

samples, both Cu<sup>+</sup> and Cu<sup>2+</sup> were detected, both incorporated in the glass matrix, the second one being responsible for the colour of the artefacts.

**Keywords:** archaeometry, glass, EXAFS

#### MS58.28.5

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##### Maya Blue: a Long Lasting Mystery Revealed

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The composition of Maya Blue, one of the most important pigments in antiquity, has puzzled scientists for decades. Recent studies using different analytical techniques including synchrotron and neutron powder diffraction, proved that the pigment is a combination of palygorskite (characterized by large channels), and the organic dye indigo.

Pigment preparation was repeated successfully and is easy (mix clay and dye and heat at ~100°C for a few hours). Chemical modelling showed indigo fitting the channels without impediment, thus it was assumed that indigo would fully or partially occupy the channels. However, energy calculations and thermal analyses showed indigo cannot penetrate into channels, since the water present does not leave the channels at synthesis temperature and strong H-bonds formed by the first molecule in the channels need to be broken.

A new concept of Maya Blue structure is presented, based on the fact that indigo only fill the grooves present at the crystal's surface. These grooves, which can be thought of as half channels split along cleavage planes, can equally well accommodate the dye molecule, forming one or two H-bonds explaining the stability and colour of the complex. A possible line of study to determine the provenance of Maya Blue is based on mutual abundance of the monoclinic and orthorhombic polymorph of palygorskite, determined via Rietveld refinement. . On the basis of the new theory all the facts previously hard to explain, become comprehensible.

**Keywords:** maya blue structure, palygorskite, synchrotron and neutron powder diffraction

#### MS59 APPLICATIONS OF SYNCHROTRON AND NEUTRON FACILITIES IN STRUCTURAL CHEMISTRY

**Chairpersons:** Paul Raithby, Trevor Forsyth

#### MS59.28.1

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##### Microcrystal X-ray Diffraction and MAS NMR Studies of Zeolites

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Zeolites are notoriously difficult to prepare as large single crystals. Until the last decade we have had to rely on powder diffraction as our major tool for determining their structure. With the advent of single crystal X-ray diffraction as a standard tool at synchrotron sources this limitation has been somewhat reduced. In this presentation I will discuss some of our recent work on studying the structure and properties of zeolites using the single crystal X-ray diffraction station at the Synchrotron Radiation Source, Daresbury, UK.

Not only have new structures been solved using this facility, but we have also shown how the details of previous powder X-ray diffraction work have sometimes been incorrect. In addition, the facility has also allowed us to crystallographically study the thermal properties of zeolites, such as negative thermal expansion, in more detail than was previously possible.

I will also explain how solid state MAS NMR studies can be used to improve the accuracy of our crystallographic models, and I will discuss the possibilities for solving structures from NMR data.

**Keywords:** zeolites, microcrystal diffraction, NMR

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##### Combined X-ray and Neutron Charge Density Studies on C-H activation catalysts

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The new single crystal diffractometer RESI (*RE*ciprocal Space Investigator) at the new high-flux neutron source FRM-II (www.frm2.tum.de) has been optimized for the demands of combined X-ray and neutron charge density studies (high resolution data at low backgrounds) by employing an X-ray and neutron sensitive imaging plate detector, a flexible  $\kappa$ -goniometer geometry and a focusing neutron guide for thermal neutrons. The new diffractometer concept will be outlined, and the advantage of combined X-ray and neutron charge density studies illustrated by first applications in the field of catalyzed C-H activation. We will demonstrate that so-called 'ligand-induced charge concentrations' in the valence shell of main group and transition metal complexes (*i*) can be identified by experimental charge density studies; and (*ii*) act as controlling parameters in C-H activation processes.[1,2] Systematic experimental studies of molecular charge distributions will thus lead to significant advances in the design and chemical control of catalysts for C-H activation and other processes, with central relevance to many reactions of academic and commercial importance.

[1] Scherer W., McGrady G.S., *Angew. Chem. Int. Ed.*, 2004, **43**, 1782. [2] Scherer W., Sirsch P., Shorokhov D., Tafipolsky M., McGrady G.S., Gullo E., *Chem. Eur. J.*, 2003, **9**, 6057.

