15. X–4 TIME-RESOLVED X-RAY DIFFRACTION AND SPECTROSCOPY. By D. M. Mills, Cornell High Energy Synchrotron Source (CHESS), and School of Applied and Engineering Physics, Cornell University, Ithaca, New York.

Although the pulsed nature of the radiation emitted from storage rings has for some time been exploited for studies in the vacuum ultra-violet region of the spectrum, only recently have synchrotron radiation users begun to perform time-resolved diffraction and spectroscopy at x-ray energies. Time-resolved x-ray experiments performed at synchrotron radiation sources fall naturally into two catagories, those which do not depend on the actual time-structure of the emitted radiation but rather rely on the high flux and those which take explicit advantage of the modulated or pulsed nature of the x-ray beam. It is with these experiments that this presentation is concerned.

A survey of recently performed time-resolved x-ray experiments will be given with emphasis on the techniques used. Future directions for this field will also be discussed.

15. X–5 GENERAL PROBLEMS IN THE STRUCTURAL ANALYSIS BY EXAFS. By P. Rabe, Institut für Experimentalphysik, Universität Kiel, D-2300 Kiel, FRG

The evaluation of structural parameters from the extended X-ray absorption fine structure follows several steps each of which may introduce uncertainties in bond lengths and coordination numbers:
1. Recording the spectra: Absorption spectra are subject to statistical noise. An increasing noise is directly related to an increasing uncertainty in the bond lengths, coordination numbers, and Debye-Waller factors determined in the subsequent steps of the data analysis.
2. Normalization procedure: To convert the experimental spectra to a form which can be compared with the single scattering formalism of EXAFS the atomic background has to be removed. Generally this background is assumed to behave monotonous with photon energy. Several experiments have shown however that an atomic extended fine structure which is caused by multielectron excitation is underlying the EXAFS. This low frequency fine structure may interfere with the EXAFS especially in cases where the amplitudes are small due to thermal damping or structural disorder.
3. Fourier transform or curve fitting:The finite range over which the EXAFS can be observed leads to a substantial broadening of peaks in the Fourier transform. As a result close lying coordination shells cannot be resolved unambiguously. Moreover the electron-atom scattering phases and amplitudes have to be known. In fortunate cases reference samples with electronic and structural properties comparable to those of the sample under investigation are available from which these parameters can be extracted.In other cases a combination of experimental and calculated phase shifts lead to reliable bond lengths. Finally at photon energies close to the absorption edge the spectra are dominated by multiple electron scattering. This range is permanently lost for an interpretation with the single scattering formalism and leads to a loss of information about a long range order. A way out of this dilemma is to resort to multiple scattering calculations or to complete the EXAFS spectra with X-ray scattering data in the photon energy range of anomalous dispersion.

15. X–6 APPLICATIONS OF X-RAY STANDING WAVES FOR BULK AND SURFACE STUDIES. By G. Materlik, Hamburger Synchrotronstrahlungslabor HASYLAB, Hamburg, Germany, INVITED PAPER at the Microsymposium organized by C.J. Sparks.

Recent progress in studies with x-ray standing waves which has been realized by using synchrotron x-radiation is described in this paper. Most of the measurements were carried out by using the ROEMO instrument installed at the storage ring DORIS in Hamburg (A. Krolzig, G. Materlik and J. Zegenhagen, Nucl. Instr. & Meth. 208, 613 (1983)).
The movement of the x-ray interference field across the crystal net-planes, generated by passing a Bragg reflection, was used in following studies: 1. Position distribution, lattice relaxation and limits for vibrational amplitudes were determined by higher order measurement on shallow layers of implanted bulk impurities (G. Materlik and J. Zegenhagen, Phys. Lett. subm.) 2. Chemisorbed (Br on Si & Ge, M. Bedzyk and G. Materlik, subm.) and electrodeposited (Cd and Tl on Cu, G. Materlik, J. Zegenhagen and W. Uelhoff, subm.) sub-monolayer coverages of adsorbates were studied to characterize the adsorbate structure perpendicular to the diffraction planes which were oriented parallel to the surface. 3. The position of 1/4 monolayer of Br on Si was measured with a Si x-ray interferometer parallel to the (111) surface plane of the analyzer crystal (G. Materlik, A. Frahm and M.J. Bedzyk, Phys. Rev. Lett. 52, 441 (1984)). 4. The electron emission yield was measured to determine the crystal perfection layer-by-layer perpendicular to the surface using the electron energy loss process (M.J. Bedzyk, G. Materlik and M. Kovalchuk, subm.) and 5. The electron emission yield of a non-centrosymmetric GaAs crystal was measured and reveals the shift of the diffraction planes relative to the atomic planes as a function of photon energy E as described by f'(E) and f"(E).

