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Intrinsic Local Distortions and charge carrier behavior in CMR manganites and cobaltites¹

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We compare and contrast the local structure and electronic configurations in two oxide systems $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ (LSCO) and $\text{La}_{1-y}\text{Ca}_y\text{MnO}_3$ (LCMO). Although these oxides may appear quite similar they have rather different properties. At $x=0$, LaCoO_3 (LCO) has unusual magnetic properties - diamagnetic at low T but developing a moment near 100K. The Sr doped LSCO materials show ferromagnetism for $x > 0.2$. For LCO, one of the possible spin state configurations called the intermediate spin (IS) state ($S=1$), should be Jahn-Teller (JT) active, while the low spin ($S=0$) and high spin ($S=2$) states have no JT distortion. Early local structure measurements suggested a JT distortion was present in LCO and therefore supported an IS spin model. However we find no evidence for any significant JT distortion (and hence no support for the IS model) for a range of bulk and nanoparticle cobaltites $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, $x = 0 - 0.35$. In contrast there are large JT distortions in the manganites LCMO, $0.2 < x < 0.5$ (Mn-O bonds), for which CMR behavior is observed. We have shown that the JT distortions in the manganites depend on both temperature T and magnetic field B, and from the B-field dependence, propose the size and nature of the polarons in LCMO. We also present Co K-edge XANES data that shown no significant shift of the edge for the cobaltites as the Sr concentration increases from $x = 0$ to 0.35 indicating essentially no change in the electronic configuration about Co; consequently, the holes introduced via Sr doping appear to go primarily into the O bands. In contrast there is a large shift of the Mn K-edge with Ca doping indicating a change in the average Mn valence, and a corresponding change in the Mn electronic configuration. We briefly discuss some possible models.

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