**Keywords:** electron density, neutron diffraction, agostic interactions

#### MS59.28.3

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##### Structure and Dynamics of Co-ordination Compounds by Neutron Scattering

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The importance of transition metal hydrido-complexes, both classical and non-classical (i.e. compounds containing the M-H or M-H<sub>2</sub> moieties) in catalytic reactions, in particular hydrogenations, is well known, and much work has been carried out in recent years to obtain a detailed understanding of the nature and reactivity of the M-H and M-H<sub>2</sub> moieties.

Single crystal neutron diffraction, at low temperature, has been instrumental in establishing the correct co-ordination geometry in non-classical hydrides. It has been established that the H-H separation can cover a wide range of distances, from ~ 0.8 Å (strong H-H bond) to ~ 1.4 Å (weak H-H bond), corresponding to various degree of the H-H activation, thus neatly spanning the oxidative addition pathway and giving support to the mechanistic studies.

However, it is worth noting that a complete description of the reactivity in hydrido-compounds can only be achieved by combining the diffraction results with the knowledge of their dynamics that can be obtained from neutron incoherent inelastic scattering (INS) experiments.

I will discuss some recent structural results on transition metal poly-hydrides and show how, by combining neutron diffraction, INS and DFT calculations, the H<sub>2</sub> dynamics can be explained.

**Keywords:** transition metal hydrides, molecular hydrogen complexes, neutron scattering

#### MS59.28.4

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##### Location of a 4-coordinate H Atom via Neutron Diffraction

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A four-coordinate H atom has been unambiguously located, by single-crystal neutron diffraction for the first time, in the centre of the tetrahedral metal complex  $Y_4H_8(Cp')_4(THF)$  [ $Cp'=C_5Me_4(SiMe_3)$ ]. The core of the molecule consists of a tetranuclear cluster with one interstitial, one face-bridging and six edge-bridging hydride ligands. At the present stage of structural refinement, the four individual Y–H distances to the unique interstitial hydride ligand are 2.184(16), 2.189(16), 2.221(13) and 2.168(12) Å. The compound was prepared via the reaction of  $YCp'(CH_2SiMe_3)_2(THF)$  with  $PhSiH_3$  and gaseous  $H_2$ , and an initial x-ray analysis suggested the present geometry. [1]

The existence of 4-coordinate hydrogen now completes the series of high-connectivity hydride ligands located in the interstitial cavities of molecular cluster complexes. We had previously reported the existence of 6-coordinate H in the octahedral cavity of  $[HCo_6(CO)_{15}]^-$  in 1979, [2] and 5-coordinate H in the square pyramidal cavities of  $[H_2Rh_{13}(CO)_{24}]_3^-$  in 1997, [3] via single-crystal neutron analyses.

[1] Tardif O., Nishiura M., Hou Z., *Organometallics*, 2003, **22**, 1171. [2] Hart D.W., Teller R.G., Wei C.W., Bau R., Longoni G., Campanella S., Chini P., Koetzle T.F., *Angew. Chem. Internat. Edit.*, 1979, **18**, 80. [3] Bau R., Drabnis M.H., Xie Z., Garlaschelli L., Klooster W.T., Koetzle T.F., Martinengo S., *Science*, 1997, **275**, 1099.

**Keywords:** 4-coord-H, neutron-diffraction, interstitial-hydride

#### MS59.28.5

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##### Neutron Cryocrystallography of Proteins

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Neutron diffraction can directly determine the hydrogen isotope positions of a protein and its bound solvent. By collecting the data at cryo-temperatures the quality of the resulting maps can be improved. It has proved possible to cryo-cool very large concanavalin A protein crystals ( $> 1.5 \text{ mm}^3$ ) suitable for high resolution neutron and X-ray structure analysis. We can thereby report the neutron crystal structure of the saccharide-free form of concanavalin A to 2.5 Å resolution [1]. This is the first cryo- neutron protein crystal structure ever to be reported and the first 15K to 293K neutron protein crystal structure comparison. Comparison with the 293K neutron structure [2] shows that the bound water molecules are better ordered and have lower average B-factors than those at room temperature. Overall, twice as many bound waters (as  $D_2O$ ) are identified at 15K than at 293K.

Methodologically, this successful neutron cryo protein structure refinement opens up new categories of neutron protein crystallography, including freeze trapped structures. Other large crystals of proteins have also proved amenable to cryo-cooling and examples of these will be presented too (Blakeley, Meilleur, Myles, Bau *et al* to be published).

