

Understanding the role of *f*-electron in Mn^{III}-Ce^{IV}-Mn^{III}

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The perovskite manganites AMnO₃ and their doped analogues A_{1-x}B_xMnO₃ (A and B = main group and lanthanide (Ln) metals) are a fascinating family of magnetic oxides exhibiting a rich variety of properties, not least of which is multiferroicity in members such as BiMnO₃ and DyMnO₃, opening up potential applications in memory and resistive switching elements. The molecular compound [Ce₃Mn₈O₈(O₂CPh)₁₈(HO₂CPh)₂] (Ce^{III}₂Ce^{IV}Mn^{III}₈; hereafter Ce₃Mn₈) bears a striking structural resemblance to the repeating unit seen in the perovskite manganites. First-principles theoretical calculations reveal the expected nearest-neighbor Mn^{III}₂ exchange couplings via superexchange pathways through bridging ligands and also an unusual, direct Mn^{III}-Ce^{IV}-Mn^{III} metal-to-metal channel involving the Ce^{IV} *f*-orbitals. An excellent agreement between theory and experiment for the magnetic susceptibility curve is reached along with the establishment of an unprecedentedly rich physical picture of magnetic interaction. With high throughput computational approach, we investigate divalent and trivalent cation substitution in Ce₃Mn^{III}₈ molecules and its effects on ground state magnetic configuration using first-principles based approaches.