ML.11–H 2 CRYSTALLOGRAPHY WITH SYNCHROTRON RADIATION. By M. Hart, Department of Physics, King's College, Strand, London WC2R 2LS, UK.

Synchrotron radiation sources are still only showing "great promise" for crystallography almost ten years after their virtues were proclaimed at the Tenth Congress in Amsterdam. Use of EXAFS has grown apace and its interpretation has matured to the extent that a routine service is now available. At long last the crystallographic communities in Europe, Japan, USSR and the USA either have or are about to have access to sources dedicated to their needs; the days of "great promise" are over, serious work begins!

Since the last congress in Ottawa there have been very significant changes in the nature of crystallographic work done at synchrotron radiation sources. Traditional work, for example precession photographs of proteins, x-ray diffraction topography and EXAFS has become routine. On the other hand, sufficient beamtime has become available for more speculative research to become feasible. Our x-ray interferometers now routinely measure f' and f'' with very high precision while others have been used to locate surface atomic sites using Borrmann wavefields. In the time domain, surface Rayleigh waves, magnetic domains in motion, muscles in action and crystal growth during laser annealing have all been studied. Our understanding and manufacturing capability in x-ray optics has been refined to the point that many new experiments are under construction; in powder diffraction, diffuse scattering, surface studies and scattering tomography.

I hope to present a comprehensive review of the state of the art.

ML.11–H 4 SURFACE STUDIES BY ELECTRON MICROSCOPY. By K.Yagi, Department of Physics, Tokyo Institute of Technology, Oh-okayama, Meguro, Tokyo 152 Japan.

Recently great progress has been made in surface science due to the deveopement of UHV techniques and related surface analyzing methods such as LEED, RHEED, AES, UPS, ISS. Information on structures and chemical compositions given by such methods, however, is an averaged one over the area covered by the electron, photon or ion beam. Microtopograpic information on surfaces is very important for the understanding of surfaces and surface phenomena. Various methods have been deveoped to get surface images as listed in the table. One general method is to reduce the probe size to get images in the scanning mode. However, their spacial resolution was not high enough to be compatible with needs in modern surface science except in the case where high resolution STEM was used.
In the present lecture direct observations of surfaces and surface processes with use of conventional transmission electron microscopes(CTEM) are reviewed(Yagi et al.Crystals,vol 7 Springer-Verlag 1982) and contrasted with the other methods in the table.
One of the characteristics of the CTEM method is that EM image contrast is determined by a electron diffraction(ED) process at surfaces and in crystals. Therefore, the images obtained have crystallographic information on the surfaces relative to the underlying bulk crystals. There are two modes of surface observations: transmission mode(TEM-TED) to observe surfaces of thin films through them and reflection mode(REM-RED=RHEED) to observe surfaces of bulk crystals with glancing angle. In both modes observations should be done under the UHV condition on specimens with clean and well-defined surfaces. Therefore, UHV EM and in-situ specimen treatment techniques must be developed. With these techniques, surface atomic steps, reconstructed surface structures and adsorbate structures and their domains and dynamic surface processes such as step motions due to sublimation and deposition, surface and adsorbate structure phase transitions and adsorption processes on silicon and metal surfaces were observed. High resolution imaging of surface and adsorbate structures on atom resolution level was also done.

TABLE: Surface Imaging Methods

(1) Scanning method for imaging.
  a) high resolution scanning transmission electron microscope (STEM).(in transmission and reflection modes(SREM))
  b) imaging by secondary electrons(SEM).(low energy electron incidence)
  c) imaging by singnals through analytical techniques (AES, EELS, X-ray)
  d) imaging by emitted ions (SIMS)
  e)...
(2) Conventional Electron Microscope(CTEM)
  a) indirect method(step decoration, replica)
  b) direct method(transmission mode:TEM-TED)
  (reflection mode :REM-RED)
(3) Photo Emission Electron Microscope(PEEM)
(4) Scanning Tunneling Microscope(STM)
(5) Field Ion(Emission) Microscope(FIM,FEM)

ML.12–H 2 POWDER'S PROGRESS. By R. A. Young, School of Physics, Georgia Institute of Technology, Atlanta, Georgia, 30332, USA

In its new status as a "beautiful swan" (Langford, 1981), the powder diffraction field continues to enjoy rapid progress, much of it driven by new developments in hardware (sources, detectors, diffractometers) and software, the declining cost of computing and the proliferation of microcomputers for control and analysis.

With spallation neutron sources, both intensity and resolution are maintained unusually far out in $(\sin\theta)/\lambda$, which leads to improved precision in the results. Synchrotron sources offer high intensity, high resolution, wavelength tunability, and a polarized beam. Linear position-sensitive detectors (PSD) decrease data collection times by a factor of 100. Curved PSD's are particularly good for maintaining resolution in focusing geometries. Transmission methods are receiving increasing attention and Guinier geometry with a curved PSD, either stationary or moving on a diffractometer arm, will clearly become more used.

Time-resolved x-ray studies have been reported in the manosecond range for a repetitive process and <10 sec for non-repetitive ones.

