In our previous studies of binding properties and conformational adaptability of a known nitrate/sulfate receptor *N*,*N*'-3-azapentane-1,5-bis[3-(1-aminoethylidene)-6-methyl-3*H*-pyran-2,4-dione] (**L**) [4] toward various charge-dispersed monoanions (HSO_3^-, ClO_4^-, IO_4^-, PF_6^- and SbF_6^-) we have shown that **L** is able to discriminate anions on the basis of their charge density.

Herein we present two structures whit the same anion, SCN^-, achieves two different complexes with **L**, thus displaying versatile binding nature of this podand. Geometry and (hydrogen-bonding) acceptor properties of SCN^- allow two distinct binding modes. When anion uses a sulfur atom as an acceptor, all strong hydrogen bond donors of the podand become coordinatively saturated by interactions with the oxo-functionalities from neighboring podands, so the only weaker C−H groups are accessible for anion binding. On the other hand, when anion uses nitrogen atom as a hydrogen-bonding acceptor then podand uses its N−H groups to accomplish optimal binding.

[1] J.W. Steed, , *Chem. Commun.* **2006**, 2637. [2] P.D. Beer, *Acc. Chem. Res.* **1998**, *31*, 71–80; H. Miyaji, J.L. Sessler, *Angew. Chem. Int. Ed.* **2001**, *40*, 154–157; *Angew. Chem.* **2001**, *113*, 158–161 [3] G.M.J. Schmidt, *Pure Appl. Chem.* **1971**, *27*, 647–678; G.R. Desiraju, *Angew. Chem., Int. Ed.* **2007**, *46*, 8342–8356; C.B. Aakeröy, *Acta Crystallogr., Sect. B*, **1997**, *53*, 569–586. D.–K. Bučar, G.S. Papaefstathiou, T. D. Hamilton, Q.L. Chu, I.G. Georgiev, L.R. Macgillivray, *Eur. J. Inorg. Chem.* **2007**, 4559–4568. [4] K. Užarević, I. Đilović, D. Matković-Čalogović, D. Šišak, M. Cindrić, *Angew. Chem. Int. Ed.*, **2008**, *47*, 7022−7025.

Keywords: anion receptors, podans, binding modes

MS74.P01

Recent Advances in Two-dimensional X-ray Diffraction

Bob He, *Bruker AXS, Madison, WI, (USA).* E-mail: bob.he@bruker-axs.com.

The two most important developments in two-dimensional x-ray diffraction are area detectors and algorithms in analyzing 2D diffraction patterns [1]. Recent advances in area detectors, particularly the one based on the MikroGap technology, and the diffraction vector approach in 2D data analysis are discussed with experimental examples in phase identification, stress measurement, texture analysis and grain size determination.

The VÅNTEC-500 area detector, based on proprietary MikroGap technology, achieves high resolution and low detector noise with a very high dynamic range by combining the advantages of a gaseous detector with the new resistive anode micro-design. It is designed and optimized for the two-dimensional x-ray diffraction system for analytical applications in various materials research, such as nanotechnology, thin films, polymers, metals, biomaterials, forensics, and process control. The detector features a large active area and a tapered geometry which makes it possible to capture diffraction patterns in a large solid angle and to access high diffraction angles.

Two-dimensional diffraction pattern contains information in a large solid angle. The 2D image can be described by the diffraction intensity distribution in both 2θ and γ directions. Unit diffraction vector is used in the data analysis of the 2D diffraction pattern. The unit diffraction vector for all the pixels in the 2D pattern can be calculated in the laboratory coordinates. The data analysis requires the unit diffraction vector to be expressed in the sample coordinates, which can be obtained by vector transformation. The the unit vector in the sample coordinates for Eulerian geometry are given by its three components $\{h_1, h_2, h_3\}$:

$$h_1 = \sin\theta\,(\sin\phi\,\sin\psi\,\sin\omega + \cos\phi\,\cos\omega) + \cos\theta\,\cos\gamma\,\sin\phi\,\cos\psi$$
$$- \cos\theta\,\sin\gamma\,(\sin\phi\,\sin\psi\,\cos\omega - \cos\phi\,\sin\omega)$$

$$h_2 = -\sin\theta\,(\cos\phi\,\sin\psi\,\sin\omega - \sin\phi\,\cos\omega) - \cos\theta\,\cos\gamma\,\cos\phi\,\cos\psi$$
$$+ \cos\theta\,\sin\gamma\,(\cos\phi\,\sin\psi\,\cos\omega + \sin\phi\,\sin\omega)$$

$$h_3 = \sin\theta\,\cos\psi\,\sin\omega - \cos\theta\,\sin\gamma\,\cos\psi\,\cos\omega - \cos\theta\,\cos\gamma\,\sin\psi$$

The three components can then be used to derive fundametal eauation for many applications or data corrections. The fundamental equation for stress analysis, for instance, is given by the scalar product of the strain tensor ε_{ij} with the unit vector components $\{h_1, h_2, h_3\}$:

$$\varepsilon_{(\gamma,\omega,\psi,\phi)}^{\{hkl\}} = \varepsilon_j \cdot h_i \cdot h_j$$

where $\varepsilon_{(\gamma,\omega,\psi,\phi)}^{\{hkl\}}$ is the measured strain at the Eulerian angles ω, ψ and φ, and on the portion of the diffraction ring given by γ.