15. X–7 ANOMALOUS SCATTERING STUDIES OF AVERAGE DISTRIBUTION PARAMETERS IN SIGMA AND TAU PHASES. By H. L. Yakel, Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830, U.S.A.

If synchrotron radiation (SR) with energy near an atomic absorption edge is used to measure Bragg or diffuse diffracted intensities, anomalous dispersion can change scattering cross sections enough to reveal long- or short-range structural features in materials whose constituent elements are near-neighbors in the periodic table. We present results of long-range site-occupation parameter estimations, derived from single-crystal diffraction experiments with SR and conventional Mo Kα x radiation, for sigma (σ) and $M_{23}C_6$ tau (τ) phases composed of such elements.

The σ crystals examined with conventional radiation were selected from phases containing Cr and Fe; Cr, Fe, Ni, Mo and Mn; Cr and Mn; and W and Re. SR diffraction data were obtained from a Cr-Fe crystal and from the polynary σ crystal. Tau crystals chosen from $(Cr_{23-x}Fe_x)C_6$ phases with $x = 7.3_6$, 4.1_3, 1.7_0 and 0.7_4, and from a $(Cr_{15.73}Mn_{4.18}Fe_{3.09})C_6$ phase, were studied with conventional radiation; intensities of Bragg reflections from the binary crystal with $x = 0.7_4$ were also measured with SR tuned near Cr and Fe K edges.

Analyses of these data sets show that usefully accurate, moderately precise long-range site-occupation parameters can be derived from extensive, precisely measured Mo Kα Bragg reflection intensities for all the binary Cr-Fe σ and τ phase crystals examined. However, site-occupation parameters could not be recovered by analyses of conventional data from crystals of the Cr-Mn and W-Re σ phases and the Cr-Mn-Fe τ phase. Distribution parameters of Mo atoms on the 5 sites of the σ structure could be derived from conventional data for the polynary σ crystal, but

parameters for the major 3d elements could only be found from the SR data sets. While site-occupation parameters obtained for the binary Cr-Fe σ crystal studied with SR were more precise by a factor of 3 than those recovered from conventional data, precisions of parameters for the binary τ crystal with x = 0.74 were not materially improved. In both cases, differences between parameters obtained from conventional and SR data were of marginal significance.

This work has confirmed that the success of SR diffraction experiments using dispersion to differentiate scattering cross sections depends on the precision with which dispersion correction terms can be measured or predicted. Results of analyses of SR data measured just below the Cr K edge energy from the binary τ crystal with x = 0.74 show that reasonable agreement factors can only be obtained if f'(Cr) is allowed to decrease in magnitude with $\sin\theta/\lambda$. There is need for improved theoretical treatments and expanded experimental estimates of dispersion terms for particular elements in particular crystallographic environments.

Descriptions of local departures from average structures should also be improved if SR tuned near absorption edge energies is used to measure diffuse scattering from crystals whose components have similar atomic numbers. Methods will be presented that use variations in anomalous dispersion terms at multiple wavelengths to separate data sets into functions from which short-range structural parameters of binary and ternary alloys can be derived.

15. X–8 BAND STRUCTURE APPROACH TO THE X-RAY SPECTRA OF METALS. By J.E. Müller, Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5170 Jülich, West Germany.

A formalism to compute X-ray spectra due to core excitations in metals using single-particle band structure techniques is presented and illustrated with a calculation of the K and L absorption edges of transition and rare-earth metals. The scheme is based on a new linearized version of the augmented plane wave method specifically designed to cover large energy ranges (200 ev).

