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SYNOPSIS

Investigation of Structural and Magnetic Properties of Spin-chain Oxides

In the recent years, the low dimensional magnetic materials have attracted a lot of attention due to their unique electronic and magnetic properties. Here, the low dimensional systems refer to the compounds where the arrangements of the magnetic ions are in less than three spatial dimensions e.g. 2D- layers, 1-D or quasi 1-D spin chains, etc. Some of the interesting properties of these compounds are geometrical frustration, multiferrocity, superconductivity, highly anisotropic physical properties, and quantum phase transitions.

Among the low dimensional magnetic materials, quasi-one-dimensional spin-chain compounds of type $A_3MXO_6$ [$A = Ca, Sr, and (M, X) = alkali or transition metal ions$] have recently attracted much interest due to their peculiar physical properties. The crystal structure of these compounds consists of chains, made up of alternating face-sharing $MO_6$ trigonal prisms (TP) and $XO_6$ octahedra (OCT) running along the crystallographic $c$ axis. These chains, separated by non-magnetic $A^{2+}$ ions, are arranged on a triangular lattice in the $ab$ plane and each chain is surrounded by six chains. One-dimensional character in the magnetic properties of these compounds is expected because the distance between the magnetic ions along the chain is approximately half of the interchain distance. The ferromagnetic intrachain and antiferromagnetic interchain interactions, combined with a triangular arrangement of spin-chains may give rise to a geometrical frustration in these compounds. Since the electronic and magnetic properties are governed by the charge, spin and orbital degrees of freedom, a large number of opportunities exist in these compounds to modify these properties by a suitable substitution of the transition metal ions at the $M/X$ sites.
In this thesis, we concentrate on the structural and magnetic properties of the compounds \( \text{Ca}_3\text{Co}_2\text{O}_6 \), \( \text{Ca}_3\text{Co}_{2-x}\text{Fe}_x\text{O}_6 \) \((x = 0.1, 0.2, 0.4, \text{ and } 1.0)\), and \( \text{Ca}_{2.75}\text{Ru}_{0.25}\text{Co}_2\text{O}_6 \) \((R = \text{Lu and Dy})\). In the compound \( \text{Ca}_3\text{Co}_2\text{O}_6 \), spin-chains are made up of alternating face sharing \( \text{CoO}_6 \) octahedra (with Co1) and \( \text{CoO}_6 \) trigonal prisms (with Co2) with a Co-Co separation of \( \sim 2.6 \text{ Å} \) (along the chain). The different crystalline electric fields at the OCT and TP sites lead to the different spin states of the \( \text{Co}^{3+} \) ions in this compound; low spin \((S = 0)\) and high spin \((S = 2)\) states at the OCT(6\(b\)) and TP(6\(a\)) sites, respectively. The \( \text{Co}^{3+} \) spins at the TP sites have an Ising-like magnetic anisotropy and are aligned along the crystallographic c axis. The choice of the iron substitution at the cobalt site was motivated by the consideration that the \( \text{Co}^{3+} \) ions at the TP site, in the compound \( \text{Ca}_3\text{Co}_2\text{O}_6 \), has large orbital moment \((1.7 \mu_B)\), while the \( \text{Fe}^{3+} \) ions have zero orbital momentum (a closed subshell without orbital degrees of freedom). Moreover, the ionic radii of the \( \text{Co}^{3+} \) and \( \text{Fe}^{3+} \) with six oxygen coordination are very close \((0.61 \text{ and } 0.645 \text{ Å}, \text{ respectively})\). No strong lattice effect will, therefore, be introduced, and changes only due to the different magnetic character of the spins of \( \text{Co}^{3+} \) and \( \text{Fe}^{3+} \) are expected. The choice of rare earth \((R^{3+})\) doping at the \( \text{Ca}^{2+} \) site is motivated by the theoretical prediction from the band structure calculations that magnetic properties for the compound \( \text{Ca}_3\text{Co}_2\text{O}_6 \) can be tuned by electron doping. The difference in the ionic radii of the rare earth \((R^{3+})\) and the calcium \((\text{Ca}^{2+})\) may change the distance between magnetic ions. The difference in the oxidation state of the \( R^{3+} \) and \( \text{Ca}^{2+} \) is expected to vary the oxidation state of \( \text{Co}^{3+} \) in the compound \( \text{Ca}_3\text{Co}_2\text{O}_6 \). These factors can change the intrachain and interchain magnetic exchange interactions, which can modify the magnetic properties of these spin-chain compounds. The thesis comprises of seven chapters.

