Chapter 7
Summary and Conclusions

Double perovskites have attracted attention due to unusual magnetic properties and half metallic nature of the charge carrier transport. The itinerancy and ferrimagnetism in these systems are found to arise from a double exchange type of mechanism in which the ordering and electronic configuration play a critical role, the characteristics of this type of ordering stem from the fact that it combines features of both ferromagnetic and antiferromagnetic systems. LaSrCoRuO$_6$ is an archetype double perovskite which offers a unique opportunity to examine the interplay of the cationic order, charge balance, transport and magnetic interactions between Co and Ru species. The main aim of the present work is the study the effect of thermal and substitutional disorder on the structural, magnetic and transport properties of LaSrCoRuO$_6$.

LaSrCoRuO$_6$ is an ideal double perovskite with Co and Ru octahedra arranging themselves in NaCl fashion. The valence of Co and Ru are $+2$ and $+5$ respectively. The degree of ordering of B-site cations in double perovskites is known to play an important role in deciding the magnetic, transport and structural properties of these systems. Any disturbance of this order will result in the formation of additional magnetic species like Ru$^{4+}$ and Co$^{3+}$ which add to the magnetic interactions already present and interesting
magnetic ground states. The main highlight of this work is the observation of “magnetic compensation” and “negative magnetization” due to creation of thermal or substitutional disorder in LaSrCoRuO$_6$. This reversal of magnetization has been explained on the basis of magnetic interactions that result due to the disorder in the occupancy of B-site of LaSrCoRuO$_6$ double perovskite.

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The archetype double perovskite LaSrCoRuO$_6$ is a AA'B'B'O$_6$ type double perovskite crystallizing in a monoclinic structure. This structure allows for ordering of B-site cations in a NaCl fashion with the ordering being favored due to a charge difference ($\delta q \geq 3$) between Co and Ru. In the perfectly ordered LaSrCoRuO$_6$(LSCR13), the Co$^{2+}$ and Ru$^{5+}$ magnetic ions are found to couple antiferromagnetically leading to an antiferromagnetic ground state that can be seen from neutron diffraction measurements. In order to induce disorder in the occupancy of B-site different annealing procedure was employed. This disorder in Co and Ru site occupancy results in Ru-O-Ru type linkages which are known to align ferromagnetically. The presence of ferromagnetic interactions are clearly seen in the disordered compound of LaSrCoRuO$_6$ (LSCR12) which has a larger B-site occupancy disorder in terms of an increased value of magnetization as compared to that in the ordered compound LSCR13 and hysteresis in M vs H loop. Due to such a disorder in occupancy of Co and Ru sites, octahedral distortions set in, as the immediate neighbor of a Ru octahedra could either be a Ru octahedra or a Co octahedra. The EXAFS results in the disordered compound LSCR12 bear a clear testimony to this fact, with the Co-O and Ru-O bond lengths being shorter, the mean square displacement being higher
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and the Co-O-Ru bond being straighter. These changes are a result of of Ru-O-Ru ferromagnetic linkages which due to their presence alter the Ru-O-Co antiferromagnetic interactions. The negative magnetization seen in the low field ZFC magnetization is due to Ru-O-Ru ferromagnetic interactions which below $\approx 150K$ are found to polarize the Co spins in a direction opposite to the applied field giving rise to magnetic compensation and negative magnetization.