The main features of the spectra are interpreted in terms of band structure and EXAFS concepts and the connection between both forms of description is discussed.

The calculated spectra are compared with available experimental data: All the experimental features are reproduced by the calculation. However, for the heavier elements the actual placement of the features shows discrepancies, which point to a limitation of the ground state potentials for calculating high energy states.

15. X–9 X-RAY EXCITED OPTICAL LUMINESCENCE (XEOL) : POTENTIALITY AND LIMITATIONS FOR THE DETECTION OF SITE SELECTIVE EXAFS SPECTRA

by

J. GOULON[1,2], P. TOLA[1], J.C. BROCHON[2], M. LEMONNIER[2]

[1] E.R.A.(CNRS)n°22 "Interactions Moléculaires" Université de NANCY I - B.P. n°239 - 54506 VANDOEUVRE LES NANCY FRANCE

[2] L.U.R.E. (L.P. CNRS), Université de PARIS-SUD Bâtiment 209C - 91405 ORSAY FRANCE

The optical luminescence induced in various materials by X-ray excitation has been used for many years as a sensitive analytical tool. This phenomenon however deserves further attention from the spectroscopis because :

(i) the differences between UV or X-ray excited spectra can be very useful in the assignment of weak transitions in multiple site systems : e.g. in C-Y_2O_3 doped with Eu^{3+} cations, three lines assigned to transitions occurring at the centrosymmetrical Eu^{3+} (C_{3i}) site are strongly enhanced in the XEOL spectrum.

(ii) X-ray excitation spectra were reported to reproduce, in few cases (e.g. CaF_2, ZnO...) either positive or negative edges and EXAFS oscillations.

(iii) we have recently established that in the case of mixtures of different species (e.g. ZnO + Zn:porphyrin), the X-ray absorption spectrum of one specific species (i.e. ZnO) could be obtained by this method.

The XEOL and optical EXAFS/XANES spectra of several inorganic or organometallic systems will be presented. Time resolved XEOL spectra have also been obtained, taking advantage of the pulsed structure of the synchrotron radiation light. Finally a simple formulation of the phenomenon predicting either positive or negative edges will be developed and the requirements for site selectivity discussed.

15. 1–1 A NEW INSTRUMENT FOR PROTEIN CRYSTALLOGRAPHY ON THE WIGGLER BEAM LINE AT THE SRS PROVIDING A FOCUSSED, TUNABLE BEAM AT SHORT X-RAY WAVELENGTHS. By

J R Helliwell[1], M Papiz[2], P R Moore[1] and A W Thompson[1].

[1] SERC, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, Cheshire, England.

[2] Department of Physics, University of Keele, Keele ST5 5BG, Staffordshire, England.

A new instrument has been constructed on the wiggler beam line at the Daresbury Synchrotron Radiation Source (SRS). The wiggler provides much harder x-radiation wavelengths than are available on an ordinary bending magnet at the SRS; the critical wavelengths of the emitted spectrum of radiation being 1Å and 4Å respectively for the SRS operating at 2 GeV. Hence, the new instrument provides shorter wavelengths than the first protein crystallography workstation at the SRS which has been routinely operational from 1981 (Helliwell et al (1982) J.Phys.E. 15, 1363). The optimization of the anomalous dispersion coefficients f' and f" for those elements with absorption edges with wavelengths $0.8Å < \lambda < 3Å$ is possible. The range $0.8 < \lambda < 1.1Å$ encompasses the L absorption edges of the heavy atoms which are usually used as derivatives in protein crystallography (eg Pt, Au, Hg). We present details of the spectral characteristics of the new wiggler magnet source, the parameters of the x-ray optics, the remote control alignment system and the computer configuration. In addition, an electronic area detector diffractometer (the FAST) has been supplied by Enraf-Nonius whose performance has been successfully tested. The diffractometer is capable of being mounted 'on its side' to move the detector in a vertical plane on the workstation to allow for the horizontal polarization of the SRS beam. Data collected on the system at Daresbury will be described.