8 01-Instrumentation and Experimental Techniques (X-rays, Neutrons, Electrons)

01.01 – Time Resolved Structural Studies

MS-01.01.01 TIME–RESOLVED STRUCTURAL STUDIES. By J.R. Helliwell, Department of Chemistry, University of Manchester, Manchester, M13 9PL, U.K.

Synchrotron radiation has considerably reduced the time taken to record data in; for example, X–ray crystallography, fibre diffraction, EXAFS, and powder diffraction. It has become more generally feasible therefore to perform time–resolved studies of molecules either of biological interest (e.g. enzymes and muscle) or in materials science during chemical reactions. An introduction to this topic will be given to open this microsymposium, which is organised under the auspices of the Commission on Synchrotron Radiation. A comparison will then be made of the currently available single crystal methods, particularly concerning exposure times and the elapsed times in acquiring a data set. This work shows that, even in X–ray crystallography of biological macromolecules, data sets can be rapidly recorded whilst of good quality and completeness.

MS-01.01.02 THE USE OF SYNCHROTRON RADIATION INSTRUMENTATION FOR TIME RESOLVED STRUCTURAL STUDIES: MUSCLE DIFFRACTION. By J. Bordas, N. Bliss, G. Diakun, C. Hall, J. Harries, R. Lewis, G. Mant, M. Martin-Fernandez, A. Svensson and E. Towns-Andrews*, SERC, Daresbury Laboratory, Warrington, U. K.

In recent years it has become evident that synchrotron radiation is essential for dynamical studies of biological structures. Biological specimens are inherently weak scatterers and hence time resolved measurements on systems of this type pose great demands on the experimental station design (e.g. station optics, data acquisition and detection systems). We are now able to collect two dimensional x-ray data in the millisecond time regime. Some data will be presented from time resolved diffraction studies of frog sartorius muscle. Experimental results and technical difficulties associated with such measurements, along with new instrumentation design, targeted specifically towards experiments of this nature, will be discussed. The layout of station 16.1, a high intensity fixed wavelength diffraction station at the SRS will be presented. This station will provide an increased x-ray flux at the specimen , approximately five times that of the existing time resolved diffraction station at the SRS. This will enable sub-millisecond data to be obtained and hence the possibility of following structural changes in biological systems in real time.

MS-01.01.03 TIME-RESOLVED X-RAY ABSORPTION SPECTROSCOPY by A.Fontaine.LURE (CNRS-CEA-MENC), Bât 209d F91405 Orsay -Cedex

X-ray Absorption Spectroscopy has proved to be a powerful tool to elucidate number of questions in materials science. Great interest exists in time-resolved experiments achieved with extreme energy resolution to take a full benefit of the strong correlation between the stereochemical environment of the absorbing atom and the exact shape and position of the absorption edge of the core levels. Time-resolved experiments based on XAFS invole generally mass transportation which means relatively slow processes. Selected experiments in electrochemistry are presented and different options to improve the time-resolution are rewieved.

Fast energy dispersive X-ray spectroscopy allows in-situ observations with data collected in a short time. A great benefit is expected from the forthcoming storage ring (ESRF) which should be able to give flux larger by at least 3 orders of magnitude. It is no longer possible to use the dispersive geometry to study samples at concentrations of about 100 µmol.They require a scanning monochromator, detecting the fluorescent decay. Related to this field are the quick-Exafs spectrometers developed initially at Hamburg under R.Frahm and at LURE under P.Lagarde, C.Prietto, H.Dexpert et M.Verdaguer which have been able in these three last years to open new routes in a wide variety of science. But the very first experiment to look for any kind of time-resolved X-ray Absorption Spectroscopy dealt with a stroboscopic approach.

MS-01.01.04 *IN SITU* DIFFRACTION EXPERIMENTS: RECENT ADVANCES AND RESULTS. By W. Depmeier, Inst. f. Mineralogie, Universität Kiel, D-W 2300 Kiel, Germany.

The scientific purpose of our group's *in situ* diffraction experiments is to follow structural changes of a given compound, observed by the changes of the corresponding diffraction pattern as a function of temperature, pressure, electron transfer rate, etc. The variables may be altered alone, or in combination. In pursuit of this idea our group has developed and built various sample environments for x-ray and neutron diffraction, and continues to do so. Such devices include

- a heatable high pressure cell for neutron powder diffraction (K. Fütterer)
- a microfurnace for use within a closed-cycle cryorefrigerator, allowing x-ray Guinier diffractometry at temperatures between 12 and, hopefully, 700 K (G. Hermeler)
- a heatable electrochemical reaction cell for *in situ* intercalation studies (H. Katzke).

The names in parentheses indicate the principal responsible scientist. Plans exist to further improve the instruments and to broaden the range of accessible variables.
Descriptions of the various sample environments will be presented and experiences discussed. Recent examples of results of our experiments will also be given. Materials studied include

- Li intercalated V_2O_5
- an ionic superconducting halide perovskite
- aluminate sodalites
- silica sodalites
- clathrasils.