Structure solution from powder diffraction data has been systematically carried out for >20 structures. The powder pattern must first be decomposed into the Bragg intensities, which can then be used in MULTAN or other structure solution programs. Successful decomposition is materially aided by knowledge of the unit cell parameters (e.g. Werner; Pawley; Hewat), although success has also been reported with other methods (e.g. Parrish, Will & Huang; Rubia, Soria & Cano). Many hundreds of structures have now been refined with the Rietveld method. X-ray, neutron, fixed energy and fixed angle

data have been used. At least 3-4 computer programs handle multi-phase refinement. In zeolite ZSM-5, 180 parameters were refined from x-ray data (Baerlocher). Applications to polymers have been made effective by use of constrained-molecule refinements (e.g. Pawley; Immirzi). A particularly fruitful new development is the use of the Rietveld method with intense pulsed neutron(time of flight) data,used for most of the >50 powder diffraction studies reported from the IPNS-Argonne from 1981 on. Precision in atomic parameters comparable to good single crystal results is usual with non-hydrogenous materials.

Some developmental needs outstanding for Rietveld analyses are better modeling of reflection profile shapes, better handling of preferred orientation, how to recognize and avoid false minima, improvement of techniques and methods so that good individual temperature factors can be routinely determined simultaneously with site occupancy factors, resolution of the current discussions of standard deviations, and an equivalent of the Hamilton R-ratio test.

Appropriate modeling of the reflection profiles can be crucial to several types of analyses. Further progress has been made on the problem, both by use of simpler geometries (HDS) and with improved models.

Recent progress in line profile analysis includes advances in single-line analyses, incorporation of size and strain parameters in a Rietveld refinement program, and very sophisticated analyses to determine the detailed nature of disorders in lamellar structures (e.g. Tchoubar, et al.)

Progress in the phase identification and quantitative analysis is being enhanced by improved precision of data, pattern decomposition, and instrumental resolution.

ML.12–H 4 FUNCTIONAL SIGNIFICANCE OF FLEXIBILITY IN PROTEINS. By Robert Huber and William Bennett, Max-Planck-Institut für Biochemie, 8033 Martinsried/München, FRG.

The structural basis and the functional implications of large-scale flexibility are discussed for three systems: trypsin-trypsinogen, immunoglobulins, and citrate synthase. The trypsin-trypsinogen system provides an example in which an order-disorder transition is used as a means to regulate enzymatic activity. Immunoglobulins demonstrate how flexibly linked domains may be used to allow the binding of ligands with diverse arrangements. In citrate synthase, domain motion forms an active site that is shielded from solvent. Analogous large-scale flexibility has been observed in a number of other systems.

ML.13–H 2 CRYSTALLOGRAPHIC CONCEPTS IN THE DESIGN OF MATERIALS FOR THE DISPOSAL OF NUCLEAR WASTE. By F.P. Glasser, Department of Chemistry, University of Aberdeen, Old Aberdeen AB9 2UE, Scotland.

Radioactive wastes must be immobilized in a form which effectively isolates them from re-entering the biosphere for long periods of time, ranging up to 10^5 - 10^6 years. The species requiring immobilization lie mainly in the atomic number range 40 - 72, together with Th, U and other actinides. Geological barriers may be insufficient for their containment, especially for those having high geochemical mobility. Matrix isolation, siting individual atoms in dilute solid solution in the lattice of a crystalline phase or phases, can be used to design high-integrity waste forms. The waste form is typically achieved by balancing the waste composition with oxide additives, tailored to achieve the desired phase combination after a ceramic fabrication and firing stage. The principles of crystallochemistry and phase equilibria are used to design satisfactory phase combinations. Examples are presented showing how these principles have been applied. Special applications arise for crystalline host phases which are suited to the immobilization of normally gaseous elements, e.g. tritium. Degradation of crystalline host lattices may occur by leaching, accelerated by lattice damage arising from radiation, transmutation, fission product accumulation, etc. These effects are discussed. The science of developing high-integrity materials which are durable in a wide range of natural environments is in its infancy. However, the fruits of decades of crystallochemical and phase equilibria research have enabled remarkable progress to be made, thereby offering hope that radioactive wastes can be effectively immobilized by a combination of man-made and natural barriers.

ML.13–H 4 MEASUREMENT AND USE OF ANOMALOUS X-RAY SCATTERING. By Wayne A. Hendrickson, Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D. C. 20375, U.S.A.

X-ray scattering factors are affected by resonance of the incident radiation with natural frequencies of bound electrons in atoms. This anomalous scattering grows very large as the absorption edges of certain ionic species are approached, but it is also substantial at wavelengths remote from edges. In practical terms, for all but the lightest of atoms, anomalous scattering is the norm at wavelengths of interest for diffraction experiments. Appropriately designed experiments can isolate the contributions of a few anomalous scattering centers from among many normal scattering light atoms. The distinctiveness of these centers and the accompanying phase shifts make anomalous scattering useful in structure determination -- particularly so in macromolecular crystallography. Phase information from anomalous scattering measured at a single wavelength is inherently ambiguous and must be combined with other information to be definitive. The combination with isomorphous replacement results is standard. Recent advances have been made in methodology for using partial structures, solvent leveling, and direct methods to resolve this phase ambiguity. In addition, it has long been recognized that, in principle, multiple wavelength analyses can yield definitive solutions. Measurement and processing techniques to eliminate systematic errors are essential for anomalous scattering data. But although small, the effects can be powerful. For example, the actual signal in Bijvoet differences arising from the sulfur anomalous scattering ($\Delta f''=0.6e$ at $\lambda=1.54\text{Å}$) of the protein crambin averaged only 2.1% of $|F_{obs}|$, yet this sufficed for a direct determination of the structure. Resolved anomalous phasing procedures have subsequently been used in other structure determinations. Several laboratories are engaged in synchrotron experiments to exploit anomalous dispersion at multiple wavelengths.