10 01-Instrumentation and Experimental Techniques (X-rays, Neutrons, Electrons)

PS-01.01.10 COMBINED QEXAFS-XRD, A NEW TECHNIQUE COMBINING *IN-SITU* FAST SCANNING X-RAY ABSORPTION SPECTROSCOPY AND X-RAY DIFFRACTION.

G N Greaves, A J Dent, B R Dobson, S M Clark*, C A Ramsdale, SERC Daresbury Laboratory, Warrington, UK.
G Sankar, P A Wright, S Natarajan, J M Thomas, The Royal Institution, 21Albemarle Street, London, UK.
R H Jones, Department of Chemistry, The University of Keele, Keele, UK.

We have recently demonstrated the value of the combined use of Energy Dispersive X-Ray Absorption Spectroscopy and X-ray Diffraction (XRD) in tracing the *in-situ* conversion of a mineral precursor, aurichalcite (Cu_{5-x} Znx $(OH)_6$ $(CO_3)_2$) through its various intermediate stages to an active (Cu, ZnO) catalyst using a dispersive monochromator. (Couves J W, Thomas J M, Waller D, Jones R H J, Dent A J, Derbyshire G E, Greaves G N, Nature, (1991), *89*, 119). Two detectors were operated in tandem: a photodiode array to record the dispersed transmission XAFS and a curved position sensitive detector to record the angular dispersed Debye-Scherrer patterns. Time-resolved XAFS and XRD pattern were obtained within a few seconds of one another under in-situ conditions. We now report a separate, but related development pioneered at the Synchrotron Radiation Source at Daresbury Laboratory, whereby quick scanning XAFS (QEXAFS) technique (Frahm R, Physica B, (1989), *158*, 342) has been combined with the previous method of XRD detection to collect high quality X-ray spectra at elevated temperatures in a few minutes.

The layout of the experiment is such that the sample is housed in a variable atmosphere high temperature (Linkam) furnace at the centre of a 120° (INEL) position sensitive detector. the XAFS is collected by rotating the Bragg angle of the double crystal monochromator continuously, thereby practically eliminating the deadtime associated with conventional angle-by angle scanning. The rapid slewing rate of the monochromator is then used to collect the XRD at a wavelength away from the edge region.

We have tested the QEXAFS/XRD combination to follow the cause of production of a commercially important example: the ceramic material cordierite, idealised formula $Mg_2Al_4Si_5O_{18}$. We made the chance discovery that cordierite is preparable from Mg^{2+} zeolite B when traces of ZnO are present. We will present data showing from diffraction the zeolite transitions from crystalline to amorphous, then to a transitory ''stuffed quartz'' phase before finally becoming cordierite. The Zn environment was followed by means of the XAFS and it will be shown that the Zn, at least in part, is incorporated into the final product.

PS-01.01.11 SYNCHROTRON RADIATION FOR MICROCRYSTAL STRUCTURE DETERMINATION AND FOR LAUE TIME RESOLVED STUDIES

BM Kariuki, MM Harding*, IM Dodd, GMT Cheetham, Chemistry Department, Liverpool University, Liverpool L69 3BX.

1. Monochromatic synchrotron radiation (wavelength 0.90 A) from the SRS wiggler beamline (Daresbury) and the Enraf-Nonius FAST area detector diffractometer have allowed data collection and structure determination for a number of microcrystals of moderate complexity and different chemical types. Examples include:

a gold cluster, $Au_{10}(PPh_3)_7$..., 10x10x30 μm reference 1
$AlPO_4$-CHA, $Al_3P_3O_{12}F.C_4H_{10}NO$, 35x20x15 μm reference 2
Aurichalcite, $(Zn/Cu)_5(OH)_6(CO_3)_2$, 40x100x5 μm
This is a natural mineral and catalyst precursor[3]; it is monoclinic, a=13.86, b=6.417, c=5.294 A, β =101,0°, space group $P2_1/m$, twinned on $(20\bar{1})$. 410 unique intensities were measured, each of which has two component reflections because of the twinning; the structure was solved and refined to R1=0.07, wR2=0.19 (at present), with SHELXL-92 (our thanks to George Sheldrick). The structure is similar to that of hydroxyzincite[3]. There are four metal sites, two are distorted octahedral (probably Cu), one tetrahedral (probably Zn) and the other trigonal bipyramidal.

2. The SR Laue method with white radiation has allowed complete structure determination for a small crystal of a new organometallic compound, $AuOs_3(CO)_8PPh_3dppm.PF_6$. This includes unit cell determination, and refinement (to R=.075) allowing for the wavelength dependence of the atom scattering factors, and is to be described in a related poster (IM Dodd, Hao Quan, MM Harding).

3. Laue diffraction has great potential for time resolved studies. As a pilot project we have studied the transition (at *ca*67°C) in single crystals of $P_4N_4Cl_8$ from the metastable form containing 'boat' molecules to the stable form containing 'chair' molecules (crystals from Dr K Venkatesan, Bangalore).
The experimental part of the work has been described[4]. Selected results from one series of Laue diffraction photographs show how many reflections can be recorded from each film pack and used in structure refinement:

time/min	0	5	7	9	12	22	32
T/ °C	52	62	67	72	77	87	102
n reflns	234	229	228	318	315	301	276
%boat	79	76	55	43	38	24	12

Analysis of this and other series should allow the effects of time, temperature and crystal variation to be understood better.

