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

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演題：**Self organized structures in ferroelastic and co-elastic systems**

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Self organized mesoscopic structures in ferroelastic materials display as basic excitation mobile twin walls. These twin walls form hierarchical structures with needles and corner domains (level 1), combs, zig-zag domains, multiple junctions (level 2), and tweed and tartan structures (level 3). Walls and segments can easily be modified chemically and ,sometimes, structurally so that they can be used as templates for the fabrication of electronic devises (e.g. superconducting wall patterns in insulating matrices for the formation of arrays of Josephson junctions).

In co-elastic structures the elastic degrees of freedom couple with order parameters with different physical properties and, often, different symmetries. This disallows for the formation of switchable domain patterns. Instead more complex patterns emerge, often related to incommensurate phases (e.g. in quartz). In case of Dauphine twin walls in quartz, it is shown that transport along the crystallographic c-axis is reduced rather than enhanced while transport in the perpendicular directions is highly anisotropic. It is argued that ions such as Li(+) are more mobile in the incommensurate structure while their activation energy changes dramatically between the two commensurate structures

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The Chemical Control of Electronic Oxides

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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, $<r_A>$ (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; $RBaMn_2O_6$ (*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.