Site-specific magnetically frustrated \( \text{Sr}_5\text{Mn}_5\text{O}_{13} \) and \( \text{Sr}_4\text{LaMn}_5\text{O}_{13} \) perovskites

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LaxSr\(_{1-x}\)MnO\(_3\)-d manganites are among the most intensely studied perovskites because of the plethora of interesting properties and potential applications. The possibility of obtaining compounds with the Mn valence that can change between 2+ and 4+ by varying the La and oxygen contents allows for a wide range of magnetic, conducting and dielectric properties. The subtle relations among various degrees of freedom, combined with the flexibility of the perovskite framework made these compounds a very interesting test-case for study of the structure-properties correlations.

The Sr-rich side of the system showed an interesting series of compounds \((\text{LaxSr}_{1-x})_4+n\text{Mn}^{4+n}\text{O}_{10+3n}\) with a systematic progression of oxygen vacancy ordering and the related Mn charge and orbital occupation/ordering [1]. In this series, the La-free compounds \((x=0)\) have been observed for \(n=0\) (Sr4Mn4O10), \(n=1\) (Sr5Mn5O13) and \(n=3\) (Sr7Mn7O19) [2]. Only the \(n=0\) and \(n=1\) members have been observed for the La-containing samples \((x=0.1\) and 0.2) and only the \(n=1\) member was found for the \(x=0.3\) due to the subtle correlation of Mn charge and oxygen vacancy ordering.

The \(n=1\) member \((\text{LaxSr}_{1-x})_5\text{Mn}_5\text{O}_{13}\) shows an interesting evolution with \(x\) [3]. The structure (left figure) is formed by a very stable “pinwheel” pattern of Mn\(_3^+\) pyramids linked by the Mn octahedron, which is the only structural site susceptible to change of valence from Mn\(_4^+\) \((x=0)\) to Mn\(_4^+/\text{Mn}_3^+\) for \(x=0.1\), Mn\(_3^+\) for \(x=0.2\) and Mn\(_3^+/\text{Mn}_2^+\) for \(x=0.3\). The space group symmetry of the compounds changes from P4\(/m\) \((x=0)\) to P2/m \((x=0.2)\) with increasing La content to accommodate the Jahn-Teller Mn\(_3^+\) ion in octahedral environment. This structure was reported to show an unusual averaged compressed Mn\(_3^+\) octahedral environment, produced by averaging of the elongated octahedra disordered in the \(x\)-\(y\) plane [3].

Neutron powder diffraction patterns obtained at 10 K for Sr5Mn5O13 and LaSr4Mn5O13 compounds showed peaks of the magnetic origin suggesting an antiferromagnetic ordering pattern of spins with propagation vector \(k=(1/2,1/2,1/2)\). The magnetic structures of both compounds was solved in the I2'/\(m\) magnetic space group \(#12.3.68\), showing that the pinwheel pattern of pyramids with half-occupied dz2 orbital pointing towards the apex of the pyramids has all Mn\(_3^+\) cations aligned ferromagnetically. The four close-by clusters, separated by an oxygen vacancy, are antiferromagnetically coupled. The intermediate Mn\(_4^+/\text{Mn}_3^+\) octahedron is, therefore, sharing corners with two couples of inverted spin pinwheel clusters. Due to the orbital ordering, also associated with the magnetic and oxygen vacancy ordering, the Mn4+ cations in Sr5Mn5O13 show only antiferromagnetic interactions with the neighbouring pinwheel clusters, therefore the Mn4+ spins are not able to order magnetically with the two pairs of opposite spins (right figure). The Mn3+ cations in LaSr4Mn5O13, on the contrary, may couple ferromagnetically with two pinwheel clusters (through the half-occupied dz2 orbital that lays in the \(x\)-\(y\) plane), and antiferromagnetically with the second pair (through the empty dx2-y2 orbitals), allowing for magnetic ordering. This would require, however a perfect orbital ordering of Mn3+ in the octahedral sites, which is not observed in this compound [2], instead nano-scale magnetically ordered regions with different magnetic orientations are observed.


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