

1,2-benzoquinone, formed by electron transfer between metal d and semiquinone 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

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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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The possibilities offered by the Java language to run on any computer platform linked to Internet has motivated a large number of scientists in creating interactive applications or applets, aiming at a better understanding of scientific phenomena.

Crystallographers have been early adopters of the new possibilities offered by Internet with the aim to illustrate various concepts specific to crystallography. Presently, a quick search on the Internet reveals already the existence of numerous web sites containing interactive applets dedicated to crystallographic teaching.

The current generation of personal computers equipped with the most recent graphical hardware and software and the enormous local CPU capacity, allows to create very powerful applets which were not conceivable with previous generations.

Almost all the aspects of crystallographic teaching can be currently accessed on the web. Notions of point and space group symmetry, Fourier transform and diffraction theory, crystal structures and many others related topics are covered on various sites, freely accessible on the web.

However, for the student wishing to learn more about crystallography, the problem is to find the logical path among all the possible sites and applets providing the best sequence of subjects in order to acquire the expected knowledge.

We are currently setting up a web-based interactive environment on crystallography, building not only on our own developments but also on the vast amount of already existing tools available on Internet.

Keywords: teaching of crystallography, simulation software, web resources

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Teaching Crystallography with a Laser, Two Lens and ...Einstein's Tongue

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Teaching crystallography to students in Biology is a difficult task, particularly because many of them arrived there because 'there are no more Maths or Physics in Biology'. After 10 years of practice, we have tried as much as possible to limit (not suppress !) the recourse to Mathematics and, also, to show really what diffraction means.

For that goal we make use of a classical optical bench requiring a LASER ($\lambda=0.6328 \mu\text{m}$), a pinhole as a beam expander and two lens. We use as crystals 24x36 B&W photographs of a 80x60 repeats of the well-known 'Einstein's tongue' (cell parameters $a = 0.45 \text{ mm}$, $b = 0.4 \text{ mm}$). This allows to record a diffraction pattern on films mounted in the back focal plane of the second lens. The diffraction data extend to order 21 (more than 500 visible Bragg's spots), which correspond to 20 μm resolution.

In order to illustrate the principle of the MIR method, we have made 'heavy atom derivatives' by adding small dots on Einstein's face (one site per derivative), and we have 'collected new data'. Our hope is to go really all the way through with experimental data to 'solve the structure'. For now, this structure solution step is illustrated with calculated data. This shows very well how a recognizable picture is obtained after 'MIR phasing' with only 50 reflections, and what is the effect of experimental noise.

All programming was performed with *Mathematica* (Wolfram Research), which allowed to develop very rapidly the necessary code. This aspect will also be shown in the oral presentation.

Keywords: teaching, optical diffraction, mathematica

MS97 BIO-INORGANICS IN BIOLOGICAL MACROMOLECULES

Chairpersons: Adriana Bigi, Enrico Rizzarelli

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Structural Biology of Lignolytic Enzymes: Laccases and Heme Peroxidases

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Laccases (Lac) and certain peroxidases, e.g. lignin peroxidase (LiP), manganese peroxidase (MnP), and versatile peroxidase (VP) are employed by filamentous fungi to degrade the recalcitrant biopolymer lignin a major constituent of woody plants. While LiP, MnP, and VP are heme-containing glycoproteins utilizing hydrogen peroxide as co-substrate to attain the redox state needed for activity, laccase is a blue multi-copper oxidase using molecular oxygen for activation. These fungal metalloenzymes are used in biotechnological applications and have a high potential to be employed in other industrial processes. We have been engaged in structural-functional work on LiP/MnP and VP since many years. This work resulted in the finding of a unique, unprecedented amino acid modification in LiP, which initiated further investigations employing crystallography, protein chemistry, site-directed mutagenesis, spectroscopy, and spin-trapping. The conclusions drawn from the outcome of these experiments had far reaching consequences for the understanding on LiP substrate interaction and on the redox behavior. More recently, we have extended our interest towards fungal laccases, yielding the first crystal structure of a laccase in its glycosylated, fully functional form, containing a full complement set of coppers. In this presentation the current state on structural-functional aspects of the above metalloenzymes is reviewed, spanning from the description and analysis of 3D-structures to mechanistic aspects, e.g. substrate binding and specificity and redox potential.

Keywords: lignolytic enzymes, radicals, substrate binding

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Inhibitor Binding to Aldose Reductase Studied at Subatomic Resolution

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Aldose reductase (ALR2; EC 1.1.1.21), which reduces D-glucose into D-sorbitol, is believed to cause the development of severe degenerative complications of *diabetes mellitus*. Therefore, ALR2 is the target of an extended effort in inhibitor development. We have solved the X-ray structure of complexes with ALR2 and a large number of inhibitors, of which several are at atomic and subatomic resolution, with either a carboxylate head (IDD 594, 0.66 Å) or an hydantoin head (fidarestat, 0.92 Å; minalrestat, 1.10 Å). Inhibitors bind to a charged "anionic site" in the active site cleft. The structure of IDD 594 showed very precise details, with departures from standard stereochemistry, as well as hydrogen atoms and unusual contacts for a Br atom in the inhibitor. The structure of fidarestat showed the presence of Cl⁻ ions replacing buried water molecules in the active site. The Cl⁻ ion has been clearly identified in an anomalous difference map. These observations explain inhibitor binding, which is crucial for drug design.

Keywords: aldose reductase, inhibitor interactions, diabetes