The substitution at the B-site in the archetype ordered LaSrCoRoO$_6$ double perovskite allows an opportunity to probe the changes in the structural, magnetic and transport properties due to the creation of Co$^{2+/3+}$ and Ru$^{5+/4+}$ redox couples in an environment with a fixed A-site variance and linearly varying the Goldschmidt tolerance factor. Here two types of substitution at B-site has been probed. In the first case Co and Ru antisite disorder has been created by selectively increasing the composition of one of them with respect to other resulting in LaSrCo$_{1-x}$Ru$_{1+x}$O$_6$. In the second case Cu$^{2+}$ has been substituted for Co$^{2+}$. It is expected that partial substitution of Co by Cu will inhibit some of the magnetic interactions giving a better understanding of magnetic interactions at play in LaSrCoRuO$_6$. In the entire doping range, for both the series namely, LaSrCo$_{1-x}$Ru$_{1+z}$O$_6$ and LaSrCo$_{1-y}$Cu$_y$RuO$_6$, the double perovskite structure is preserved. As is known from chapter 3, in the case of the undoped LaSrCoRuO$_6$, there are two competing magnetic interactions, the linear Co-O-Ru-O-Co and the 90° Co-O-O-Co. The magnetic and transport properties of the doped LaSrCo$_{1-x}$Ru$_{1+z}$O$_6$ show significant changes due to the creation of Ru$^{4+}$ and Co$^{3+}$ species in both the Co and Ru doped compounds. The linear Co-O-Ru-O-Co and the 90° Co-O-O-Co interactions are diluted in the Ru and Co doped compounds at the expense of new interactions of the
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type Ru\(^{4+/5+}\)-O-Ru\(^{5+/4+}\) and those involving the HS/IS Co\(^{3+}\). The sharp rise in magnetization seen at about 160K in all the Co and Ru doped compounds can be attributed to ferromagnetic interactions arising due to Ru-O-Ru nearest neighbour interactions leading to the filling up of the \(\pi^*\) bands and lowering of the resistivity as compared to the undoped LaSrCoRu\(_6\). The temperature induced magnetization reversal displayed by the Ru rich compounds in low applied fields has been explained to be due to the polarization of the paramagnetic Co spins by Ru-O-Ru ferromagnetic interactions below the Ru sub-lattice ordering temperature of 160K. The Co spins are polarized in a direction opposite to the applied magnetic field giving rise to magnetic compensation and negative magnetization. However, in the case of the Co rich compounds, no negative magnetization is seen although there exists a steep rise in magnetization below 160K, instead only a large variation between the ZFC and FC magnetization curves is seen, which is also indicated by a decrease in the strength of ferromagnetic interactions with increasing Co content. Doping of Co and Ru results in the formation of Co-O-Co and Ru-O-Ru networks respectively. It is known that the Co-Co pairs favour the trivalent state and likewise, the Ru-Ru pairs favour the tetravalent states. Hence, the observed magnetic behavior reflects the general competition between the itinerant ferromagnetism and the antiferromagnetic superexchange coupling between Co-Co pairs, that are further modified by the interactions between Ru and Co.

The strong competition between magnetic interactions that lead to a decrease in the ordered moment of Co and Ru is reduced or eliminated with the substitution of Cu for Co in LaSrCoRu\(_6\). The magnetic properties clearly indicate the presence of antiferromagnetic interactions from the negative \(\Theta_{CW}\) and the magnetization behavior in
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the entire temperature range. With Cu\textsuperscript{2+} substituting Co\textsuperscript{2+}, the charge on Ru remains unaltered, and the ionic sizes of the two ions being similar, no major structural changes are observed, resulting in nearly similar magnitude of resistivity as in the case of the undoped LaSrCoRuO\textsubscript{6}. The Cu substitution does not favour the formation of Ru-O-Ru or Co-O-Co networks, it instead disturbs the existing magnetic interactions especially the 90° Co-O-O-Co interaction with the result that antiferromagnetism appears to be strengthened.

Another possible way of modifying magnetic and transport properties is by forming the solid solutions of antiferromagnetic LaCoO\textsubscript{3} and ferromagnetic SrRuO\textsubscript{3}. These perovskite solid solutions of the form Sr\textsubscript{1-x}La\textsubscript{x}Ru\textsubscript{1-x}Co\textsubscript{x}O\textsubscript{3} will have a strong interplay of cationic order, charge balance and complex magnetic interactions between the two B-site cations. The charge transfer between Ru and Co in LaSrCoRuO\textsubscript{6} is very sensitive to local atomic structure such as cation order. Any disturbance in this cation order leads to compensation of antiferromagnetic interactions by the ferromagnetic interactions most likely associated with Ru-O-Ru interactions. Investigations on the structural, magnetic and transport properties of solid solutions of SrRuO\textsubscript{3} and LaCoO\textsubscript{3} which form double perovskite compounds of the type La\textsubscript{2x}Sr\textsubscript{2-2x}Co\textsubscript{2x}Ru\textsubscript{2-2x}O\textsubscript{6}, where 0.25 ≤ x ≤ 0.75 have been carried out. With the increase in Co content, ferromagnetic interactions are found to weaken and at x = 0.75 the compound orders antiferromagnetically at T\textsubscript{N} = 34K. This interplay of ferromagnetic and antiferromagnetic interactions is attributed to presence of Ru\textsuperscript{4+}/Ru\textsuperscript{5+} and Co\textsuperscript{2+}/Co\textsuperscript{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 archetype double perovskite. The presence of different
magnetic sublattices leads to magnetic compensation and negative magnetization. This can be explained by polarization of paramagnetic Co spins by the ferromagnetic Ru$^{4+}$ sublattice in a direction opposite to applied field.