MS-01.01.05A NEW TYPE OF DIFFRACTOMETER FOR QUICK DATA COLLECTION By Y. Ohashi,* H. Uekusa, A. Sekine and Y. Takenaka, Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan and T. Higashi and T. Sato, RIGAKU Corporation, Akishima, Tokyo 196, Japan

We found that the chiral alkyl group bonded to the cobalt atom in some cobaloxime complex crystals was racemized by X-ray or visible light without degradation of the crystallinity (Ohashi, *Acc. Chem. Res.*, 1988, **21**, 268-274). When the reactive alkyl group was replaced with more bulkier groups, the structural changes were so fast that the three-

dimensional intensity data were unable to be collected with an usual four-circle diffractometer. This indicates that if the data collection may be performed more quickly, a wide variety of reactions would be made clear on the basis of the structure analysis. We have designed and constructed a new type of diffractometer, which is composed of a κ-type goniometer, a no-screen type Weissenberg camera with two imaging plates as detectors and a reader for the imaging plate with a laser. The crystal is mounted on a κ-type goniometer and is aligned automatically by two still photographs. Then the three-dimensional intensity data were collected within an hour with the Weissenberg camera using two imaging plates alternately for recording and reading the data. All the operations are computer-controlled. Some examples showing the dynamical structural changes have been obtained using the new diffractometer.

MS-01.01.06 SUB-NANOSECOND TIME RESOLUTION IN LAUE DIFFRACTION USING A THIRD GENERATION SYNCHROTRON

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The high brilliance of third generation synchrotrons will make it possible to shorten the exposure time in diffraction measurements by a factor ~ 10^2-10^4 compared to existing SR sources. Of particular interest for time resolved crystallography is the Laue method which makes optimal use of the polychromatic synchrotron spectrum and permits the recording of near complete data sets in a single shot for high symmetry crystals.

We present here the design of the white beam station BL3 at the ESRF, which will use a soft wiggler with 48 poles and a maximum field of 0.76 T at 20 mm gap giving a critical energy of 16 keV. The deflection parameter K can be varied between 2 and 5. The polychromatic radiation is focused by a toroidal mirror and ray-tracing calculations show that the 10 mA single bunch mode will produce $4x10^{10}$ photons onto a small 0.2x0.2 mm^2 sample from one electron bunch. The duration of the single bunch is 50 psec and simulations of the diffraction pattern from myoglobin predicts 500-750 usable reflections.

Single bunch exposures may therefore open up the possibility of capturing short lived excited states in a reaction scheme, but it has also the advantage that the diffraction pattern may be free of radiation damage since the time scale associated with the migration of free radicals is supposed to happen on a much longer time scale. The beamline will be installed in September 1993 and first beam is expected in the 4th quarter of 1993.

PS-01.01.07 DECONVOLUTING LAUE MULTIPLE DIFFRACTION SPOTS BY THE DENSITY MODIFICATION METHOD.

By Q. Hao* and M. M. Harding, Chemistry Department, Liverpool University, Liverpool L69 3BX, U.K.

In a Laue diffraction pattern 10-20% of the spots result from the exact superposition of two or more reflections which are 'harmonics', e.g. hkl, $2h,2k,2l$ ..... For the solution of large or difficult structures the intensities of the remaining 80-90% of the reflections, measurable as singles, may not be sufficient, and evaluation of the intensities of the components of the multiple spots is therefore important. A new procedure for this deconvolution using real-space density modifications on the Patterson map is given. This is a further development based on a procedure in reciprocal-space related to Direct Method (Hao, Campbell, Harding and Helliwell, *Acta Cryst.*, 1993, A49, in the press). It has been tested with Laue diffraction data from 4-Zn insulin and Cytochrome C Peroxidase (CCP). 304 and 1134 reflection intensities were evaluated from multiple spots of insulin and CCP respectively; the R-factors showing the agreement with the high quality monochromatic data are 0.24 and 0.21.

PS-01.01.08 DEVELOPMENT OF X-RAY FOCUSING OPTICS FOR MICRODIFFRACTION.

By W. Yun*, B. Lai, Z. Cai, D. Legnini, K. Randall, Advanced Photon Source, Argonne National Laboratory, U.S.A, A.A.Krasnoperova, and F.Cerrina, Center for X-Ray Lithography, University of Wisconsin at Madison, U.S.A., E. Di Fabrizio, Institute of Solid State Electronics, Italy.

X-ray microfocusing optics capable of focusing hard (5-30 keV) x-rays to submicron focal spot size with high focusing efficiency are of great importance for spatially resolved microdiffraction as well as many other applications such as microscopy, microspectroscopy, and microanalysis. The availability of such optics opens up new opportunities to extend the capabilities of many conventional x-ray techniques with high spatial resolution. For example, identification of crystallographic phase, orientation, local structure, and strain can be studied using the spatially resolved microdiffraction technique. For this purpose, we have developed two types of microfocusing optics, transmission phase zone plates and reflecting focusing optics using an ellipsoid mirror. A 0.6-micron spatial resolution and a 33% focusing efficiency were measured from a phase zone plate using synchrotron x-rays. In this paper, we will present the recent developments in x-ray focusing optics for x-ray microdiffraction and other applications. The parameters that are relevant to microdiffraction experiments will be discussed.

PS-01.01.09 TIME-RESOLVED ENERGY-DISPERSIVE POWDER DIFFRACTION STUDY OF THE FORMATION OF CORDIERITE FROM A CHROMIUM DOPED CORDIERITE GLASS.

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The crystallisation of cordierite and spinel from a non-stoichometric chromium doped cordierite glass has been studied at a number of temperatures under isothermal conditions using energy-dispersive powder diffraction. A quartz like intermediate was found to briefly exist before the on set of crystallisation. A complete kinetic analysis will be presented together with a detailed discussion of the chemistry of formation of cordierite.