[1] Blakeley M.P., Kalb (Gilboa) A.J., Helliwell J.R., Myles D.A.A., *PNAS*, 2004, **101**(47), 16405. [2] Habash J., Raftery J., Nuttall R., Price H.J., Wilkinson C., Kalb (Gilboa) A.J., Helliwell J.R., *Acta Cryst.*, 2000, **D56**, 541.

**Keywords:** cryocrystallography, neutron diffraction, bound solvent structure

#### MS60 MICROSTRUCTURAL PROPERTIES FROM POWDER DIFFRACTION DATA

**Chairpersons:** Davor Balzar, Paolo Scardi

#### MS60.28.1

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##### Subgrain Size-Distributions, Dislocation Structures, Stacking- and Twin Faults and Vacancy Concentrations in Crystalline Materials Determined by X-ray Line Profile Analysis

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X-ray diffraction patterns, especially when measured with high precision, are a detailed fingerprint of the microstructure of crystalline materials. Up to date computer assisted numerical methods enable to describe whole diffraction patterns by physically well established profile functions based on specific microstructural models. Size profiles are modelled by assuming log-normal size-distribution of grains of subgrains. Distortion or strain profiles are based on the dislocation model developed by Wilkens. Stacking- and twin faults are incorporated by the method developed by Treacy *et al.* and are parametrized for the density of intrinsic-, extrinsic and twin faults, respectively. The diffuse background scattering is interpreted in terms of point defects, especially vacancies. It is shown that subgrains can be separated either (i) by tilt- or twist angles produced by geometrically necessary dislocations, or (ii) by dipolar dislocation walls which no tilt or twist between the adjacent subgrains. Both types of subgrain boundaries break down the coherent scattering of X-rays, thus delineate undistorted crystalline regions in terms of X-ray scattering. Stacking- and twin faults are analysed in terms of splitting of dislocations, and are discussed as a function of grain- or subgrain size. Diffuse background scattering or background scattering, which is usually discarded as a disturbing part of diffraction patterns, is discussed in terms of vacancy concentrations within the grain interior and grain boundary regions, respectively. In plastically deformed copper it is shown that, when the deformation and the diffraction measurements are carried out at temperatures lower than the annealing temperatures of vacancies, relatively large vacancy concentrations, of the order of  $10^{-7}$  -  $10^{-6}$  are accumulating within the grain interior regions. More surprisingly, it is found that, within the grain-boundary or subgrain-boundary regions the vacancy concentration values can reach values corresponding to the melting temperature of copper, i.e.  $5 \times 10^{-5}$  -  $10^{-4}$ . The microstructural parameters provided by X-ray line profile analysis will be discussed in specific case studies.

**Keywords:** microstructure, line profile analysis, subgrain size-distribution dislocations

#### MS60.28.2

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##### Microstructural Studies of Nanocrystalline Materials Using WPPM

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Whole Powder Pattern Modelling (WPPM) is a recently proposed and continuously evolving procedure for the microstructural analysis of materials using X-ray powder diffraction [1-4]. The procedure is based on the analysis of the whole information contained in a powder pattern, without relying on an *a-priori* arbitrarily imposed peak profile function. Through the use of WPPM, microstructural features of nanocrystalline materials such as domain size distribution, quantity of line & plane defects can be obtained non destructively in a matter of minutes. Even if it can be used for the analysis of any sample, WPPM performs at best for nanocrystalline materials.

Ball milling is an easy and cost effective technique for the production of nanocrystalline powders. The deformation energy introduced in the powders during the milling causes both a reduction of the domain size and an increase in the defect content, features that can be easily monitored using WPPM. In this contribution, the application of WPPM for the analysis of nanocrystalline materials produced by ball milling will be shown and features/drawbacks with respect to traditional techniques, discussed

[1] Scardi P., Leoni M., *Acta Cryst.*, 2002, **28**, 1293. [2] Scardi P., Leoni M., *Diffraction Analysis of the Microstructure of Materials*, E.J. Mittemeijer & P. Scardi, Springer-Verlag, Berlin, 2004, 51-91. [3] Leoni M., Di Maggio R., Polizzi S., Scardi P., *J. Amer. Ceram. Soc.*, 2004, **87**, 1133-1140. [4] Leoni M., Confente T., Scardi P., *Z. Kristallogr.*, 2005, *in press*.

**Keywords:** line profile analysis, materials characterization using X-rays, in-situ experiments