Chapter 1 gives a brief overview of some of the most important features of the
low dimensional magnetic systems. A brief introduction about the geometrically frustrated magnets, their interesting physical properties, and why one should study them, is given. The crystal structure of the $A_3MXO_6$ type quasi-one-dimensional spin-chain compounds and how the geometrical frustration arises in these compounds are discussed. An outline of the thesis is given at the end.

In the succeeding chapter, a brief description about the sample preparation techniques used to synthesize the polycrystalline compounds studied in the thesis is given. A brief introduction and working principles of the various experimental techniques (x-ray diffraction, neutron diffraction, dc magnetization, and Mössbauer spectroscopy) employed to investigate the structural and magnetic properties of the compounds are also described. A brief description about the Rietveld method, to refine the crystal structures and to determine the magnetic structures from the powder diffraction data, is also given.

Chapter 3 presents the structural properties of the compounds $Ca_3Co_2O_6$, $Ca_3Co_{2-x}Fe_xO_6$ ($x = 0.1, 0.2, 0.4,$ and $1.0$), and $Ca_{2.75}R_{0.25}Co_2O_6$ ($R =$ Lu and Dy). The Rietveld refinement of x-ray and neutron diffraction patterns confirms that all compounds, except $Ca_3CoFeO_6$, crystallize in the rhombohedral structure (space group $R\bar{3}c$). For the compounds $Ca_3Co_{2-x}Fe_xO_6$ ($x = 0.1, 0.2,$ and $0.4$), the Rietveld refinement of neutron diffraction patterns and Mössbauer study confirm that the $Fe^{3+}$ ions are located only at the TP site. For the rare earth substituted compounds $Ca_{2.75}R_{0.25}Co_2O_6$ ($R =$ Lu and Dy), the refinement shows that the trivalent rare earth ions $R^{3+}$ are located at the $Ca^{2+}$ ($18e$) site, and bond lengths $Co2-O$ and $Co1-Co2$ increase significantly, as compared to the parent compound $Ca_3Co_2O_6$. The observed increase in the bond lengths $Co2-O$, with rare earth substitution, suggests that extra electrons are transferred to the $Co2$ ions at the TP site. The crystal structure of all the compounds, except for $Ca_3CoFeO_6$, contains one-dimensional
chains made up of alternating face-sharing CoO$_6$ octahedra and (Co/Fe)O$_6$ trigonal prisms, running along the crystallographic $c$ axis. For the compound Ca$_3$CoFeO$_6$, the profile matching refinement of the x-ray diffraction pattern confirms a triclinic crystal structure (space group $P\overline{1}$).

