Formation and ordering of orbital molecules in AV_2O_4 spinels

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Orbital molecules are clusters of transition metal cations formed by orbital- and charge-ordering in systems with direct d-d interactions [1]. Vanadium oxides exhibit a particularly rich variety of orbital molecule states, notably the V-V dimerisation that accompanies the metal-insulator transition in VO_2 [2]. In vanadium oxide spinels such as AlV_2O_4 and GaV_2O_4 the 3D connectivity of V-V nearest neighbours allows larger orbital molecules to form, and these also persist into a hidden high-temperature disordered state [3].

Not all AV_2O_4 spinels have orbital molecule ground states, but as the formation of V-V bonds is associated with marked lattice distortions we have employed synchrotron X-ray powder diffraction and pair-distribution function analysis to determine the structural and electronic requirements for V-V bonding to be stabilised. Studying the $Zn_xGa_{1-x}V_2O_4$ family of materials revealed that, whilst the long-range order of orbital molecules in the ground state of GaV_2O_4 is highly sensitive to A-site substitution, local V-V bonding interactions are stable to $x > 0.75$ before the ground state of ZnV_2O_4, which is orbitally ordered but without V-V bonding, emerges [4]. Furthermore, we have found a monoclinic distortion coincident with the reported pressure-driven metal-insulator transition in LiV_2O_4 that suggests it to be the result of orbital-molecule formation [5]. Overall, we have determined that the formation and ordering of orbital molecules bonds in AV_2O_4 spinels is principally dependent on the V-V nearest-neighbour distance (Fig. 1).

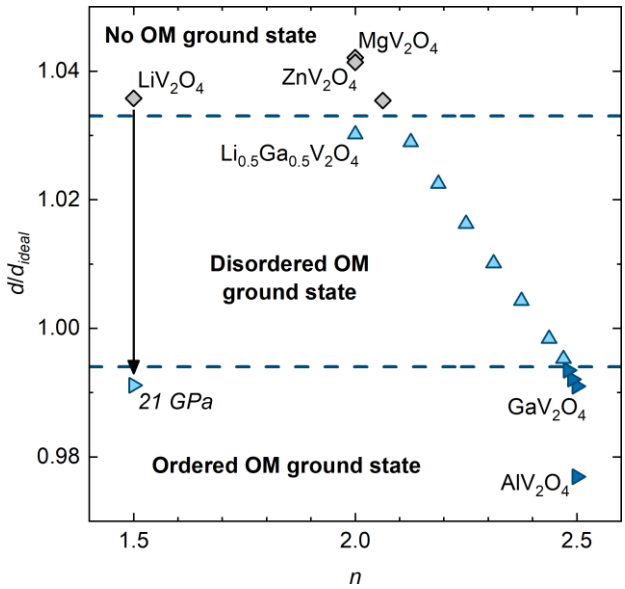

Figure 1. Phase diagram illustrating the dependence of V-V bonding in the ground states of AV_2O_4 spinels on the ratio of observed to ideal V-V nearest neighbour distances d/d_{ideal}. n is the average number of 3d electrons per V cation [4].

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