Dramatic Electronic Structure Effects in the Thermodynamic and Kinetic Behavior of Transition Metal Oxides

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The structure and properties of oxides has often been rationalized on the basis of size and charge effects. In this presentation we show two case studies where the electronic structure of the transition metal ion creates significant effects on the thermodynamic and kinetic properties of the oxide. In Li_xNiO_2, Li-vacancy ordering couples with the Jahn-Teller instability of the Ni^{3+} ion to create very long-range attractive interactions between Li ions. This causes substantially different ordering than in the equivalent Li_xCoO_2 which is metallic and not Jahn-Teller active. Li_xMnO_2 undergoes reversible and irreversible phase transitions at room temperature which involve substantial movement of the Mn ions, while the equivalent materials Li_xNiO_2 and Li_xCoO_2 do not. We show that Mn^{3+} in the presence of other Mn^{3+} attains a very high mobility due to a charge disproportionation mechanism which creates Mn^{2+} in the activated state.