Magnetic-induced ferroelectric polarization in charge-ordered $CaMn_7O_{12}$ system

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The electronic properties of $CaMn_7O_{12}$ yield to interesting physical phenomena including charge-ordering [1], non-collinear magnetism [2], and improper ferroelectricity [3]. The charge-ordered $CaMn_7O_{12}$ is a complex, distorted quadruple perovskite whose chemical formula could be rewritten in the form of $(AA'_3)(B_4)O_{12}$ as $(CaMn_3^{3+})(Mn_3^{3+}Mn^{4+})O_{12}$ where three Mn^{3+} are on the A-site (Mn1), three Mn^{3+} on the B-site (Mn2), and one Mn^{4+} on the B-site (Mn3). Three parallel c-chains with alternating Mn1 and Mn2 form a Kagome lattice with either Mn3 or Ca at the center of the hexagonal rings. The crystal structure of this material is shown in Fig. 1a and the computed electronic structure shows a ≈0.2 eV band gap for the charge-ordred structure, shown in Fig. 1b. The non-collinear magnetic ground state, shown in Fig. 1c and 1d, consists of spin moments lying on the ab-plane, forming a helical pattern along the c-axis. Antiferromagnetic and ferromagnetic interactions among these c-chains cause spin frustration, leading to 120° alignment of these spin moments. Our DFT+U+J study shows that the Mn3 spins at the center adopt (30°,90°) magnetic configuration with respect to the surrounding (Mn1,Mn2) spins, breaking the inversion symmetry and generating a Berry-phase computed ferroelectric polarization of 2975 $\mu C/m^2$ along the c-axis (Fig. 1d). Our computed ferroelectric polarization is in close agreement with experimental measurements of 2870 $\mu C/m^2$ [3]. When the magnetic helicity of the system is reversed, the ferroelectric polarization flips, reinforcing that it is a magnetic-driven process. This study aims to explore how the electronic and magnetic properties are intertwined to give rise to a multiferroic, charge-ordered state.

This work was supported by the US Office of Naval Research under Grant No. N00014-11-1-0664. Computational support was provided by the High Performance Computing Modernization Office of the US Department of Defense, and the National Energy Research Scientific Computing Center of the US Department of Energy.

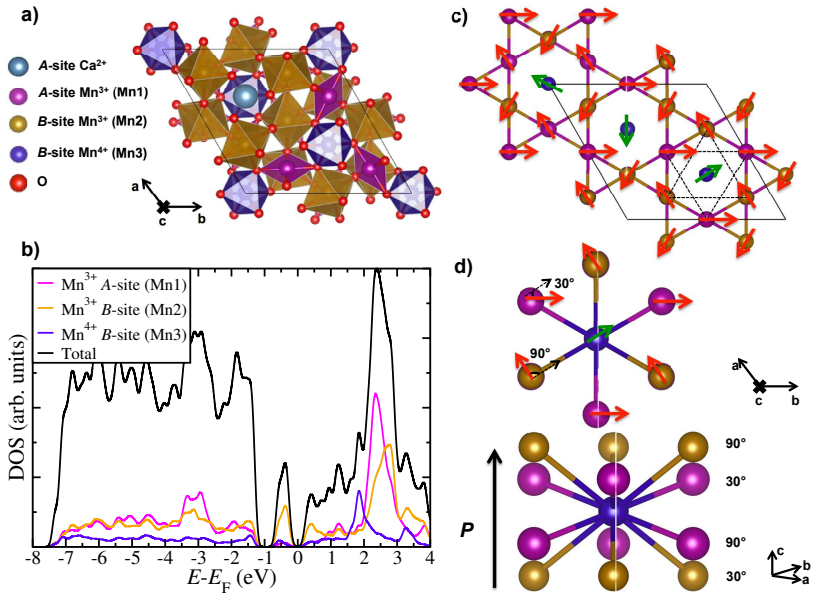

FIG. 1. Structural, electronic and magnetic properties of $CaMn_7O_{12}$. a) The crystal structure of the lowest energy and charge-ordered $CaMn_7O_{12}$ in the rhombohedral $R\bar{3}$ phase. The system has three different Mn atoms, Mn^{3+} on the A-site (Mn1), Mn^{3+} on the B-site (Mn2), and Mn^{4+} on the B-site (Mn3). b) Projected density of states shows a ≈0.2 eV band gap. The charge density is projected to Mn atomic orbitals indicating their differences in bonding character. c) Non-collinear magnetic configuration shows red arrows to represent the spin moments of either Mn1 or Mn2 and green arrows to represent the spin moments of Mn3. The dashed black lines show the Mn1 and Mn2 surrounding the Mn3. d) Top panel shows a top view of the Mn3 spins at the center within the (30°,90°) magnetic configuration with respect to the surrounding (Mn1,Mn2) spins. Bottom panel shows a side view indicating the direction of the ferroelectric polarization.

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