Abstract

Spinel compound $CoCr_2O_4$ is found to be a promising multiferroic material as it exhibits switchable electric polarization under reversal of magnetic field. In a bid to enhance the functional properties of $CoCr_2O_4$, recent experiments attempted substitution of Cr by a another magnetic atom. Substitution of Fe and Mn in place of Cr led to fascinating phenomena like temperature and composition dependent magnetic compensations, magnetostrsiction effects, composition dependent tunable exchange bias which are not observed in pristine $CoCr_2O_4$. The experimental results on various thermal, structural and magnetic properties in Fe and Mn substituted $CoCr_2O_4$ implied that there can be significant cation disorder present in these systems which renormalizes the magnetic exchange interactions and in turn is responsible for the anomalous behavior of the physical quantities with changes in the compositions of the system. In order to gain fundamental understandings into various effects like the cation disorder, the crystal fields, the magnetic exchange interactions and their interplay, the electron-electron correlations, the spin-lattice coupling on the properties of these systems and thus provide interpretations of the available experimental results, in this dissertation. We have performed systematic investigations into the structural, electronic and magnetic and vibrational properties of $Co(Cr_{(1-x)}Fe_x)_2O_4$, $0<x<1$, with first-principles Density functional theory (DFT) based DFT+U method. Our investigations into the pristine compounds $CoCr_2O_4$, $CoMn_2O_4$ and $CoFe_2O_4$ demonstrated the changes in their electronic structures as one of the magnetic component is changed systematically, and thus helped in understanding the roles of crystal fields, magnetic exchanges, structural distortions, electron-electron correlations. Such fundamental understanding helped in interpreting thee differences in their ground state magnetic structures as well and provided enough insights into the possible scenario when one of the magnetic atom is substituted with the other. Our investigations into $Co(Cr_{(1-x)}Fe_x)_2O_4$, $0<x<1$ quantified the degree of cation inversion at each composition and for a range of temperatures. Based upon this, calculations of the structural properties and the magnetic exchange interactions enabled us to discover the roles of sites-occupancies in influencing, in particular, the emergence of a collinear magnetic order from a

non-collinear one with increase in the Fe content in the system. The electronic structures as a function of composition and degree of cation inversion provided the microscopic picture of the competing magnetic exchange interactions and thus a complete picture of the physical mechanism of the magnetic properties in this system. In a similar way, $Co(Cr_{(1-x)Mnx})_2O_4$, $0<x<1$, was investigated. The variations in the degree of cation inversion in this system was non-regular in comparison to that with $Co(Cr_{(1-x)}Fe_x)_2O_4$. We found that the non-regular variations in the degree of cation disorder can be used to explain the experimentally observed non-regular variations in the magnetization, and in particular the phenomena of composition dependent magnetic compensations. We showed that the cation disorder affects the charge state, and the impart substantial influence on the variations in the overall physical properties in this system. The information on the fundamental mechanisms in these two substituted systems could be achieved due to quantification of the degree of cation disorder, for which we generalized an existing thermodynamic model and coupled it with first-principles calculations. This development is a significant contribution in this dissertation. A quest into the effects of cation disorder onto the vibrational properties in these systems, further led to a qualitative understanding of the effects of symmetry lowering due to chemical substitution and degree of cation inversion on the phonon dispersion in pristine and substituted $CoCr_2O_4$. As a further exploration into the possible coupling between magnetic and the lattice degrees of freedom, as suggested in experiments, we generalized an existing model to compute the spin-phonon coupling strength in AB_2O_4 spinels having two magnetic atoms. The result identified the vibrational modes and associated atom pairs responsible for significant spin-phonon coupling. Overall, the results presented in this thesis shed enough light on the interplay of various factors and their role in influencing the physical properties in these multi-functional systems.