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Keywords: protein-ligand docking, DPI, drug discovery

MS95 ADVANCED FUNCTIONAL MATERIALS (INCLUDING MOLECULAR BIOLOGICAL FUEL CELL BATTERY)

Chairpersons: Michele Catti, Dimitri Argyriou

MS95.30.1

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New Approach to Structure Determination of Crystalline Polymer Electrolytes

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Polymer electrolytes consist of salts, e.g. NaI, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, dissolved in high molecular weight polymers, e.g. poly(ethylene oxide) (PEO). The recent discovery of ionic conductivity in crystalline polymer electrolytes [1] was prompted by the elucidation of the crystal structure of $\text{PEO}_6\text{:LiAsF}_6$ [2] from powder diffraction data using a simulated annealing technique [3]. This challenged the established view that conduction occurs exclusively in amorphous polymer electrolytes above their glass transition temperature and opened a new avenue in polymer electrolyte research.

Recently we have established even more complex crystal structures of polymer electrolytes, such as $\text{PEO}_8\text{:NaBPh}_4$ and $\text{PEO}_4\text{:ZnCl}_2$, using a combination of single crystal diffraction data from a material prepared with a low-molecular weight polymer and powder data from a material with the same chemical composition but synthesized using a high molecular weight PEO. The combination proved to be successful when the individual methods failed to produce a reliable structural model.

We have also discovered polymorphism in $\text{PEO}_6\text{:LiAsF}_6$ and determined the crystal structure of the new phase. The differences in the crystal structure of the two polymorphs account for the difference in their ionic conductivity.

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Keywords: polymer electrolytes, ionic conductivity, polymorphism

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Magnetic Control of Electric Polarization in Magnetic Oxides with Non-collinear Magnetic Structures

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Recent observations of gigantic magnetoelectric and magnetocapacitive effects in rare-earth manganites, TbMnO_3 and DyMnO_3 [1,2], provide a novel approach to the mutual control of magnetization and electric polarization in magnetic ferroelectrics. We can control the magnitude and/or direction of the electric polarization vector by the application of magnetic field in these manganites. In comparing the results from the both manganites, we noticed that a characteristic common to the both materials is that they possess modulated magnetic structures with long wavelengths (as compared to the chemical unit cell) which arise from competing magnetic interactions. Ferroelectricity in these materials appears to originate from the competing magnetic interactions which cause lattice modulations through magnetoelastic coupling. In this talk, we show magnetic control of electric polarization in several magnetic oxides with non-collinear magnetic structures, which may provide new route to design magnetoelectrics.

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Keywords: multiferroics, magnetoelectric effect, non-collinear magnetic structure

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Crystal Structure and Magneto-transport Properties of New Cobalt Based Layered Oxides

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The search for new layered cobalt based oxides is very important to discover interesting physical properties as recently illustrated by the discovery of a large thermoelectric power in the metallic phase $\text{Na}_{0.5}\text{CoO}_2$ [1] and by the report on the superconductivity of the derived hydrated compound $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ [2]. Recent investigations in the Sr-Co-M-O systems (M = Ga, Ti...) by means of transmission electron microscopy techniques have allowed to detect new layered cobaltites. Their structure has been obtained by combining high resolution images and powder X-ray/neutron diffraction data.