1. GMT Cheetham, MM Harding, JL Haggitt, MP Mingos, HR Powell (1993) submitted to JCS Chem Comm.
2. MM Harding, BM Kariuki, LB McCusker, A Simmen (1992) in preparation for Zeolites.
3. JW Couves, JM Thomas, D Waller, RH Jones, AJ Dent, GE Derbyshire, GN Greaves (1991) Nature 354, 465-468.
4. S Ghose (1964) Acta Cryst 17, 1051-1057.
5. PD Carr, GMT Cheetham, MM Harding, RJ Rule (1992) Phase Transitions, 39, 33-43.

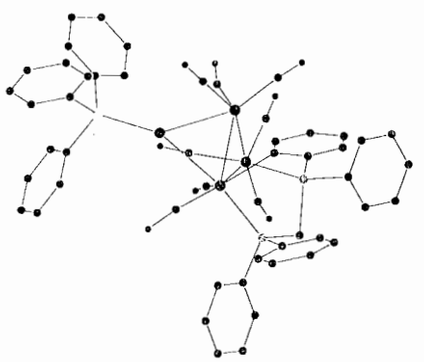
PS-01.01.12 SYNCHROTRON RADIATION DIFFRACTION FOR COMPLETE STRUCTURE DETERMINATION OF A SMALL ORGANOMETALLIC CRYSTAL, $AuOs_3(CO)_8PPh_3dppm.PF_6.0.5C_6H_5Cl$

Ian M Dodd*, Hao Quan, Marjorie M Harding, Chemistry Department, Liverpool University, Liverpool L69 3BX,UK.

For this newly synthesized material[1] only a rather small crystal was available, of dimensions 270x60x40 μm. Laue diffraction photographs were recorded on the wiggler beamline at SERC Daresbury Laboratory, with exposure times <15 s.
For one set of photographs the incident beam was attenuated by a palladium foil (0.1 mm); from these photographs, in which the minimum wavelength is sharply defined by the palladium absorption edge (0.509 A), the unit cell was determined *on an absolute scale*[2,3].
Intensity data were measured from five film packs using the Daresbury Laue software suite[4]. For these film packs the incident beam was attenuated by 0.2 mm Al and 0.114 mm Cu; these shifted the spectral distribution to shorter wavelengths, effectively 0.24-0.7 A, reducing absorption, radiation damage, and background due to air scattering. 12183 individual intensity measurements were were merged to give 7163 unique reflections from which the structure was solved and refined to R=0.12.

Subsequently an absorption correction was applied[5] and the unmerged data was refined using SHELXL-92 (for which we are most grateful to Prof George Sheldrick). In the Laue method, different reflections are measured at different wavelengths; the anomalous scattering factors, f′ and f", and therefore the structure factors, vary with wavelength, and this variation can be substantial for heavy atoms. SHELXL-92 can allow for this variation, and refinement has given R1=0.075.

1. A K Smith and J Mathews, Liverpool University.
2. P D Carr, D W J Cruickshank, M M Harding (1992) J Appl Cryst 25, 294-308.
3. I M Dodd, P D Carr, M M Harding (1993) J Appl Cryst 26, in the press.
4. J R Helliwell et al, (1989) J Appl Cryst B24, 340-348.
5. S J Maginn, M M Harding and J W Campbell (1993) Acta Cryst B49, in the press.



01.02 – Synchrotron Data Collection for Macromolecules

MS-01.02.01 MACROMOLECULAR CRYSTALLOGRAPHY AT LURE: INSTRUMENTATION FOR X-RAY DIFFRACTION DATA COLLECTION AND RESULTS. by R. Fourme*, R. Kahn, W. Shepard and A. Beniley, LURE, Bat. 209D, Universite Paris-Sud, 91405 Orsay, France

The X-ray sources available at LURE using the positron storage ring DCI are generated from bending magnets (critical wavelength λ_c=3.4A) and from a 5-pole wiggler (λ_c= 1.1A). Synchrotron radiation is provided 90 hours per week, for 31 weeks of the year. The ring is refilled only every 2 days since the decay time of the beam is 4-5 days. Such characteristics are favorable for uninterruped and accurate diffraction data collection. A total of five stations (including W11 and W32 on the wiggler line) will soon be available for macromolecular crystallography. Two of these are full-time stations, while the other stations are 50% shared with other disciplines.
The station W11, in the process of being assembled, is a setup for unfocussed Laue data collection. It will be equipped with a large imaging plate, as well as films, W32, our work horse for monochromatic data collection, has been running successfully since 1991. It features double focussing optics (two elliptically curved reflectors, a crystal and a multilayer) and a Hendrix-Lenfer imaging plate scanner with an off -axis translation. Exposure times with X-rays from a Ge(111) crystal (λ=1.5A) are 1-30s/deg and 8-240 s/deg from a Si(111) crystal (λ= 0.9A). This station will soon be upgraded by increasing the diameter of the imaging plate from 18cm to 32cm. The smaller imaging plate will then be transferred to the part-time D43 station, which is equipped with a curved crystal monochromator.
For high precision data collections, large spherical drift MWPCs (in collaboration with G. Charpak's team, CERN) have been installed on the stations D23 and D41. The detector on D23 has been routinely used since 1988, and is associated with a sagittal focusing two-crystal monochromator for mutiple wavelength experiments. The detector on D41, an improved model with a higher spatial resolution, allows for data collection of crystals with larger unit cells. This station is equipped with a single bent crystal monochromator and is close to completion.
Selected results obtained by various user groups will be discussed, with emphasis on high resolution, large unit cells, MAD data collection and diffuse scattering measurements. The data quality obtained from MWPCs and imaging plate detectors will be compared.