Orbital ordering in transition-metal spinels
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Transition-metal spinels (general formula $AB_2X_4$) have been for many years the subject of intense experimental and theoretical activity. Structurally, the most interesting feature of these systems is the fact that the $B$ cation occupies the nodes of a pyrochlore lattice, which is known to be geometrically frustrated. Therefore, one can explore how their natural tendency to order in the charge, magnetic and orbital sectors is affected by geometrical frustration. Orbital Ordering (OO) occurs when the orbital degeneracy of an extended concentrated system is lifted, typically through a distortion of the lattice. This may result in either single orbital occupation or alternation/modulation of the orbital occupancy, with or without an associated charge ordering. The degree of charge localization is another important issue: in highly localized systems, one can speak of a cooperative Jahn-Teller (JT) effect, but this paradigm is no longer sufficient in the present of significant electronic hopping. Both $e_g$ and $t_{2g}$ orbitals are relevant for transition-metal spinels; $e_g$ systems, such as ZnMn$_2$O$_4$, tend to display the strongest JT effects, with direct coupling to the lattice. More recently, significant attention has been devoted to the possibility of orbital ordering in ions with partial $t_{2g}$ occupation, such as Ti$^{3+}$ and V$^{4+}$ ($3d^1$) and V$^{3+}$ ($3d^2$) and their electron/hole-symmetric counterparts. With respect to $e_g$ systems, $t_{2g}$ systems have a greater degeneracy and weaker coupling to the lattice, and can give rise to significant hopping, due to the direct overlap of the $t_{2g}$ orbitals along the $<110>$ crystallographic directions of the spinel structure. Recent results on Ti, V, Fe and Ir spinels will be discussed, with particular reference to the relation between the complex crystallographic superstructures and the changes in transport (metal-insulator transitions) and magnetic (paramagnetic-diamagnetic transitions) properties at the ordering temperatures.