HASYLAB Hamburger Synchrotronstrahlungslabor

Research with Synchrotron Radiation

A wiggler at DORIS III.

Synchrotron radiation emitted from the DORIS III storage ring is used at the Hamburger Synchrotronstrahlungslabor HASYLAB in many different ways for fundamental and applied research. Groups involved in preparing and carrying out experiments in 1993 involved more than 890 scientists from Germany and elsewhere; they came from 183 institutes and laboratories. It was largely thanks to special programmes of the European Union that the HASYLAB facilities could be opened to a wide European users community.

The DORIS storage ring has been used exclusively since June 1993 to produce synchrotron radiation and is providing about 4250 hours of beam time each year. It is generally operated in 5-bunch mode at an electron energy of 4.5 GeV, with storage maintained in reduced bunch mode part of the time to allow for experiments which make use of the ring's time structure. DORIS III started operating this year with positrons and this has led to an important increase in the lifetime of the stored beam. The maximum injection current is presently 90 mA, which decays continuously over 8 hours to a value of 50 mA; the time needed for a new injection is of the order of 10 minutes. These running conditions will improve in the course of the 1994, so users of the HASYLAB facilities can look forward to productive years of exciting research using synchrotron radiation. Fig. 1 compares the spectral brightness obtained at the DORIS III dipole magnet sources and at its wiggler and undulator beam-lines. For the many experiments which do not need a very small source size or beams with a very high degree of coherence, the HASYLAB facilities are competitive with the most modern third-generation synchrotron sources over a wide range of wavelengths.

An aerial view of HASYLAB taken in 1990 before the construction of two new experimental halls accompanying the installation of seven insertion devices. The DORIS storage ring can be seen in the upper part.

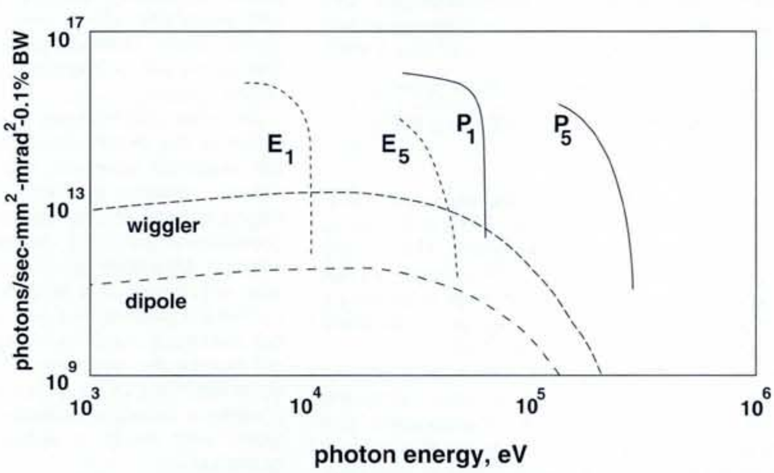


Fig. 1 — Comparison of the spectral brightness of synchrotron x-ray sources. Spectra for a DORIS III dipole bending magnet at 5.3 GeV, for a standard DORIS III x-ray wiggler, and for the 1st and 5th harmonics (P_1, P_2) of the planned PETRA undulator (for an electron energy of 14 GeV) are compared with spectra (E_1, E_5) for a standard ESRF undulator at the European Synchrotron Radiation Facility.

Experiments are performed simultaneously at some 40 experimental stations (10 of the stations are located at wiggler or undulator beam-lines), where altogether about 80 instruments are available. HASYLAB's main fields of research in the x-ray region involve structural biology, diffraction from solid and liquid surfaces and interfaces, small-angle scattering, and absorption spectroscopy. However, there is a long tradition of synchrotron radiation research in the VUV and soft x-ray regime at DESY.

EXPLOITING HIGH-BRIGHTNESS SOURCES

An important advantage of radiation from a magnetic undulator (a periodic magnetic structure through which a beam passes) compared to radiation from a bending magnet or a wiggler is its narrow spectral distribution (see Fig. 2). However, for applications such as Extended X-ray Absorption Fine Structure spectroscopy (EXAFS) where a broad scanning range is needed, this feature is an obvious disadvantage. A solution is to change the gap between the undulator's magnet arrays while scanning the x-ray monochromator to allow EXAFS scans over a wide energy range with undulator radiation. Synchronized movement of the undulator gap and the optical elements of the high-flux SX-700 monochromator has been implemented recently at the XUV-undulator beam-line BW3. The gap is changed in steps of 0.05 mm and fluctuations in photon flux owing to its incorrect positioning are less than a few percent; the beam position at all the other beamlines is essentially unaffected by the movement of the undulator.

