Studying mechanical properties by in-house electron and X-ray diffraction

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X-ray and electron diffraction are the prime methods for analyzing and characterizing mechanical properties of crystalline materials. Rigaku offers a range of home laboratory-based diffractometers, that are an excellent match for these very specific challenges. A wide range of mechanical effects in crystals can be explored and thus also a broad range of Rigaku instruments can be employed in their analysis. This presentation will focus on Rigaku's latest developments and ultimate solutions for investigating mechanical effects in crystals.

The SmartLab series general diffractometer can determine the exact orientation of single crystalline and quasi-crystalline multilayer materials. Furthermore, the pol figure can be analyzed, residual stress and lattice strains be determined, and a wide variety of temperature stages allows for investigating temperature-dependent phase changes.

The XtaLAB Synergy-S/R Series instruments allow for the structure determination of crystals in the micrometer scale. A special focus with respect to mechanical properties lies in the elucidation of high-pressure phases. High-pressure crystallography is nicely supported by the instrument's hard- and software layout.

The XtaLAB Synergy-ED electron diffractometer on the other hand allows for structure determination of crystallites in the nanometer scale. Unprecedented structures are elucidated from extremely small crystals within only few minutes, opening the way to a completely new realm of crystallography. One special application of electron diffraction is the probing of macroscopically bent crystals and subsequent determination of the local structure.

SmartLab, XtaLAB Synergy-R and Synergy-ED

Understanding the Mechanisms Bending in Flexible Crystals

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A crystal is normally thought of as *a homogenous solid formed by a periodically repeating, three-dimensional pattern of atoms, ions, or molecules.* Indeed, the regular arrangement of molecules, in a single crystal lead to many useful characteristics (in addition to diffraction!) including unique optical and electrical properties, however, molecular crystals are not typically mechanically robust, particularly compared to crystals of network solids like diamond. Upon the application of stress or strain, these crystals generally irreversibly deform, crack or break resulting in the loss of single crystallinity.

We have recently discovered a class of crystalline compounds that display the intriguing property of elastic flexibility – that is they are capable of reversibly bending without deforming, cracking or losing crystallinity. A number of these crystals are flexible enough to be tied into a knot! (See Figure 1). We have developed a unique approach to determine the atomic-scale mechanism that allows the bending to occur which employs mapping changes in crystal structure using micro-focused synchrotron radiation. We have applied this technique to understand the deformation in both elastically[1] and plastically[2] flexible crystals. Most recently we have used it to show that previous theories regarding the requirement of "interlocked" crystal packing for flexibility is incorrect.

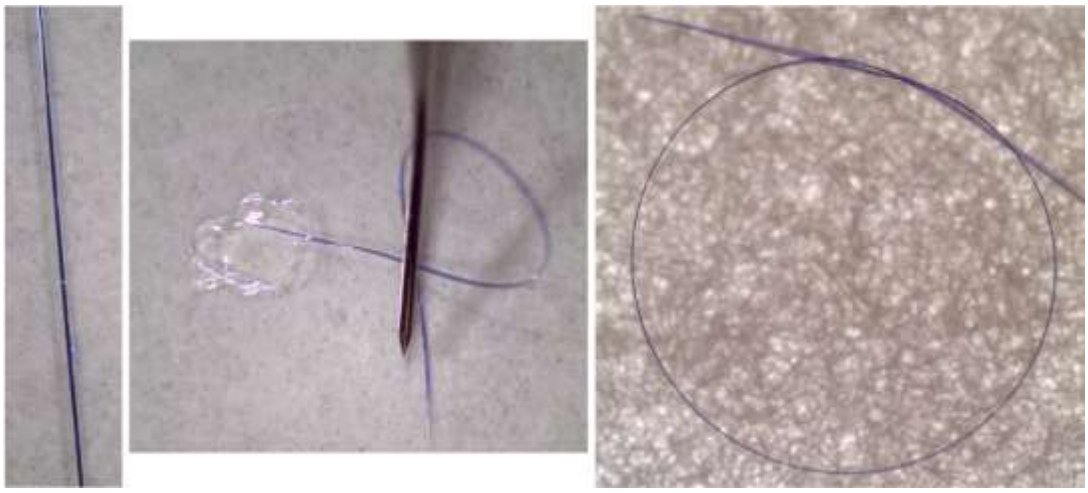

Figure 1: A crystal of [$Cu(acac)_2$] showing elastic flexibility.