Firstly, a new oxide, $(\text{Ga}_{1/3}\text{Co}_{2/3})_2\text{Sr}_2\text{CoO}_{6+\delta}$, has been isolated [3]. Its complex structure is described from a modulation vector $q^* = q_1a^* + q_2c^*$. For the as-prepared sample ($\delta \approx 0.4$), it can be described in an orthorhombic supercell $Bb2b$ ($q_1=1/3$ and $q_2=1$) with the unit cell parameters $a=3a_p\sqrt{2}$, $b=a_p\sqrt{2}$ and $c=19.2034(4)$ Å. The layer stacking consists in an intergrowth between a $[\text{SrCoO}_3]$ perovskite-type block and a block of triple [AO] layers, $[(\text{SrO})(\text{Co}_{2/3}\text{Ga}_{1/3}\text{O}_{1+\delta/2})(\text{Co}_{2/3}\text{Ga}_{1/3}\text{O}_{1+\delta/2})]$ in which several kinds of GaO_x and CoO_x polyhedra coexist. Low resistivities ($\rho_{300\text{K}} \approx 10^{-1}\Omega\cdot\text{cm}$) depending on the δ value have been measured whereas a positive thermoelectric power $S_{300\text{K}} = 30\mu\text{V/K}$ indicates the presence of holes (Co^{4+}) in the CoO_2 conducting layers. This value can be compared with those observed in the $\text{Na}_{0.5}\text{CoO}_2$ and the misfit $[(\text{A}'_{1-x}\text{Co}_y)_{n-2}\text{A}_{2+x-y}\text{O}_n]^{\text{RS}}[\text{CoO}_2]_{b1/b2}$ ($\text{A}'=\text{Bi, Tl}$.. and $\text{A}=\text{Ca, Sr}$..) related cobaltites. Secondly, two hydrated oxyhydroxides have been prepared in air [4]. The structural study coupled to thermal analyses has shown that $\text{Sr}_3\text{Co}_{1.7}\text{Ti}_{0.3}\text{O}_5(\text{OH})_2 \cdot x\text{H}_2\text{O}$ and $\text{Sr}_4\text{Co}_{1.6}\text{Ti}_{1.4}\text{O}_8(\text{OH})_2 \cdot x\text{H}_2\text{O}$ are derived from the Ruddlesden-Popper $n=2$ and $n=3$ members, respectively. The T-dependence of the structure shows upon warming two broad structural transitions from hydrated oxyhydroxides to oxygen deficient RP structures via an anhydrous oxyhydroxide form. The phenomenon of water loss during warming up to 1000°C to obtain the parent RP structures is found to be reversible. The magnetic behavior of these phases is governed by the substituted amount of Ti^{4+} (d^0) for cobalt species: cluster-glass and spin-glass like properties are observed for the hydrated $n=2$ and $n=3$ members, respectively.

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Keywords: crystal and powder X-ray diffractometry, electron microscopy technique, topotactic transformations

MS95.30.4

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Single-component Molecular Conductor Formed by Electron Transfer between d and π Orbitals

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Recently, research on conducting systems that consist of a single-component molecule has attracted a lot of attention.[1] Herein, we report the crystal structure and electronic properties of novel linear chain rhodium(I,II) mixed-valence complex, $\{\text{Rh}(3,6\text{-DBDiox-4,5-Cl}_2)(\text{CO})_2\}_\infty$ (**1**) where 3,6-DBDiox-4,5-Cl₂ is used to indicate the semiquinonate or catecholate form of 3,6-di-*tert*-butyl-4,5-dichloro-

1,2-benzoquinone, formed by electron transfer between metal d and semiquinonate π^* orbitals.

X-ray crystal structure analysis of **1** was performed at 302 and 56 K using synchrotron radiation at BL02B1 beamline at the SPring-8 facility. Compound **1** only consists of linear chains of $[\text{Rh}(3,6\text{-DBDiox-4,5-Cl}_2)(\text{CO})_2]$ molecules and these complex molecules form trimer units in the linear chain at 302 K. At 56 K, the trimer units in the linear chain dimerized and form hexamer units. Compound **1** shows a significantly large conductivity ($17\text{--}34 \text{ S cm}^{-1}$) at room temperature regardless of the neutral molecule. The temperature dependence of the electrical conductivity shows a semiconducting behavior. The observed dimerization of trimers in the 1-D chain is considered to originate from Peierls distortion.

[1] Tanaka H., Okano Y., Kobayashi H., Suzuki W., Kobayashi A., *Science*, 2001, **291**, 285–287.

Keywords: conducting molecular crystals, mixed-valence compounds, synchrotron X-ray diffraction

MS95.30.5

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In Field Incommensurate-Commensurate Phase Transition in the Multiferroic TbMnO_3

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Orthorhombic TbMnO_3 [1] is a multiferroic compound that exhibits a flop in the electrical polarization from c to the a-direction with an applied magnetic field either along a or b axis. We have studied the magnetic field dependence of the incommensurate wave vectors (q_{Mn} , q_{Tb}) associated with the polarization and the magnetic ordering by neutron and x-ray single crystal diffraction with $H\parallel a$ and b. The polarization flop transition corresponds to first-order transition from an incommensurate multi-q-structure to a commensurate single q-structure with $q=1/4$ at $H\parallel a$, $H>9\text{T}$, $T_c\sim 28\text{K}$. In our X-ray measurements, the induced magneto-elastic coupling is observed as a structural modulation at twice the magnetic wavevector ($2q_{\text{Mn,Tb}}$). The temperature and field dependence of the magnetic and superlattice reflections are consistent with a soliton formalism which predicts a stable commensurate single $q=1/4$ -phase.

