Charge and orbital ordering in spinel vanadates

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Orbital degrees of freedom of triply degenerate t_{2g} states often play important roles in early transition-metal oxides. We discuss the following two spinel vanadates, both of which show intriguing properties arising from such orbital degrees of freedom.

(1) AlV_2O_4
Since the average valence of V is half integer (2.5+), there is instability of charge disproportionation in this compound. From electron diffraction, synchrotron x-ray diffraction, and magnetic measurement, we conclude that vanadium "heptamers" are formed below 700 K in this compound. The stability of this V heptamer is given by a strong bonding of vanadium t_{2g} orbitals, and thus, it can be regarded as a formation of "molecules" in the crystal. [1]

(2) MnV_2O_4
This compound exhibits a structural phase transition (from cubic to tetragonal) and a ferrimagnetic phase transition (where the Mn^{2+} spins and V^{3+} spins are aligned to the opposite direction) at the same temperature (57 K). We found that the crystal structure of this compound can be switched from cubic to tetragonal with applied magnetic field [2]. We also obtained the evidence by x-ray diffraction measurement that this structural phase transition is dominated by the ordering of V t_{2g} orbitals.

References

[1] Y. Horibe et al., Phys. Rev. Lett. 96, 086406 (2006).
[2] K. Adachi et al., Phys. Rev. Lett. 95, 197202 (2005).