[1] A. Worthy, A. Grosjean, M. Pfrunder, Y. Xu, C. Yan, G. Edwards, J. K. Clegg and J. C. McMurtrie, "Atomic Resolution of Structural Changes in Elastic Crystals of Copper(II) acetylacetonate", *Nature Chemistry*, **2018**, 65-69.

[2] S. Bhandary, A. J. Thompson, J. C. McMurtrie, J. K. Clegg, P. Ghosh, S. R. N. K. Mangalampalli, S. Takamizawa, and D. Chopra, "The mechanism of bending in a plastically flexible crystal." *Chem. Commun.*, **2020**, 12841-12844.

Challenging Structure Determination on Deformed Crystals - How Modern X-ray Instrumentation can Help

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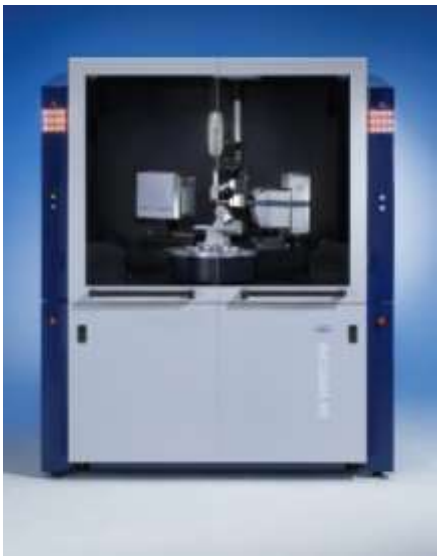
Although new methods, such as cryo-EM and electron diffraction, expand the spectrum of methods for 3-D structure investigations, in house X-ray diffraction remains the gold standard for obtaining precise models within reasonable time and efforts. Large research facilities like synchrotron beam lines or neutron diffraction beam lines require more effort to operate on the on hand, on the other hand, such facilities are adding valuable information either by improving the model quality or enabling the investigation of a particular sample at all. However, it should be noted that the majority of large research facilities are running an in-house system in parallel to pre-check samples or to compare the results obtained from the different diffraction methods. Highly integrated platforms such as Bruker's D8 QUEST and D8 VENTURE are offer many advantages compared to large research facilities. For example, in-house instrumentation is available 24/7 and allows even non-specialists to work effectively on today's ever more complex crystallographic targets. At the same time these platforms provide experts with an assortment of tools to collect the best possible data for dedicated investigations. New features in both automation hardware and software design have emerged and are at the scientist's service for challenging projects. Instant access, often with fewer time restrictions are another important point to mention in advantage of in-house solution.

The presentation will start on key components, such as the goniometer, the IμS DIAMOND and the METALJET D2 PLUS X-ray sources and the PHOTON III detectors. We will discuss key features of these X-ray components and demonstrate along the D8 VENTURE platform how they are integrated into a complete high-performance system. We will show how the latest software advances in APEX and PROTEUM make data collection more efficient and also provide newly added features. Using selected application examples we will demonstrate the integration of accessories, such for high pressure research or automated sample handling.



D8 VENTURE X-ray diffraction solution featuring two IμS 3.0 microfocus sources and a PHOTON III 14 detector.