[1] Kimura et al., *Nature*, 2003, **426**, 55.

Keywords: 1/4-phase, polarization flop, soliton formalism

MS96 CRYSTALLOGRAPHIC TEACHING

Chairpersons: Åke Oskarsson, Randy Read

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Crystallography Boot Camp at Cold Spring Harbor Laboratory
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A theoretical and practical course teaching the fundamentals of macromolecular crystallography has been held at Cold Spring Harbor Laboratory for the last 16 years. This course exposes participants to basic diffraction theory, crystallization (proteins, nucleic acids and complexes), crystal characterization, X-ray sources and optics, synchrotrons, crystal freezing, data collection, data reduction, multiple isomorphous replacement, multiwavelength anomalous diffraction, molecular replacement, solvent flattening, non-crystallographic symmetry averaging, electron density interpretation, molecular graphics, structure refinement, structure validation, coordinate deposition and structure presentation. Participants learn through extensive hands-on experiments in which one or more proteins are crystallized and the structure(s) determined by several methods, in parallel with lectures on the theory and informal discussions behind the techniques.

Several core tenets have served to make this course well-regarded. First, extremely experienced instructors both lecture and run practicals. For example, the mathematical theory of crystallography and the practical side of growing crystals is anchored by the

irreplaceable Alex McPherson. Another core feature of the course is a dedicated fully equipped laboratory with bench space, microscopes, and computer workstations which are always available during the long hours of the course. Finally, the extraordinary venue with nearby housing and dining facilities keeps the participants fully focused on the demanding, yet flexible, training schedule.

Keywords: education, teaching, training

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Introducing Twinning

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Twinning is a relatively common phenomenon in crystallography, but it has long been considered to be amongst the most serious obstacles to successful structure determination. A twinned crystal is an aggregate in which different domains are joined together according to a specific symmetry operation - the twin law. Reflections from different domains may overlap, and twinned crystals fall broadly into two categories in which either all reflections or only certain zones of reflections are affected by overlap. The former occurs when a crystal lattice belongs to a higher point group than the crystal structure itself, the latter frequently occurs when the twin law is a symmetry operation belonging to a higher symmetry supercell.

Software has now developed to such an extent that some twin problems can now be tackled using a black-box approach. More commonly, successful use of these tools depends of some understanding of twinning and its basis in symmetry. This talk will describe some of my experiences in teaching students about twinning.

Keywords: crystallographic education, twins, software for crystallography

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Real versus Virtual aids in Teaching Crystallography

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Crystallography is a special discipline, impossible without models. Our macroscopic models of the microscopic world are only crude approximations of the atomic reality. Those artificial "reflections" of the real world can be expressed using material "substance" or as virtual reality. The explosive development of computer graphics tools has provided a tremendous boost to both structural research and teaching. Without the use of computers it would be impossible to teach about the expanding frontiers of biocrystallography. In addition to being the scenes and tools for displaying and manipulating molecular models, computers are also invaluable in modernizing the teaching/learning process, facilitating distance education, individual learning pace, exchange of teaching aids, etc. Despite the possibilities offered by computer tools, many educators believe that the use of traditional "real" models is essential. Classroom experience shows that some aspects of space and symmetry, almost intuitively obvious with solid models, are complicated or inconvenient when handled on the computer screen. At the introductory level, where simple models and hand-waving can be very appealing, there is no need to strive to recreate three dimensions in the computer. There is also a psychological aspect of using solid objects as material models, even if not perfect, seem to have some physical properties that make them closer to the real world than the idealized computer representation. Besides, computer models can only display what had been foreseen by the programmer, while the use of pliers, plasticine, glue, and imagination can lead to almost unlimited creativity.

Keywords: computer graphics, models, teaching aids

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Towards a Web-Based Interactive Environment for the Teaching of Crystallography

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