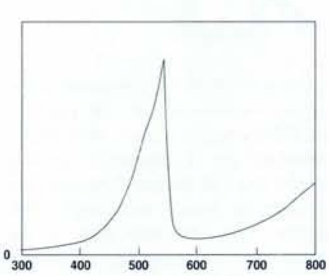


Fig. 2 — Photon flux of the 44-period undulator at beam-line BW3 with a 50 mm gap, measured at the sample position using a GaAs photodiode.

Major new research opportunities have been opened up in the photon energy range between 50 and 1500 eV owing to the high photon fluxes (typically $\approx 10^{12}$ photons per 0.1% energy band-width normalized to 100 mA at 1000 eV) and the high spectral resolution that have been achieved. At the N_2 and Ne K-edges at 400 and 870 eV, respectively, bandpass energies of less than 50 and 200 meV are obtained, which are the best values reported up to now for this energy range.

Thanks to the excellent performance of the new BW3 beam-line, many interesting experiments are being performed covering a broad range of topics in atomic and solid-state physics. The angular distributions of photo-electrons of simple atoms and molecules have been measured using time-of-flight photo-electron spectrometers. Data analysis shows that the degree of polarization of the undulator radiation in the first harmonic is 97%. Topics that have been studied include:

– the electronic structure of atoms (many-body effects) and solids using soft x-ray fluorescence spectroscopy;

– the recently discovered, linear magnetic dichroism of Fe at the Fe 2p-edge using spin-polarized photoemission;

– resonant and non-resonant Auger decay processes in atoms, molecules and free-standing C_{60} clusters.

Absorption Spectra of Clusters

A molecular-beam experiment has been built up at HASYLAB to examine the geometric and electronic structures of free-standing clusters. The goal is to perform absorption and photo-emission studies of inner shells of clusters. Time-of-flight techniques are used for the analysis of the photo-electrons as well as for the detection of clusters. The first inner-shell photo-electron spectra of free clusters have been obtained using the set-up.

Of particular interest is the evolution of electronic energy levels with cluster size and its relation to the geometrical structure. Rare-gas clusters play an important rôle here because their size can be easily varied and they are model systems with a simple electronic structure, without problems asociated with directed bonds or electron correlation. However, data from fluorescence spectroscopy of the lowest valance excitations is difficult to analyze owing to spin-orbit splitting and other complications. These problems can be avoided by studying resonant K-shell excitations. The resulting absorption spectra are characterized by a single Rydberg series ($1s \rightarrow np$, where n is an integer) and the excitations are localized at a given atom owing to the small overlap between core orbitals. However, in order to extract detailed information, the $1s^{-1}np$ state must be well resolved. This has become possible using new monochromators and high-brightness undulator sources. Fig. 3 plots, as a function of cluster size, the energy of the $1s \rightarrow 3p$ excitation in Ne clusters determined using an undulator source at HASYLAB's BW3 beam-line.The data indicate that for small sizes, the 4p-state is largely located outside the cluster, acting as a Rydberg orbital for the whole system. The energy required for the corresponding excitation is reduced owing to screening of the core hole by other atoms so the transition energy decreases with cluster size. As the cluster grows, this Rydberg orbital no longer exists and the 4p-excitation transforms to a higher energy, bulk-like state inside the cluster.

Photodissociation

The photodissociation of water represents a good example of the types of photo-ionization experiments that make full use of the of the DORIS time-structure as well as the high intensity and the high resolution available at beam-line BW3. Fig. 4 shows partial ion-yield curves of H_2O excited close to the oxygen K-edge. It is seen that the fragmentation intensity of water vapour follows the spectral variation of the absorption almost independently of the ion produced (H^+ is the most prominent ion, but O^+ and OH^+ ions are also present in large numbers, while H_2O^+ and O^{2+} appear at the percent level). In addition, it is possible to check for correlation of ion fragments by recording ion-ion coincidences. Fragmentation into one or two protons plus an additional ion seems to be the dominant process, and virtually independent of the excited valence state. Another, particularly interesting channel of this dissociation is the production of neutral hydrogen atoms. This is a strong indication for a very fast dissociation of a neutral, core-excited molecule, *i.e.*, in this case the dissociation is even faster than the ionization of the molecule. A schematic drawing of this unusual dissociation process is shown in Fig. 5.

