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Some Examples of Polyoxometalates Crystal Structure Defects

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The study of Molybdenum and Tungsten polyoxometalate complexes is of fundamental importance in the context of both oxidation catalysis and biology. The possibility to build complexes with different structures and to attach to them varied organometallic molecules is related to oxygen and electron transport during enzymatic reactions [1].

X-ray crystal structure solution and refinement of poly-oxometalate single crystals often involves some difficulties usually related to different disorders in their crystal packing. The structural framework of these compounds is formed by joining complexes W, Mo – O, which can be presented in variety of different shapes, like spheres, ellipsoids, wheels and others. The complexes can be connected to each other by a network of solvent water molecules and cationic counter ions or by different organic or organometallic groups. Large accessible voids between the complexes usually allow inserting additional atoms or groups. The sufficiently weak bonds between different structural groups and the inherent high symmetry of the polyoxometalate can cause several types of disordering. Metal atoms of the complexes may also be partially substituted by other metal atoms, which in turn can be disordered distributed inside of the complexes.

Different types of disordering and partial or mixed occupancies at certain positions can cause small changes in the symmetry of the crystals, which can give rise to supersymmetry or even to an aperiodic structure. Lack of small reflections with high resolution can prevent from finding correct symmetry group and thereafter from obtaining structure solution.

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Supercell approximation for an incommensurately modulated crystal of profilin:actin

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A crystal structure from an incommensurately modulated protein crystal has never been reported, mainly due to a lack of methods for solving these unique structures. Here we report the first modulated protein structure that was determined using q-vectors to accurately integrate the diffraction data followed by a commensurate supercell approximation. Crystal modulation is characterized by a loss of short-range translational symmetry, where a single unit cell is no longer sufficient to accurately describe the structure. Such a loss of periodicity is often caused by dynamic processes within the crystal arising from, for example positional modulations. Experimentally, the incommensurately modulated state is characterized by the appearance of distinct satellite reflections surrounding the main Bragg reflections on the diffraction pattern that cannot be indexed with a supercell. In order to fully describe the modulated structure, and hence the dynamic processes within the crystal, one must explore higher-order space over multiple unit cells. By careful examination of atomic positions over higher dimensional space, a modulation function can be calculated that traces the atomic disorder. Such a function is periodic, but incommensurate with the crystal lattice. Another form of modulation occurs when the atomic disorder is commensurate with the main lattice. In this case, the intensities can be indexed as a large, or 'supercell'. In the case of incommensurately modulated profilin:actin crystals, the data was not able to be indexed as a supercell by use of existing software. The diffraction data had to be indexed and integrated using the q-vector approach. Data were observed to 2.4 Å and were processed with a single q-vector with *EVAL15* software. The main and satellite reflections were indexed and described by an orthorhombic main unit cell of a=37, b=71, c=185 Å and the q-vector q=0.2829…b*. From this q vector we know that the modulation repeats at approximately, but not exactly, three and a half unit cells in the b direction. To approximate the supercell, the data was then reindexed using a supercell approximation (assuming the q vector is close to 2/7; then h=h, k=7k+2m, l=l). The supercell dimensions were a=37, b=498, c=185 Å with space group $P2_12_12_1$. A previously refined periodic PA structure was used as a search model and molecular replacement using *MOLREP* produced a ribbon structure with 6 PA copies. Analysis of electron density maps made clear the position of the 7th copy, which was fit manually. Then refinement was performed with *REFMAC* using 7 rigid groups for each actin and one for profilin. In the resultant map there was interpretable density for ATP. In this preliminary structure the motion appears to involve a rotation in the ac plane and is in general agreement with the analysis of the average structure, which by analysis of Fourier electron density maps indicate major motion in actin subdomains 2 and 4. The position of profilin seems to change the least. The structural information gleamed from this approximation will help bootstrap the solution of the incommensurate structural refinement in (3+1)D superspace.

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Service crystallography at the university of santiago de compostela

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The latest technological developments in X-Ray production, optics and detection, the automation of crystallization, sample handling and conditioning, and the improvement in computing facilities combined with new methodologies have converted crystallographic analysis to routine in many cases, mainly for small and medium-size molecules. The standardization of these techniques allowed their use by non-specialized users inside Departments and to be included in the general services offered by Universities and other research institutions. However, there are still many situations, even in simple systems, where the assistance of an expert crystallographer is required.

We describe here our experience with the set up and development of the X-Ray Unit at the University of Santiago de Compostela (USC)

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as a general crystallographic service to the scientific community either at USC or at any other national or international research organization or industry.

The X-Ray Unit at the USC offers nowadays the following techniques:

- Single crystal diffraction for all size of molecules.
- General X-Ray diffraction: powders, micro-diffraction, high resolution, grazing incidence.
- Small Angle Scattering (SAXS).
- Reflectometry.
- Energy dispersive X-Ray fluorescence.