Chapter 4 is divided into two parts. The first part of this chapter describes the magnetic structure of the compounds Ca$_3$Co$_2$O$_6$ and Ca$_3$Co$_{2-x}$Fe$_x$O$_6$ ($x = 0.2$ and 0.4). In the first approximation, two different commensurate magnetic structures, (i) amplitude-modulated structure with a propagation vector $k = \{0, 0, 1\}$ and (ii) partially disordered antiferromagnetic (PDA) structure, are able to fit the same neutron diffraction patterns, below their respective Néel temperatures ($T_N = 25, 20, \text{ and } 17 \text{ K}$, for $x = 0, 0.2, \text{ and } 0.4$ compounds, respectively). However, a detailed analysis reveals that these compounds order magnetically in an incommensurate spin density wave (SDW) structure, having a modulation and an alignment of the spins along the crystallographic $c$ axis, below $T_N$. Further, a coexistence of the magnetic long-range and short-range ordering has been observed down to 1.5 K (below $T_N$). For the parent compound Ca$_3$Co$_2$O$_6$, in addition to the magnetic Bragg peaks corresponding to the SDW structure, a second set of magnetic peaks corresponding to the commensurate antiferromagnetic (CAFM) structure with a propagation vector $k_2 = \{0.5, 0.5, 0\}$ appears in the neutron diffraction patterns below $\sim 15$ K. Moreover, the magnetic Bragg peaks, corresponding to the CAFM and SDW structures, exhibit time dependence at some fixed temperatures below $\sim 14$ K. Our analysis (for the parent compound Ca$_3$Co$_2$O$_6$) shows that the magnetic ground state is a coherent superposition of the magnetic structures belonging to the propagation vectors $k_1 = \{0, 0, 1.009(3)\}$ and $k_2 = \{0.5, 0.5, 0\}$. The second part describes Mössbauer spectroscopy studies of spin-spin relaxation in the compounds Ca$_3$Co$_{2-x}$Fe$_x$O$_6$ ($x = 0.2$ and 0.4), and nature of magnetic ordering in Ca$_3$CoFeO$_6$. 
The compounds with $x \leq 0.4$ are paramagnetic above $\sim 90$ K, and the iron exhibits slow spin relaxation phenomena even at room temperature. However, for the compound Ca$_3$CoFeO$_6$, which crystallizes in the triclinic space group $P\bar{1}$, the iron resides almost equally in two different crystallographic sites and exhibits a very high magnetic ordering temperature $T_N \sim 500$ K. Both iron sites exhibit quadrupole interactions of almost equal size; however, with an opposite sign. These results agree well with the magnetic susceptibility measurements, in which a sharp drop in magnetization is observed above 200 K. The net magnetic interaction is antiferromagnetic, however, with a small ferromagnetic component displaying hysteresis along with a saturation magnetization of about 0.02 $\mu_B$/f.u. at 1.5 K.

Chapter 5 describes the effect of an external perturbation viz. magnetic field on the nature of magnetic ordering in the compounds Ca$_3$Co$_{2-x}$Fe$_x$O$_6$ ($x = 0, 0.1, 0.2, \text{ and } 0.4$). For all compounds, high temperature magnetic susceptibility obeys the Curie-Weiss law. The value of paramagnetic Curie temperature decreases as the concentration of iron increases ($\theta_p = 27.8$ for $x = 0$ compound) and it becomes negative (-1.6 K for $x = 0.4$) for higher concentration of iron. From the dc-magnetization study, we have derived the value of intrachain and interchain exchange interactions for the compounds Ca$_3$Co$_{2-x}$Fe$_x$O$_6$ ($x = 0.0, 0.1, 0.2, \text{ and } 0.4$). A decrease in the intrachain positive exchange constant $J'$ and an increase in the interchain negative exchange constant $J$ have been observed with substitution of iron, which result in deviation from “1D character” in these spin-chain compounds. In the dc magnetization study, we have observed an indication of the presence of a field induced transition from a ferri to a ferromagnetic state. Neutron diffraction study has been carried out to study the spin-spin correlations in the compound Ca$_3$Co$_{1.8}$Fe$_{0.2}$O$_6$, by directly investigating the evolution of the magnetic structures as a function of applied magnetic field (0, 2 and 4 T) and temperature (1.5-100 K). Under an applied
field of $\sim 2$ T, a phase transition from the zero field SDW structure ($T_N \sim 20$ K) to a commensurate amplitude modulated (AM) structure has been observed. With a further increase in the magnetic field ($\sim 4$ T), the AM structure transforms into a ferrimagnetic structure. In zero applied field, a magnetic short-range ordering (SRO) coexists with the SDW long-range ordering (LRO) at all temperatures below $T_N$. In the applied magnetic field (2 and 4 T), the SRO is converted into the LRO only over the temperature range $12 - 20$ K, however, below $\sim 12$ K, an increase in the volume fraction of the SRO has been observed. The correlation length for the SRO (below $\sim 12$ K) also gets affected by the application of field. The magnetic properties of the compounds $\text{Ca}_3\text{Co}_{1.8}\text{Fe}_{0.2}\text{O}_6$ are very much different from the parent compounds $\text{Ca}_3\text{Co}_2\text{O}_6$. A field induced transition from the zero field modulated PDA structure to a ferrimagnetic structure in the magnetic field of 1.7 T, and then a transition to a ferromagnetic state in the magnetic field of 3.6 T was reported for the parent compound $\text{Ca}_3\text{Co}_2\text{O}_6$. However, no transition from the modulated PDA structure to the AM structure (before transition to the ferrimagnetic structure) was reported.