Combining Surface Diffraction and Local Probes

Since in grazing incidence, only a small number of atoms or molecules contribute to the scattering, beams of very high intensity and angular collimation that are only available at modern synchrotron radiation facilities are indispensable for x-ray studies of the geometrical and electronic structure of surfaces and interfaces in solid and liquid systems. Such studies are being conducted with great success at HASYLAB. The interest stems from the fact that atoms and molecules adsorbed on metal or semiconductor surfaces can form different structural modifications, details of which have to be known for modern research and for development work in areas such as microelectronics and catalysis. The large variety of structures in which atoms can be arranged on surfaces, so-called reconstructions, is a result of the small difference in energy between the various configurations.

As an extension of classical crystallography, the long-range structure of surfaces can be determined with synchrotron radiation to very high accuracy, *i.e.*, with an uncertainty in the atomic positions of the order of ± 0.001 nm. However, using this technique only the structural parameters of the average structure are determined, and local defects are in general not identified. This is unfortunate because these local defects play a major rôle in important processes such as the formation of reconstructed structures and in the nucleation and growth of layers. This serious lack of information in x-ray surface diffraction can be overcome by combining the method with scanning tunnelling microscopy (STM), which is a local probe capable of providing the necessary information about steps, domain boundaries, short-range disorder, dislocations, and different local structures coexisting on the surface. On the other

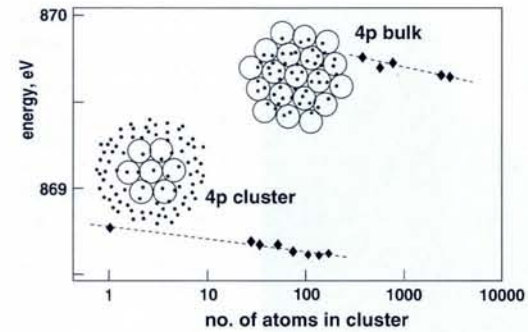


Fig. 3 — Transformation from a Rydberg-type excitation of an entire cluster to the bulk excitation of a solid. The shift of the energy of the $1s \rightarrow 4p$ excitation is plotted as a function of the size of neon clusters. The electron orbitals and sites of excitation are illustrated schematically. The absolute energy scale has been adjused to agree with spectroscopic data for the atomic $1s \rightarrow 3p$ transition.

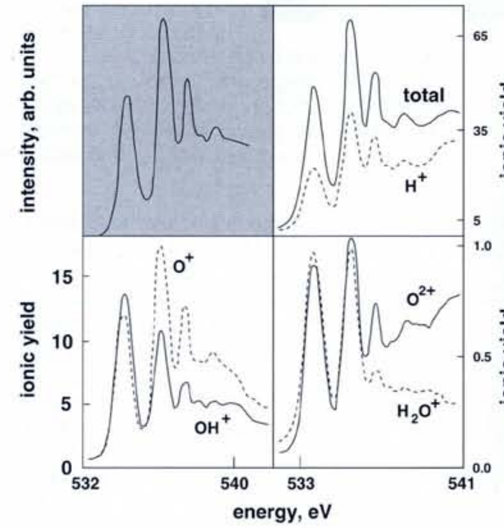


Fig. 4 — Ionic fragmentation of water following core excitation. Shown are the ionic yield spectra as a function of energy, measured with a time-of-flight mass spectrometer.

