Bi $6s^2$ lone-pair-induced magnetic order in $BiMn_7O_{12}$

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Manganese oxides $A Mn_7O_{12}$ (*A*=Na, Ca, La) with *quadruple* perovskite structure display charge, spin and magnetic orderings not observed in *simple* perovskites, such as $LaMnO_3$ and related doped compounds [1-3]. In fact, despite the similar crystal structure and the common electronic properties determined by the Jahn-Teller (JT) Mn ions, quadruple perovskites $AA'_3B_4O_{12}$, differ from simple ones ABO_3 in the following: (*i*) the crystal structure hosts *two*, instead of one, JT sites, *A*' and *B*; (*ii*) the JT distortion of the *A*' site leads to a doubling of the *a* axis of the pseudocubic cell of simple perovskites and to a larger buckling of the corner-sharing BO_6 octahedra; (*iii*) such denser and more strongly buckled structure prevents the formation of oxygen defects.

Thanks to the absence of defects and structural inhomogeneities inherent to simple perovskites, quadruple perovskites constitute a model system for studying competing orderings in JT systems with perovskite-like structure [2]. Here we study the magnetic structure of the single-valent compounds $LaMn_7O_{12}$ and $BiMn_7O_{12}$, the quadruple perovskite counterpart of $LaMnO_3$. By means of a detailed neutron diffraction study, we found that in both compounds the *A*' and *B* ions order antiferromagnetically (AFM) at low temperatures in an independent fashion. However, in spite of the common Mn^{3+} properties, the magnetic structures are strikingly different in the two compounds. In particular, in $LaMn_7O_{12}$ the structure of the *B*-site is of C-type [1], which contrasts the A-type structure reported for $LaMnO_3$. In $BiMn_7O_{12}$, the structure of the *B*-site is more complex, being characterized by two distinct propagation vectors. We discuss the origin of these differences in terms of the polar properties of the Bi $6s^2$ lone pair, which also accounts for the centre of symmetry breaking in the crystal structure of $BiMn_7O_{12}$ [3]. Finally, we discuss the role of symmetry of the JT sites and of the Mn-O-Mn bond angle on the stability conditions of competing magnetic structures.

References

[1] A. Prodi *et al*., Nature Materials **3**, 48 (2004)

[2] A. Prodi *et al*., Phys. Rev. B **79**, 085105 (2009)

[3] F. Mezzadri *et al*., Phys. Rev. B **79**, 100106 (R) (2009)