

Structural and Magnetic Properties of Multiferroic
 TbMnO_3 and quasi-one Dimensional Quantum
Spin System LiCuVO_4



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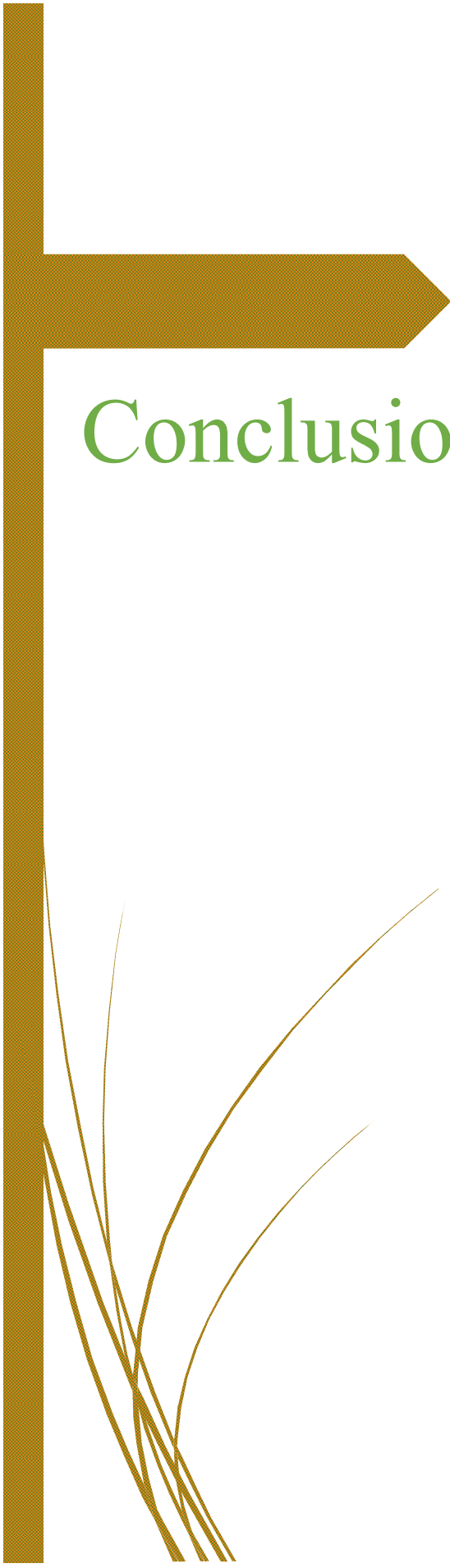
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Chapter 7

Conclusion of Thesis

In this thesis the magnetic and structural properties of Zn, Co and Mn doped LiCuVO_4 and Y, Ni and Ce doped TbMnO_3 have been investigated.

When Zn and Co are doped in quasi-one dimensional spinel compound LiCuVO_4 the antiferromagnetic interaction increases. On the other hand Mn-doping induces the short range ferromagnetic ordering. It is also observed in Mn-doped sample from the fitting with the HTSE (High Temperature Series Expansion) model that nearest neighbor (NN) (J_1 ~Ferromagnetic) interchain exchange interactions play a dominating role over next nearest neighbor NNN (J_2 ~Antiferromagnetic) and in other doped sample J_2 is dominating over J_1 . Neutron diffraction study does not show any indication of long range magnetic ordering. Neutron diffraction study also indicates that with Mn doping the V-O lengths are changed. The exchange interactions are somehow modified with Mn doping which in effect induces short range ferromagnetism. Moreover, after XPS analysis doping of Mn on the Cu site of LiCuVO_4 converts very few Cu^{2+} ions into Cu^{3+} ions due to which few Mn^{+2} are converted into Mn^{+3} . Exchange interaction between $\text{Mn}^{+2}/\text{Mn}^{+3}$ (double exchange) might be the origin of induced ferromagnetism. Further study is required to explain the actual origin of ferromagnetism in LiCuVO_4 with Mn doping. This short range ferromagnetic ordering is not stable as inclusion of further Mn-doping decreases the coercivity of the system. It is due to release of strain developed upon Mn ($x=0.05$) doping that is confirmed by XRD and Raman analysis of undoped and Mn-doped samples. Relaxation of strain play a role in canting of spin. This canted spin reduces the short range of ferromagnetic ordering. Swift heavy ion beam irradiation also reduces this short range ferromagnetic ordering. It is due to the defects created during irradiation. The lattice expansion in the irradiated samples can be explained on the basis of energy deposition mechanism in the irradiation process which demonstrates that the high electronic excitations have induced the structural modifications.

Moreover, Y doping in TbMnO_3 decreases unit cell volume whereas Ni-doping in Mn-site of TbMnO_3 first decrease but further increment of Ni content is constant. In room temperature Raman spectra of Y doped and undoped TbMnO_3 , eight feature are observed, on the other hand Ni doped TbMnO_3 modes due to MnO_6 bending and in-plane O_2 stretching broaden and few modes disappear. This might be due to the lattice disorder which is induced by Ni doping. Both Y and Ni doping decrease the Neel temperature, T_N . Y doping reduces

effectively both the $J_{\text{Tb-Tb}}$ and $J_{\text{Mn-Mn}}$ exchange interactions, whereas Ni doping on the Mn site decreases only the $J_{\text{Mn-Mn}}$ exchange interaction. The reduction in T_N in the Ni-doped sample cannot be explained with simple exchange integral where Mn^{3+} ions are assumed to form a perfectly hexagonal network. Ni^{2+} doping might change the polarization flop in TbMnO_3 which in effect may change the exchange interaction. Both Exchange bias and Griffith phase have been observed in TbMnO_3 . The Griffith phase has been attributed to the Oxygen vacancy which converts some Mn^{3+} states to Mn^{2+} states. The exchange interaction between $\text{Mn}^{3+}/\text{Mn}^{2+}$ induces ferromagnetism. Furthermore, Ce doping also converts some Mn^{3+} states to Mn^{2+} states. As a consequence, Ce doped TbMnO_3 also show Griffith phase. Moreover, The Oxygen vacancy/ Mn^{3+} - Mn^{2+} may change the Mn-O-Mn angle which in effect induces the canted AFM ordering. The canted AFM might be the origin of exchange bias.