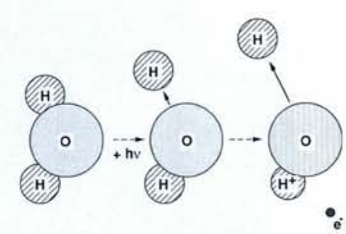
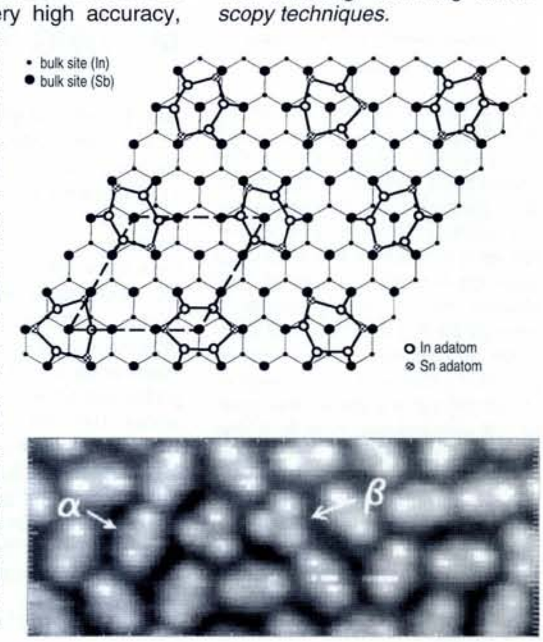


Fig. 5 — Illustration of the fast, photo-induced dissociation of core-excited water molecules followed by ionization.

Fig. 6 — a, lower) STM topography of the InSb(111)-B(3x3) surface reconstruction in an area of (40 x 100) $Å^2$ showing two different types of unit cells (α and β). b, upper) A schematic illustration of the crystallography of the reconstruction determined using a combination of x-ray diffraction and scanning tunnelling microscopy techniques.



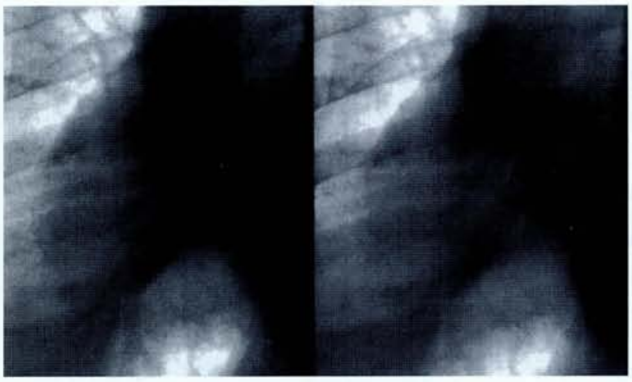
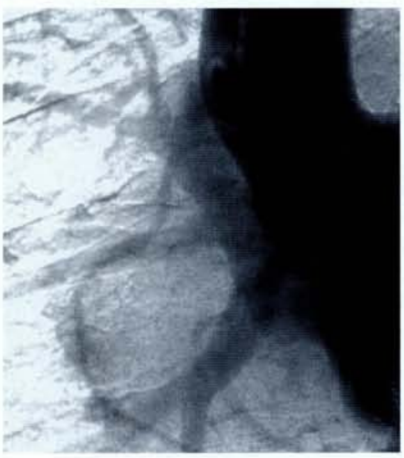


Fig. 7 — a, upper) Images of the area around a patient's heart area following the injection of an iodine contrast agent. The one on the left was taken using an x-ray beam with an energy below the K-edge of iodine, while that on the right was recorded using an energy above the K-edge. They were recorded simultaneously using a two-line ionization chamber.
b, lower) The image after computer subtraction: the right coronary artery and parts of the aorta, of the left atrium, of the left ventricle and pulmonary veins are clearly distinguished.



hand, STM is of limited value for the quantitative determination of the long-range periodic structure of the surface.

Both techniques have been applied at HASYLAB to study the metal/semiconductor systems Ag/Ge(111), Pb/Si(100), Ga/Ge(111) and Bi/GaSb(110) as well as the systems S/Ni(110), S/Ni(111) and S/Cu(111), which are of great importance in catalysis research. Fig. 6a shows the topography of the InSb(111)-B(3x3) reconstruction in an area of (40x100) $Å^2$ as recorded by STM. Two different types of unit cells (α and β) are clearly visible. The final structure determination, which could only be obtained from a combination of STM and x-ray diffraction data, is presented in Fig. 6b.

Surface diffraction experiments of the type used in this work use synchrotron radiation with wavelengths of the order of 1.5 Å, *i.e.*, with an energy of ≈ 8 keV. For bulk diffraction experiments, there is a trend to go to shorter wavelengths because of the weaker interaction with matter that allows a more accurate interpretation of the data.