Chapter 6 describes the effect of the rare earth substitution at the Ca$^{2+}$ ($18e$) site on the magnetic properties of the compounds $\text{Ca}_{2.75}\text{R}_{0.25}\text{Co}_2\text{O}_6$ ($\text{R} = \text{Lu}$ and Dy). For both compounds, high temperature (in the paramagnetic region) magnetic susceptibility obeys the Curie-Weiss law. The derived values of the paramagnetic Curie temperature ($\theta_p$) are 28.4 and 16.6 K for $\text{R} = \text{Lu}$ and Dy compounds, respectively. For the parent compound $\text{Ca}_3\text{Co}_2\text{O}_6$, the value of $\theta_p$ is $\sim 30$ K. The observed decrease in the value of the $\theta_p$ indicates a reduction in the dominant intrachain ferromagnetic interaction with rare earth substitution. In the neutron diffraction patterns, additional Bragg peaks appear for both compounds below $\sim 16$ K, indicating the onset of an antiferromagnetic ordering of cobalt spin-chains on the
triangular lattice. The magnetic Bragg peaks at 1.5 K can be indexed using the incommensurate propagation vector \( \mathbf{k} = \{0, 0, 1.02\} \). The magnetic structure corresponds to the SDW structure, having \( c \) axis as direction of the moment and the modulation. For both compounds, refined value of the maximum moment at the \( 6b \) site is zero. The refined value of the maximum moment at the \( 6a \) site is same (\( \sim 4.2 \mu_B \)) for both compounds. For the parent compound \( \text{Ca}_3\text{Co}_2\text{O}_6 \), the reported value of the maximum moment at the \( 6a \) site is \( \sim 5.1 \mu_B \). For the rare earth doped compounds, the refined zero value of the ordered moment at the OCT site confirms that cobalt ions at the OCT sites remain in the \( 3^+ \) oxidation state. The observed reduction in the value of the maximum moment at the TP site (with rare earth doping), confirms that the oxidation state of a fraction of the cobalt ions at the TP site is reduced from \( \text{Co}^{3+} \) to \( \text{Co}^{2+} \). The qualitative nature of the observed magnetic ground states for the rare-earth substituted compounds is same as that observed for the Fe-substituted compounds \( \text{Ca}_3\text{Co}_{2-x}\text{Fe}_x\text{O}_6 \) (\( x = 0.2 \) and 0.4), however, different from that observed for the parent compound \( \text{Ca}_3\text{Co}_2\text{O}_6 \).

The last chapter (Chapter 7) gives a brief summary of the research work carried out in this thesis. The effects of the intrachain and interchain exchange interactions, and external perturbation on the magnetic ground states of the geometrically frustrated compounds are discussed. A novel time dependence in the intensity of the magnetic reflections has been observed for the compound \( \text{Ca}_3\text{Co}_2\text{O}_6 \). A possibility to study the effect of an external magnetic field on the observed time dependent magnetic behavior (for \( \text{Ca}_3\text{Co}_2\text{O}_6 \)) is also discussed. The magnetic properties of the compounds \( (A_3MXO_6 \text{ family}) \) studied in the present thesis have been compared with other class of frustrated magnetic systems \([ABX_3 \ (A = \text{Cs or Rb}, \ B = \text{Co}, \ X = \text{Cl or Br})] \), in terms of the nature of the intrachain magnetic exchange interaction. The present thesis also highlights the scope for the future research work, by grow-
ing thin films and large size single crystals (necessary to investigate the anisotropic magnetic and transport properties) of these spin-chain oxides. A list of bibliographic references used in this thesis has been given after Chapter 7. A list of publication is also provided.