Influence of Valance and Magnetism on the Jahn-Teller Distortion in LiMn$_2$O$_4$ and its Lithiation Process$^1$ WEIWEI LIU, Beijing Computational Science Research Center, YANNING ZHANG, Univ of Electronic Sci Tech — We performed extensive first-principles studies on the valence and magnetic configurations of spinel LiMn$_2$O$_4$, a promising candidate of cathode materials in Li-ion batteries. We find that the ground state of LiMn$_2$O$_4$ is an anti-ferromagnetic (AFM) orthorhombic spinel structure, where AFM Mn$^{3+}$ layer and FM Mn$^{4+}$ layer alternate along the [001] direction and the 90Mn$^{3+}$-O$^{2-}$-Mn$^{3+}$ in Mn$^{3+}$-(001) planes is in AFM coupling, forming the indirect Kramers-Anderson superexchange. The coplanar Jahn-Teller (JT) ions maximize the JT distortion and the AFM magnetic orderings further strengthen the interaction between Mn$^{3+}$ cations and O$^{2-}$ anions, making the structure stable. Li diffusion in such a stable LiMn$_2$O$_4$ will go through a ring consisting of six Mn atoms, and the energy barrier of Li diffusion is dependent on the valence states of Mn atoms. Our theoretical results give insights in exploring ground state of related JT magnetic materials, and also provide information for the performance improvement of LiMn$_2$O$_4$ cathode materials.

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