Medical Imaging

The potential of synchrotron radiation in medical imaging arises from the very high intensity and the suitability for monochromatization of the white radiation. As a result one can use K-edge dichromography to image structures which contain relatively low concentrations of iodine, which is the active constituent of most clinical contrast agents. In coronary angiography, two monochromatic x-ray beams which closely bracket the K-edge of iodine at 33.17 keV are used to simultaneously record two images. The images only differ in the fact that, owing to the photo-electric effect of iodine, the image from the beam with an energy just above the iodine K-edge has a six-fold greater attenuation by iodine compared to the beam below the K-edge.

Very bright beams with photon energies of up to about 40 keV are available at DORIS III, so a medical programme to develop intravenous coronary angiography with 33 keV synchrotron radiation is being successfully conducted at HASYLAB in collaboration with the University Hospital in Hamburg. The aim of the work is to visualize coronary arteries as small as 1 mm in diameter following an intravenous injection of the iodine contrast agent resulting in a mass density of only 1 mg-cm^2, thus eliminating the risk for the patient caused by catheterization of the arteries induced by the iodine.

Seven patients were examined in 1993, and Fig. 7a shows two images of a 65-year old man taken simultaneously using two beams of appropriate energy and a pair of ionization-chamber detectors. The naked eye shows no significant difference. However, the computer subtraction image presented in Fig. 7b reveals the right coronary artery as well as parts of the aorta, of the left atrium, of the left ventricle, and of the pulmonary veins. In order to distinguish between coronary arteries and pulmonary veins, two images per injection are recorded and use is made of the fact that the contrast material enters and leaves the various types of vessels at different times. As it is essential for the method that all the coronary arteries can be detected, image-processing methods have to be used in order to visualize those parts of the coronary arteries which are masked by contrast from larger structures. It is intended that the medical parameters for the investigation of patients will be optimised within the next two years once an improved version of the twin-line ionization chamber has been installed and the image-processing techniques have been further developed.

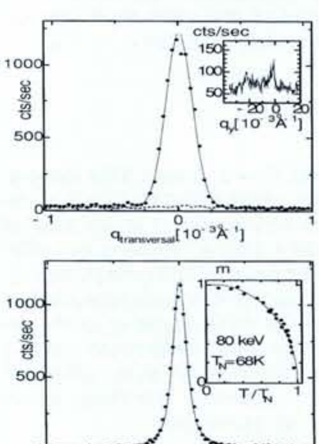


Fig. 8 — Transverse (a, upper) and longitudinal (b, lower) scans using 80 keV x-rays of the (300) reflection of MnF_2 at 40 K with the spin perpendicular to the scattering plane (the count rate is plotted as a function of the scattering distance in reciprocal space). The dashed line in (a) represents a scan at 70 K, i.e., above the transition temperature. The inset in (a) shows that a magnetic peak is not observed in a transverse scan at 4 K with the spin parallel to the scattering plane (note the change of scale). The inset in (b) gives the temperature dependence of the reduced magnetization as measured at the (300) Bragg peak. It agrees with the mean-field result calculated for pure ***S*** *= 5/2 spin.*

MOVING TO HIGHER ENERGY

Solid-State Magnetism

The most powerful methods used today to investigate magnetic structures and structural phase transitions are neutron and synchrotron x-ray scattering. The later have generally employed photons with energies of 3-15 keV which essentially probe surface layers of some 10 μm in thickness. While neutron techniques on the other hand, probe bulk properties, they usually suffer from low resolutions in reciprocal space owing to the low beam intensity. A continuous transition from a near-surface to a bulk probe can be achieved using x-rays with energies of about 100 keV. A triple-crystal diffractometer for high-energy synchrotron radiation thus combines the main advantages of both techniques, namely bulk sensitivity and high-resolution in reciprocal space. In addition, the purely magnetic cross-section in terms of the scattering angle Ω reduces to a good approximation to the simple formula:

$$(d\sigma/d\Omega)_{magnetic} = (\lambda_c^2/d^2)/S_2^2$$

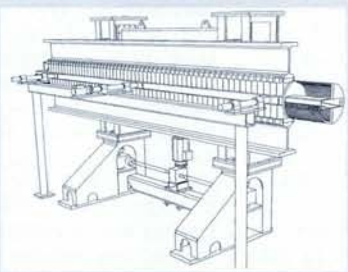
where λ_c is the Compton wavelength, d the lattice parameter, and S_2 the component of the Fourier transform of the spin density perpendicular to the scattering plane.