For texture analysis, the pole figure angles (α,β) are given by pole mapping equations:

The diffraction unit vector is also used in polarization correction, absorption correction and effective volume calculation for crystal size evaluation by γ-profile analysis.

[1] B. He, *Two-dimensional X-ray Diffraction*, John Wiley & Sons, *2009*.

Keywords: area detector, stress, texture

MS74.P02

Nullification of extinction effects in XRD analysis

I. Tomov, S. Vassilev, *Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 109, Sofia 1113, (Bulgaria).* E-mail: iv_tomov@yahoo.co.uk.

Based on the different behaviour of the empirical extinction coefficient k [1] and the secondary extinction (SE) coefficient g [2] with respect to the levels of interaction of the diffraction process, the present study outlines a pioneer approach to *analytical* nullification of the SE effects. Both the incident-beam intensity I_0 and the pole density P that represent the relative volume fraction of crystallites contributing to reflection define the variation of the levels of interaction of the diffraction process. Accounting for crystal and textural anisotropy, we have shown that the above coefficients are interconnected by $k=2g\mu/PI_0S$ or $g=PI_0S/2k\mu$ and depend on all the parameters describing the diffraction process of a reflection, excluding only the reflectivity Q. Here, S is the cross-section of the beam, and μ is the linear absorption coefficient. Whereas g is proportional to the product PI_0, the coefficient k is proportional to the g/PI_0 ratio. Therefore, by virtue of the *interdependence* between g and PI_0, any change of P or I_0 or both does not change the ratio g/PI_0 and, hence, k is constant that is independent of the level of interaction. For a pair of levels of interaction defined by variation of incident beam intensities from $I_{0,i}$ to $I_{0,i*}$, one can show that $k_i=k_{i*}$, where i and $i*$ denote a generator current values causing the respective I_0 intensity values that are related by $I_{0,i}/I_{0,i*}=i/i*=R_{i,i*}$. Here, $R_{i,i*}$ is the ratio between the generator current values. The equality $k_i=k_{i*}$ allows analytical nullifying the SE effects by using two expressions of k defined by the intensities of a reflection measured at a series of levels of interaction. The procedure for applying this approach starts with kinematic definition of the parameter (R or P) under study, and finishes with derivation of an operative formula for determining its extinction-free value. For the purposes of comparison, the extinction-affected pole density P_m is expressed using intensities measured at the same reflection of textured sample and powder standard. The object of this study was a nickel sample representing a moderate texture with <100> preferred orientation. The results show that whereas the extinction-free values

of P are invariable, the extinction-affected P_m values suffer systematic percentage errors that vary between over 6% for the highest level of interaction and less than 1% for the lowest one. The main advantage of this approach is the gain in accuracy and, hence, physical reality of the data. Another advantage is that it allows for the capability of internal experimental checks without reference to any theoretical estimates. Indeed, the degree of approximation of the $R_{i,i*}$ value to the absolute value of the $i/i*$ ratio qualifies the capability of the XRD apparatus to acquire precise and accurate data.

[1] W.L. Bragg, R.W. James, C.H. Bosanque, *Phyl. Mag.* **1921,** *42*, 1-17. [2] C.G. Darwin, *Phil. Mag.* **1922,** *43*, 800-829.

MS74.P03

Microstructural characterization of polycrystalline materials using a X-ray single-crystal diffractometer equipped with an area detector

Alejandro B. Rodríguez-Navarro, Pedro Alvarez-Lloret, *Departamento de Mineralogía y Petrología, Universidad de Granada, Granada (Spain).* E-mail: anava@ugr.es

Two-dimensional (2D) diffraction patterns collected with an X-ray area detector (i.e., CDD, Image plate), available in modern X-ray single-crystal diffractometer (i.e., SMART APEX, Bruker, Germany), contain much more information than conventional linear scans (i.e., θ-2θ scan), collected using standard X-ray powder diffractometers equipped with a point detector [1]. For instance, depending on sample microstructural characteristics (grain size, crystallinity, preferential orientation, stress, etc.), Debye-Scherrer rings displayed in the 2D pattern might be continuous, spotty or display specific variation in the intensities along them. These features facilitate to differentiate among mineral phases that might be present in a sample and posibilite to extract useful information regarding their microstructural characteristics (grain size, preferred orientation of mineral grains). To facilitate the analysis of these patterns, we have developed a software tool (XRD2Dscan).