Gathering all X-Ray related techniques in one place has many advantages: easier management in a homogeneous environment, better planning and future development, more synergy and complementarity between different techniques due to close collaboration among specialized personnel, low running costs and finally even the possibility to offer specific solutions to scientific questions asked by the researchers instead of individual techniques alone.

The X-Ray Unit facilitates the application of crystallographic techniques to inexperienced users and to an increasing number of research groups working in other fields that were not traditionally linked to crystallography. For example, the evolution with time of the number of research groups demanding single crystal diffraction experiments is displayed in the graphs below.
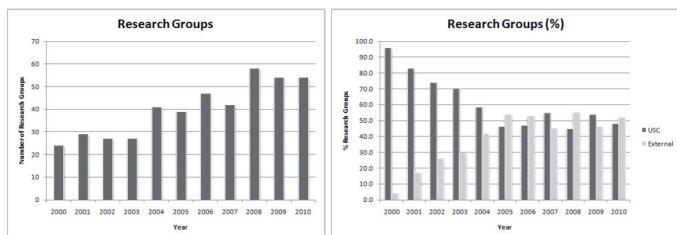
The main tasks to achieve are: keep routine techniques available, implement the most demanded ones, advice users to help them to solve specific scientific problems, provide training to enable them to perform their own experiments and data analysis, disseminate the results obtained, spread the capabilities of the techniques and finally implement and develop new methodological approaches to solve non-routine problems (disorder, twins, unstable crystals, macromolecules, etc.).

Keywords: service, X-ray, crystallography

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Improved DFT calculation of raman spectra of silicates and similar compounds

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With advances in modern technology, Raman spectrometers have become smaller, cheaper, and easier to use. As a result, Raman spectroscopy is nowadays a standard method in the characterization of materials. Beyond simple fingerprinting, vibrational analysis is extremely useful for obtaining information about structural features of molecules and solids. The theoretical tools used for vibrational analysis have also advanced very much in recent years. Among the most powerful is certainly the *ab initio* calculation of vibrational spectra from the structure alone, using quantum-mechanical methods. The benefit of this approach is not so much in the calculated frequencies

themselves, which after all are easily gained from the experimental spectrum. But the calculations yield additional information about the mode symmetries and the movements of the atoms involved in the particular vibrations. These can be used to understand changes in frequencies or other features of the experimental spectrum, like peak intensity or broadening, that result from changes in pressure, temperature, or chemical composition. Furthermore, deviations from the ideal crystal structure and its expected spectrum can be identified, and the presence of impurity phases can be spotted.

In order to join the information from the experimental spectrum with the information from the calculation, it is necessary to assign the observed bands to specific calculated modes. The foremost criterion used in this context is the agreement of the observed and calculated frequencies. To allow for an unequivocal assignment, the uncertainty of both values needs to be lower than the distance between neighboring modes. For moderately complex silicates, this is ≈ 20 cm^{-1} on average, and considerably less in some regions of the spectrum. Experimentally, this level of accuracy does not present a problem. Modern Raman spectrometers reach spectral resolutions of 2 cm^{-1} and accuracies of 0.5 cm^{-1}.

On the theoretical side, very accurate vibrational spectra of silicates are obtained from DFT calculations if the appropriate Hamiltonian is used. For silicates and compounds with similar electronic character, theoretical considerations [1,2,3] suggest that the Hartree-Fock component of ACM1 hybrid functionals should be 1/6 instead of 1/4 for this class of materials. When applied to the PBE / PBE0 [2] functional this removes the scaling error of the calculated vibrational frequencies. Calculations using this PBE(n=6) functional in combination with optimized Gaussian basis sets result in very small remaining deviations between observed and calculated Raman shifts, with standard uncertainties of ≈ 3.5 cm^{-1}, maximum deviations of ≈ 10 cm^{-1}, and no significant systematic trends. These deviations are lower than the experimental variations when comparing results from different samples or authors. This has been confirmed for a wide range of silicate structures, for which high-quality Raman spectra have been published: Forsterite α-Mg_2SiO_4 (nesosilicate), γ-$Y_2Si_2O_7$ (sorosilicate), $K_2Ca_3Si_3O_{10}$ (oligosilicate), $K_2Ca_4Si_8O_{21}$ (phyllosilicate), and α-quartz SiO_2 (tectosilictae).

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Design and characterization of high performance CMOS area detectors for X-ray crystallography

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CCD-based area detectors are well established as a principal technology for X-ray crystallography, both in the home lab and at synchrotron beam lines. However, recently CMOS detector technology has begun to replace CCD detectors in some applications. CMOS has a number of potential advantages including faster readout, shutter free operation and better detective quantum efficiency. We report on the design and operating characteristics of a new CMOS detector and compare the performance to CCD-based detectors.