As a first example, MnF_2, a representative antiferromagnet, has been studied using 80 keV synchrotron radiation at a HASYLAB wiggler beam-line. Fig. 8 giving transverse and longitudinal scans through the (300) magnetic reflection demonstrates the excellent ***k***-space resolution which was achieved. It implies that one can map mesoscopic length-scales in real space. For example, magnetic correlation lengths up to 10 μm should be visible. Taking account of the fact that magnetic scattering is about 10^6-times smaller than charge scattering, the (300) peak count rate of 1400 counts per second at 40 K with a peak-to-background ratio of almost 100 is remarkable. The temperature dependence of the measured intensity agrees well with the expected sub-lattice magnetization curve calculated using a mean-field approximation.

Multiple Bragg scattering has to be considered if weak reflections in a sea of strong Bragg peaks are measured. This is of special importance in MnF_2 where the magnetic propagation vector has integer components, *i.e.*, weak intensity of magnetic origin could be confused with charge scattering from a combination of two strong Bragg reflections *(Umweganregung)*. This source of error was excluded from the present results by a careful analysis of multiple scattering. The outcome is most encouraging because it shows that multiple Bragg scattering will not cause problems in studies of the interesting systems where the magnetic propagation vector contains non-integer components (in this case, multiple scattering will always involve weak sub-lattice reflections and *Umweganregung* is essentially negligible).

The measurements on MnF_2 show that bulk magnetic scattering of high-energy x-rays is on the way to complementing neutron and conventional x-ray scattering in studies of solid-state magnetism. It can be combined with neutron diffraction in order to separate the contributions from spin $\boldsymbol{S}$ and orbital $\boldsymbol{L}$ contributions to the magnetization density. While neutron scattering is sensitive to $\boldsymbol{L} + 2\boldsymbol{S}$, hard x-rays only measure the spin moment $\boldsymbol{S}$. Very high $\boldsymbol{k}$-space resolution is obtained with x-rays if samples of adequate quality are available, and investigations on mesoscopic length-scales are possible. Taking in account that the undulator beam-line under construction at PETRA (see insert) will provide at 100 keV a brightness which is 10^4-times that of the beam-line used so far for the experiments, it is clear that the synchrotron-based technique has a tremendous potential in determining the critical components and the form factors of spin moments.

The PETRA Undulator



A perspective view of the high-field PETRA undulator with its vacuum chamber.

The spectral distribution of the synchrotron radiation from bending magnets or insertion devices is generally shifted to higher photon energies if the storage ring is operated at higher electron or positron energies. A high-field wiggler that will be installed at DORIS III in the second half of 1994 will allow experiments with synchrotron radiation of 100 keV or even higher energies. However, experiments with very hard x-rays will profit even more from an undulator beam which is under construction at PETRA.

The PETRA storage ring is part of the injection system of HERA. Electrons are ramped from 7 to 12 GeV and protons from 7.5 to 40 GeV/*c*. During routine operation, the PETRA ring is only used for injection purposes. Between injection periods, electrons can be stored in PETRA and an undulator would produce synchrotron radiation with unique characteristics. It was therefore decided in 1993 to install an undulator test beam-line for synchrotron radiation at PETRA, to be used when the ring is not needed for injection.

The planned PETRA undulator will be built with permanent magnets and should provide very narrow energy distributions for its fundamental line (ΔE = 220 eV at an energy of E = 18.75 keV) which can be tuned over an energy range of approximately 20 keV by varying the magnetic field strength. The energies of the fundamental and higher harmonics can also be shifted very efficiently by varying the electron energy of the storage ring. Because PETRA is operated as a ramping machine for electron energies from 7 to 12, and possibly 14 GeV, it offers unique possibilities to optimise the electron energy for a given experiment. Fig. 1 includes the tuning range in the spectral distributions for 1st and 5th harmonics and for an electron energy of 14 GeV. The undulator will provide bright beams in the energy range from about 10 to at least 200 keV. By comparing its spectra with those for a standard undulator at the ESRF, it is clear that the PETRA undulator will provide a unique beam for photon energies above 20 keV.