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.
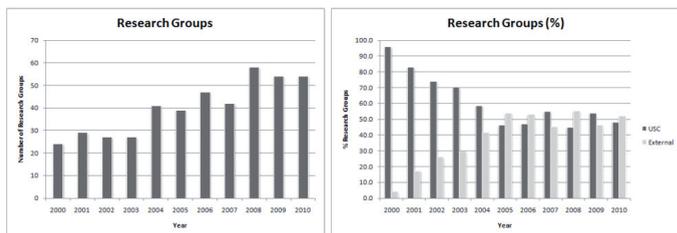
The main tasks to achieve are: keep routine techniques available, implement the most demanded ones, advice users to help them to solve specific scientific problems, provide training to enable them to perform their own experiments and data analysis, disseminate the results obtained, spread the capabilities 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

19.OT.P02

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$_2$SiO$_4$ (nesosilicate), γ-Y$_2$Si$_2$O$_7$ (sorosilicate), K$_2$Ca$_3$Si$_3$O$_{10}$ (oligosilicate), K$_2$Ca$_4$Si$_8$O$_{21}$ (phyllosilicate), and α-quartz SiO$_2$ (tectosilictae).

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Keywords: raman, calculation, silicate

19.OT.P03

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.

19.OT.P04

Simple techniques for measuring the performance of 2D X-ray detectors

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The performance of an X-ray detector depends to a large extent on the signal to noise ratio (SNR). However, this parameter is rather difficult to determine experimentally and thus it is only roughly known (if at all) for many detectors. Here we present a simple experimental technique for determining the quantum gain and the noise of a CCD detector.

In principle the simplest and most direct way to measure the quantum gain of a detector would be a measurement of the response of the detector to a single absorbed X-ray and repeat this measurement a number of times to determine the average gain. However, depending on the X-ray energy and the CCD noise it may be difficult to distinguish reliably a single X-ray "hit" above the detector noise floor, in particular at the rather low energies typically used for X-ray diffraction (e. g. 8-20 keV). Thus, the "classical" approach to measuring the gain is to use an absolutely calibrated X-ray source. However, such sources are often not easily available. Also, the use of an absolutely calibrated source requires that the measurement be corrected for the window transmission and the scintillator absorption efficiencies and these parameters are often not known with precision. Here we describe a simple method for determining the quantum gain without the use of an absolutely calibrated source and also without the need to compensate for absorption in the window and in the scintillator screen. We similarly describe the techniques for determining the total system noise so that the signal-to-noise ratio (SNR) of any given camera can be evaluated.

Specific examples for a Bruker camera will be given, but the techniques can be applied to any detector.

19.OT.P05

Identification of mineral in thin section by energy-Scanning X-ray diffraction

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The stationary sample method with polychromatic synchrotron radiation (SR) is advantageous for X-ray diffraction studies with micro-beam on minerals in a thin section. Because the irradiated area of the sample is always the same and fixed, all diffraction spots occur from the same area of the sample. However, their cell parameters, which are necessary for identification of minerals, cannot be directly obtained by this method. In order to obtain the cell parameters of the sample in a thin section even in the case of the sample stationary method, we applied energy scanning of micro-beam of monochromatic SR [1]. In the present study, an unusual mineral in a thin section of Apollo 16 lunar sample (60016) was identified using this method.

We employed the intense X-ray source of SPring-8. At the beam line 37XU the undulater is installed, and a Kirkpatrick and Baez mirror is equipped upstream of the sample giving the beam size of 0.7(V) x 2(H) μm^2 on the sample position in the thin section. Diffraction spots can be measured on the two-dimensional detector (X-ray flat panel sensor, Hamamatsu Photonics). The 60016 thin section was attached onto the sample holder, and the target silicate grain in the thin section was adjusted on the micro-beam position under an optical microscope. We applied energies of incident X-ray from 30 to 20 KeV (λ=0.4133-0.6199 Å) with the increment of 40 eV step with each exposure time being 0.5 seconds.

We obtained 17 diffraction spots in energy range above. The energy of each diffraction spot was chosen to give maximum intensity of the spot. The positions (x, y) of the diffraction spots at their maximum intensities were determined as those of the top of the diffraction profile fitting along x and y with the asymmetric Gaussian function. The reciprocal lattice vectors are calculated by the energies and the positions on the detector of the diffracted X-ray. The vectors calculated by the differences of these vectors are also used for reciprocal lattice construction. One of the domains was found as a result of analysis in a way similar to the indexing method commonly used for the four circle diffractometer, and the 7 spots obtained could be indexed by an olivine single crystal. The obtained cell parameters are a=4.751(8)$,$ b=10.199(2), and c=5.998(4)Å. These values suggest that the olivine crystal analyzed is close to near end-member forsterite composition whose Fo composition is higher than Fo_{95} [e.g., 2]. In lunar samples, forsteritic olivine is rare. Because this olivine crystal is present in a clast showing a chondrule-like texture, its forsteritic composition suggests derivation from a chondrite that impacted onto the lunar surface. This study demonstrates that the stationary sample method with energy scanning of micro-beam of monochromatic SR is a powerful tool for the non-destructive X-ray diffraction analysis of small extraterrestrial minerals in thin sections.

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19.OT.P06

The application of vacuum in the elucidation of structural changes

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The use of non-ambient conditions in order to understand structure/property correlations in the solid state is of great interest to single crystal small molecule crystallographers and chemists alike. The ability to access 3-dimensional information under short experimental time frames allow for almost real time results when combined with in-situ techniques. This combination transfers the rate limiting step from the experiment to the data processing. This approach in-turn converts the perception of a "static" single crystal "snap-shot" technique into a pseudo "dynamic" one which can be to a large range of problems and key materials ranging from sensors to pharmaceuticals.

The development of novel instrumentation and methodologies for the study of small crystals, using in-situ single crystal X-ray diffraction techniques both in-house and at synchrotron radiation facilities are presented.

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