This software allows users to take full advantage of diffractometers equiped with an area detector but that can not readily process the information of diffraction patterns from polycrystalline materials. It has many capabilities for generating different types of scans (2Theta scan, Chi scan, d-spacing versus Chi angle, pole figures) which allows users to extract the maximum information from 2D patterns and use their single-crystal diffractometer as an advanced materials research equipment [2]. It also has a database with main crystalline phases for fast mineral identication. The benefits of using area detectors as applied to polycrystalline sample characterization will be illustrated through several examples. Specifically, we will show how crystal sizes can be calculated from the intensity profile of spotty diffraction rings produced by a polycrystalline sample (i.e., quartz, SiC and α-Al$_2$O$_3$).

This technique is complementary to X-ray line-broadening analyses (e.g. Scherrer method) and size range that can be determined is from 3 to 100 microns. On the other hand, we will show how to determine pole figures describing the 3D orientation of crystals in a textured polycrystalline material. In particular, we apply this methodology to study the crystallographic properties (epitaxy, twinning) of different biomaterials such as mollusk shells which are constituted by superimposed layers of calcium carbonate (calcite or aragonite) crystals arranged in highly organized and complex shell microstructures.

[1] A.B. Rodríguez Navarro, *J. Appl. Cryst.* **2006**, *39*, 905-909. [2] C. Rodríguez Navarro, E. Ruiz Agudo, A. Luque, A.B. Rodríguez Navarro, M. Ortega Huertas, *Am. Mineral.* **2009**, *94*, 578-593.

MS74.P04

To Deuterate or not? That is the question

Paul Henry, *ESS AB, Lund, (Sweden).* E-mail: paul.henry@esss.se

Accepted wisdom when performing diffraction experiments with neutrons is, wherever possible, to deuterate the sample as collecting data from the hydrogenous analogue is complicated by the large incoherent scattering background contribution from hydrogen. Recent work has shown that high-flux, medium-resolution continuous wavelength (CW) instruments can overcome this background problem. [1-5] Here, I present the case for not deuterating small-molecule inorganics and organics as, with proper optimisation procedures for the instrument set-up, data collection strategy and correction techniques, it is possible to investigate a wide range of systems.

Specific focus will be given to the ongoing project to re-determine σ_H incoherent as a function of incident neutron wavelength. The lack of an in-depth study to accurately quantify its variation with wavelength is surprising as it is the largest contributing factor to the absorption coefficient that is used in both single-crystal and powder neutron diffraction experiments to calculate the optimal absorption correction and sample size for hydrogen containing compounds.

The practical effect is that the attenuation of the neutron beam (both incident and scattered) by the sample changes as a function of neutron wavelength and path length through the sample, with striking implications for quantitative analysis of time-of-flight (t-o-f) neutron data. The aim is to collect the necessary information to implement an empirical correction routine for CW and t-o-f data as a function of wavelength in the thermal neutron range. This correction would allow a significant number of users to perform routine data collections on hydrogenous materials without the need for deuteration (and the often observed changes in properties upon deuteration) impacting directly research in technologically important fields such as proton conductors, fuel cells and pharmaceuticals.

[1] M.T. Weller, P.F. Henry, V.P. Ting, C.C. Wilson. *Chem. Commun.* **2009**, 2973-2989. [2] P.F. Henry, M.T. Weller, C.C. Wilson. *J. Appl. Cryst.* **2009**, *42(6),* 1176-1188. [3] V.P. Ting, P.F. Henry, M. Schmidtmann, C.C. Wilson, M.T. Weller. *Chem. Commun.* **2009**, 7527-7529. [4] V.P. Ting, P.F. Henry, H. Kohlmann, C.C. Wilson, M.T. Weller. *Phys. Chem. Chem. Phys.* **2010**, *12(9),* 2083-2088. [5] V.P. Ting, M. Schmidtmann, P.F. Henry, S.E. Dann, C.C. Wilson, M.T. Weller. *Med. Chem. Commun.* **2010**, *1(5),* 345-348.

MS74.P05

Determining single-crystal elastic constants from neutron powder diffraction

JianFeng Zhang,[a] Erich H. Kisi,[a] Christopher J. Howard,[a] Oliver Kirstein,[b] *[a]School of Engineering, University of Newcastle, NSW 2308, (Australia). [b]The Bragg Institute, ANSTO, Locked Bag 2001, Kirrawee DC, NSW 2232, (Australia).* E-mail: jian.zhang@uon.edu.au