Density Functional Theory Predictions of the Mechanical Properties of Molecular Crystals

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The mechanical properties of crystalline materials are crucial knowledge for their screening, design, and exploitation. Density functional theory (DFT) is one of the most effective computational tools for quantitatively predicting and rationalising the mechanical response of these materials. DFT predictions have been shown to quantitatively correlate to a number of experimental techniques, such as nanoindentation, high-pressure X-ray crystallography, impedance spectroscopy, and spectroscopic ellipsometry. Not only can bulk mechanical properties be derived from DFT calculations, this computational methodology allows for a full understanding of the elastic anisotropy in complex crystalline systems. This talk will take the audience through practical use of DFT methodologies using the Vienna Ab-Initio Software Package (VASP) for predicting and engineering the mechanical properties of molecular crystals. The successes and limitations of DFT methods and softwares for predicting mechanical properties and effects in molecular crystals will be discussed. The purpose of the lecture will be to highlight the diverse range of tools that are available to compute and analyse mechanical properties and effects. This lecture will also cover methods for computational screening of functional molecular crystal properties such as piezoelectricity, ferroelectricity, plasticity, flexibility, twisting, shape-memory and more

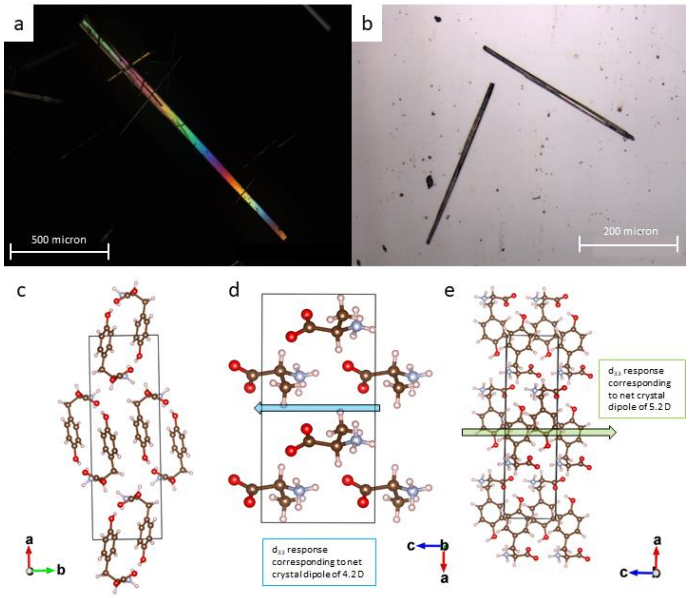

Figure 1: DFT calculations can be used to rationalise and engineer the electromechanical properties of organic crystals for eco-friendly sensing applications. Image taken from *Atomistic-benchmarking towards a protocol development for rapid quantitative metrology of piezoelectric biomolecular materials.* Applied Materials Today, 2020, 21, 100818.

Satellite meeting: Mechanical properties and phenomena in crystals

Microstructure evaluation at a glance using reciprocal space reconstructions

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Bragg peaks' analysis came a long way since these sharp intensities were first observed in single-crystal diffraction experiments. Indeed, modern crystallographic programs are well-optimized for recognizing, fitting, integrating, and correcting Bragg reflections to give us the best list of intensities for average structure refinements. But is this everything we need to know about our crystals?

When we use crystallography for structure determination of molecules or macromolecules, crystals should be generally as periodic as possible to have nicely shaped and sharp Bragg peaks and afford the most reliable crystal structures. However, when we analyze materials, non-ideal shapes of Bragg reflections and presence of broad diffuse intensities are not just a nuisance for intensities integration, but most importantly a unique opportunity to decipher the real structure of the material under study.

Ideally, total scattering analyses such as diffuse scattering simulations[1] or 3D difference pair distribution function fitting[2] provide precise information on how the real structure deviates from the average due to correlated defects and disorder, but these techniques are quite complex and still at an early stage of automation and transferability. Nevertheless, qualitatively assessing patterns from single-crystal data and learning something useful about the microstructural features of the sample is still possible, and with rather little efforts. In this contribution I will show how a general assessment on these features can be done by any crystallographer, simply based on the presence of characteristic features in reciprocal space reconstructions from single-crystal diffraction data.

1. Welberry, T. R. & Weber, T. One hundred years of diffuse scattering. *Crystallography Reviews* vol. 22 2–78 (2016).
2. Weber, T. & Simonov, A. The three-dimensional pair distribution function analysis of disordered single crystals: basic concepts. *Zeitschrift für Kristallographie* **227**, 238–247 (2012).