

Charge Ordering in Transition Metal Oxides - from Magnetite to Manganites

Dr. J. Paul Attfield, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK.

The phenomenon of charge order (CO), a long range order of different metal oxidation states in a crystal lattice, was first proposed in 1939 for magnetite (Fe_3O_4) below the 120 K Verwey transition. However, it is only in the last few years that many CO structures have been experimentally determined. We have recently studied CO in manganite perovskites, notably $\text{TbBaMn}_2\text{O}_6$ [1], and in Fe_3O_4 [2,3].

$\text{TbBaMn}_2\text{O}_6$ is a metastable, cation-ordered perovskite, prepared by low temperature oxygen intercalation into $\text{TbBaMn}_2\text{O}_5$. $\text{TbBaMn}_2\text{O}_6$ shows a wealth of ordering phenomena separated by 5 phase transitions, as octahedral rotations, $\text{Mn}^{3+}/\text{Mn}^{4+}$ charges, Mn^{3+} orbital (Jahn-Teller) distortions, and Mn spins all order at well defined temperatures. The 300 K charge and orbitally ordered structure has a subtle triclinic superstructure, ($a = 5.56044(6)$ Å, $b = 11.12021(11)$ Å, $c = 7.63668(6)$ Å, $\alpha = 89.980(4)^\circ$, $\beta = 90.234(1)^\circ$, $\gamma = 89.977(2)^\circ$). Conventional 50% doped AMnO_3 manganite perovskites such as $(\text{La}_{0.5}\text{Ca}_{0.5})\text{MnO}_3$ show a ‘striped’ charge and orbitally ordered arrangement in which ‘checkerboard’ $\text{Mn}^{3+}/\text{Mn}^{4+}$ charge ordered layers are stacked directly above each other. The 300 K structure of $\text{TbBaMn}_2\text{O}_6$ ($(\text{Tb}_{0.5}\text{Ba}_{0.5})\text{MnO}_3$) reveals an alternative CO arrangement, in which the same charge and orbitally ordered layers are stacked in an alternate fashion giving a ‘rocksalt’ three dimensional CO. This comparison reveals for the first time a *polymorphism of charge ordering* within two chemically identical frameworks (here MnO_3^{2-5-}).

The classic charge ordering problem in transition metal oxides is that of the spinel magnetite, which has been unresolved for over 60 years. Our recent structure refinements using high-resolution X-ray and neutron powder diffraction data give direct evidence for charge ordering (CO) over four independent octahedral Fe sites, two with a charge of +2.4 and the other two of +2.6. CO schemes consistent with our model do not meet the widely-accepted Anderson condition of minimum electrostatic repulsion. Instead we propose that CO is driven primarily by a [001] electronic instability, which opens a gap at the transition through a charge density wave mechanism.

The common features of CO structures such as the structural degree of CO and the CO arrangement will be discussed using the above and other examples.

Literature:

[1] Williams, A J, Attfield, J P, Phys. Rev. B, 2002, 66, 220405R. [2] Wright, J P, Attfield, J P, Radaelli, P G Phys Rev Lett 2001, 87, 266401. [3] Wright, J P, Attfield, J P, Radaelli, P G, Phys Rev B 2002, 66, 214422.