21 世紀 COE
「京都大学化学連携研究教育拠点」
化学研究所・固体化学セミナー

講師：**Prof. J. Paul Attfield**
(University of Edinburgh, U.K.)

演題：**The Chemical Control of Electronic Oxides**

日時：平成 17 年　1 月 25 日（火）16：00～
場所：化学研究所　新４Ｆセミナー室

John Paul Attfield教授はこれまで高温超伝導を示す銅酸化物、超巨大磁気抵抗効果を持つマンガン酸化物、電荷整列を起こす鉄酸化物、希土類ホウ炭化物などについて、その興味深い電気伝導性や磁性が組成及び結晶構造にどのように依存しているのかについて研究を行ってこられました。今回は最近の研究テーマのいくつかについて紹介して頂きます。

世話人：無機先端機能化学　高野幹夫（内 3120）

The Chemical Control of Electronic Oxides

J. Paul Attfield

Centre for Science at Extreme Conditions (CSEC) and School of Chemistry, University of Edinburgh, King's Buildings, Edinburgh EH9 3JZ, UK.
Visiting Professor, Institute for Chemical Research, Kyoto University, Gokasho Uji, Kyoto 611-0011, Japan

Transition metal oxides continue to offer remarkable electronic and magnetic properties for solid state science and technologies. Many of these properties result from the formation of ordered states; structural ordering of atoms or vacancies, atom displacements and polyhedral tilts; charge and orbital ordering, spin (magnetic) order, and electron-pairing order (superconductivity). Different aspects of our research in recent years concerning the chemical control of these phenomena will be presented:

(i) *Cation size effects in perovskite-related oxides.* Simple experiments on $Ln_{1-x}M_xMnO_3$ perovskites, which show colossal magnetoresistances at the metal-insulator transition, and superconducting $Ln_{2-x}M_xCuO_4$ oxides, have shown that the variations in property can be described using three parameters. These are the hole doping level x, the average radius of the trivalent Ln and divalent M (= Ca, Sr, Ba) cations at the A sites, $\langle r_A \rangle$ (equivalent to the well-known perovskite tolerance factor), and a new parameter - the variance in the A cation radius distribution, σ^2. Experiments at constant x reveal that the metal-insulator transition in $Ln_{1-x}M_xMnO_3$ perovskites and the critical temperature and superconducting properties of $La_{2-x}M_xCuO_4$ materials are both sensitive to changes in these quantities, enabling simple quadratic relationships for the size and disorder effects to be derived.

(ii) *Charge ordering in oxides.* 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. CO has become important in recent years as CO stripes or other correlations may be important to the mechanism of superconductivity in cuprates, CMR in manganites, and other phenomena in oxides. However, it is only in the last few years that many CO structures have been experimentally determined. We have recently studied CO in Fe_3O_4 and in manganite perovskites; RBaMn$_2$O$_6$ (R = Tb, Y) and $(Pr_{0.5}Ca_{0.5})MnO_3$ using high resolution powder X-ray and neutron diffraction. The results show that several CO arrangements are possible, with further variation of the orbital ordering associated with CO in manganites.

(iii) *Double Perovskites.* The discovery of CMR in Sr_2FeMoO_6 has prompted much research on related materials in which two transition metals are ordered at perovskite B-sites. Recent results on antiferromagnetic Co based materials will be presented.

(iv) *High pressure Cr oxides.* This new project is to stabilise Cr(IV) oxides with perovskite-related structures, and their solid solutions with Ru(IV) analogues, which are known to have notable magnetic, conducting and superconducting properties.