, 261 (2001).

[4] J.W.G. Boss and J. Paul Attfield, Chem. Mater **16**, 1822 (2004).

[5] W.E. Pickett, R. Weht and A.B. Shick, Phys. Rev. Lett. **83**, 3713 (1999).

[6] A.C. McLaughlin, W. Zhou, J.P. Attfield, A.N. Fitch and J.L. Tallon, Phys. Rev. B **60**, 7512 (1999).

[7] J.M. Longo, P. M. Raccah and J.B. Goodenough, J. Appl. Phys **39**, 1327 (1968).

[8] Y. Maeno, K. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J.G. Bednorz and F. Lichtenberg, Nature, **372**, 532 (1994).

[9] S. H. Kim and P.D. Battle, J. Solid State Chem. **114**, 174 (1995).

[10] P.Rozier, K. Jansson and M. Nyguen, Mater. Res. Bull. **35**, 1391 (2000).

[11] J.J. Randall and R. Ward, J. Am. Chem. Soc. **81**, 2629 (1959).

[12] A. Mamchik and I.W. Chen, Phys. Rev. B **70**, 104409 (2004).

[13] A. Mamchik and I.W. Chen, Appl. Phys. Lett, **82**, 613 (2003).

[14] K. Asai et al, Phys. Rev. B **40**, 110982 (1989).

[15] S. Yamaguchi et al, Phys. Rev. B **53**, R2926 (1996).

[16] P.M. Raccah and J.B. Goodenough, Phys. Rev. **155**, 932 (1967).

[17] L.Pi, A. Maignan, R. Retoux and B. Raveau, J. Phys. Condens. Matter **14**, 7391 (2002).

[18] S. Manoharan, R.K. Sahu, D. Eleafant and C.M. Schneider, Solid State Comm. **125**, 103 (2003).

[19] A. Mamchik, W. Dmowski, T. Egami and I.W. Chen, Phys. Rev. B **70** 104410 (2004).

[20] P.S.R.Murthy, K.R.Priolkar, P.A. Bhobe, A.Das, P.R.Sarode and A.K.Nigam, Journal of Magnetism and Magnetic Materials, **323** (2011) 822-828.

[21] G.Coa, S. McCall, M. Sheppard, J.E. Crow, R.P. Guertin, Phys. Rev. B **56** (1997) 321.

[22] J.B. Goodenough, J. Phys. Chem. Solids **6** (1958) 287.

[23] R.H. Potze, G.A. Sawatzky, M. Abbate, Phys. Rev. B **51** (1995) 11501.

[24] T.Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda, M. Takano, Phys. Rev. B **55** (1997) 4257.

[25] R. Caciuffo, D. Rinaldi, G. Barucca, J. Mira, J. Rivas, M.A.S. Rodriguez, P.G.Radaelli, D. Frorani, J.B. Goodenough, Phys. Rev. **50** (1999) 1068.

[26] P.G. Radaelli, S-W Cheong, Phys. Rev. B **66** (2002) 094408.

[27] L.Pi, A. Maignan, R. Retoux, B. Raveau, J. Phys. Condens. Matter, **14** (2002) 7391.

[28] S. Manoharan, R.K. Sahu, D. Elefant, C.M. Schneider, Solid State Commun. **125** (2003) 103.

[29] J-W.G.Boss, J.P. Attfield, Chem. Matter, **16** (2004) 1822.

[30] P.S.R. Murthy, K.R. Priolkar, P.A. Bhobe, A.Das, P.R. Sarode, A.K.Nigam, J. Magn. Magn. Mater, **322** (2010) 3704.

[31] P.Tomes, J. Hejtmanek, K. Knizek, Solid. State Sci. **10** (2008) 486.