In our studies on double perovskite with $A = Sr$, it is found that even a small disorder in Co and Ru occupancies gives rise to a competition between ferromagnetic and antiferromagnetic interactions. The ferromagnetic interactions are a result of Ru-O-Ru coupling that arise due to disorder in Co-O-Ru-O-Co arrays. It may be noted that although SrRuO$_3$ is a ferromagnetic metal, its counterpart CaRuO$_3$ does not show any long range magnetic order. Therefore in order to understand the role of Sr in magnetic and transport properties of double perovskite, LaSrCoRuO$_6$ a comparative study between its magnetic and transport properties and those of LaCaCoRuO$_6$ was made. Both the samples have the similar structural and magnetic ground states. Presence of Sr has an effect on the width of the $\pi^*$ band of Ru in the double perovskite. In the Sr containing sample, the Co-O-Ru bond angle is higher than that in LaCaCoRuO$_6$. A straighter bond angle will aid in formation of a quasiitinerant $\pi^*$ bands. Such a formation will result in weak ferromagnetic interactions. The double perovskites consists of two coupled type II antiferromagnetic sub lattices. The coupling that results due to Dzyaloshinskii-Moriya (D-M) interaction works to reduce the effective antiferromagnetic moment. Presence of weak ferromagnetic interactions in LaSrCoRuO$_6$ drives the system to a point of magnetic frustration. Any change therefore in the coupling between Co and Ru in this compound gives rise to magnetic compensation and negative magnetization.
7.2 Future Work

In this concluding segment, we mention a few fields that can be pursued in relation to double perovskites in the coming years. Double perovskite oxides are becoming more and more important in various technological applications and hence the need to improve our detailed understanding of the structural, magnetic and transport properties of such materials and how the atomic structure is related to macroscopic physical properties. The commercial potential of these materials is determined and the effort has opened up new classes for application in spintronic devices such as magnetic tunnel junctions or low field magnetoresistive sensors. The structural, magnetic and electronic properties of perovskite-related materials having the general formula AA′BB′O₆ (where A and A′ are lanthanides or alkaline-earths, B is transition metal ion and containing Ru⁵⁺ at the B′ site) have been extensively investigated by a number of research groups. The compounds that belong to this family have a wide variety of interesting magnetic properties. In light of the results presented in this thesis, it is worth looking at magnetic properties of double perovskites formed with other transition metal compounds instead of Co²⁺. For instance compounds with Mn, Fe which normally occur in +3 state may have interesting magnetic and transport properties. These could be compared with double perovskites containing Ni which would be in +2 state.

The subject of magnetization reversal in oxides and intermetallic compounds has received considerable attention. The magnetization reversal is usually achieved by applying a large magnetic field in a direction opposite to the aligned moments or by changing the temperature in moderate fields. The temperature induced magnetization reversal, which is quite rare, has been found to occur in systems having two or more different types of
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magnetic ions, that are positioned at different crystallographic sites. A few ferrimagnetic compounds are known to show temperature induced magnetization reversal effect when two antiferromagnetically coupled magnetic sublattices exhibit different temperature dependence of the magnetization. There are few other oxides and intermetallic compounds which are known to show temperature induced magnetization reversal such as LnVO₃ (Ln = Y, La, Sm, Nd etc.), (Sm, Gd)Al₂, LnCrO₃ (Ln = Gd, La₀.₅Pr₀.₅) etc, however the origin of magnetization reversal in these compounds is found to be entirely different compared to that of the ferrimagnetic compounds.

In the compound such as LaVO₃, one of the reasons for the observed magnetization reversal is the competing effects of the D-M interaction and the single ion anisotropy of the V moments, as in the case of YVO₃ in the temperature range of 75K-110K. The magnetic ordering of the Yb moments in Sr₂YbRuO₆ is considered to be purely antiferromagnetic without any canted moments. The observation for negative magnetization in Sr₂YbRuO₆ when compared with that of LaVO₃ compound, it is to be noted that in the case of LaVO₃, the D-M vector rotates against the magnetic field at the structural transition resulting from the first order magnetostrictive distortion, however since the structure of Sr₂YbRuO₃ remains the same at 10K as deduced from neutron diffraction measurements, the possibility of any structural transition and hence the rotation of the D-M vector against the field is found to be ruled out. Future investigations on whether such a rotation can be initiated by the magnetic ordering of the Yb moments need to be looked into.
Publications

• Journals:


• Conference Proceedings:


- Conference Presentations:
