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Early Work with Synchrotron Radiation at Stanford

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The use of synchrotron radiation in the soft and hard X-ray spectral region received major impetus with the start of parasitic operation of the Stanford Synchrotron Radiation Project (SSRP) in 1974. This was the first time that synchrotron radiation from a multi-GeV electron storage ring was made available in a user facility for studying the structure of matter. Here we review the early work at SSRP as well as the activities that preceded it, highlighting the scientific accomplishments (soft X-ray photoemission, EXAFS, protein crystallography), beamline instrumentation developments and source improvements. The early work using bending-magnet radiation led to the funding of several dedicated facilities in the US and elsewhere in the world – the so-called second-generation light sources. Early work with wiggler and undulator insertion devices led to funding of third-generation sources better optimized for insertion device sources, particularly undulators.

Keywords: EXAFS; protein crystallography; electronic structure; X-ray photoemission; metalloproteins; Stanford SSRP.

1. Introduction

As one of the first synchrotron radiation user facilities to significantly exploit a multi-GeV storage ring and to provide radiation from the UV to hard X-rays (Winick, 1974), many important scientific results came in the early years of the SSRP (it was called the Stanford Synchrotron Radiation Project until 1976) as well as contributions to the development of sources, beamline instrumentation and the general features of user facilities. Although severely limited by operating parasitically on the high-energy physics colliding-beam program on the SPEAR storage ring, the first beamline was an instant scientific success. Some of the initial results in surface science, materials science and crystallography are described later in this report. The initial SSRP user facility was funded with $1.2 million from the US National Science Foundation (NSF) in July 1973, with S. Doniach as director, W. Spicer as deputy director and H. Winick as associate director. The facility was based on the utilization of an existing tangential port on a bending-magnet vacuum chamber which accepted radiation with a total of 11.5 mrad of horizontal divergence. It began operation in May 1974. Related activities that preceded this are described in §3 of this report.

This first SSRP user facility beamline (see Fig. 1) served five simultaneously operating stations, each with a monochromator, spanning the photon energy range from ~6 eV to ~30 keV. On one of these stations the first extended-range VUV/soft X-ray grazing-incidence grating monochromator (the Grasshopper) was implemented, providing access to core levels up to ~1 keV for surface studies and atomic and molecular physics experiments. The Grasshopper was the first monochromator above ~40 eV with fixed entrance and exit slits, the former a requirement for use on a synchrotron radiation source. More details about the early VUV/soft X-ray results are given in §4.

On another station a rapidly tunable hard X-ray monochromator with fixed exit direction was implemented. With this instrument EXAFS spectra could be taken in minutes, even with only a few milliamperes of stored current, which was typical of parasitic operating conditions in 1974. This is to be compared with the hundreds of hours it took to obtain similar spectra (with poorer signal-to-noise ratios) on rotating-anode sources. This improvement in flux on the sample (about five orders of magnitude) made it possible to measure EXAFS spectra in a broad range of materials, including biological materials where the atoms of interest are present in low concentrations, leading to the transformation of EXAFS from a laboratory curiosity to a powerful tool of structural analysis. More details about the early EXAFS results are given in §5.

On a curved-crystal/bent-mirror double-focusing hard X-ray station the first protein crystallography studies were performed showing, among other results, that the high intensity of synchrotron radiation allowed structural data to be taken before radiation damage set in. More details about the early crystallography results are given in §6.

Early in the process of developing the five experimental stations on beamline 1, the SSRP formed participating research teams with other institutions (Bell Laboratories, California Institute of Technology, US Naval Weapons Center at China Lake California, Xerox Corporation, Stanford University and the University of Washington). This brought in expertise and additional funding and

instrumentation to complete and commission the five experimental stations. In return, these groups were given priority access for their experiments for a fraction of the available time.

To provide rapid and convenient experimenter-controlled independent access to each of these stations, the hutch system and associated hutch personnel protection system were developed (Winick, 1974). Other early developments on the first beamline included cooled grazing-incidence total-reflection mirrors, photon-beam steering using local bumps in the electron orbit and photon-beam position monitors, computer control of monochromator scanning, and an X-ray pinhole camera to measure the size and shape of the stored electron beam.

The immediate success of the first beamline led to NSF funding of \$741 000 in 1975–1976 for a second bending-magnet line at the SSRP. This line began operation in June 1976 serving three experimental stations with hard X-rays. Two of these employed toroidal grazing-incidence focusing mirrors accepting up to 5 mrad of horizontal divergence to increase the flux density. The high power density on monochromator crystals provided by these focusing systems led to the development of the first water-cooled silicon-crystal monochromators.

While beamline 2 was in construction, evidence for the existence of superheavy elements was reported in experiments using proton-induced X-ray fluorescence. To check these results using more sensitive X-ray-induced X-ray fluorescence a temporary experiment was set up on beamline 2 by a group from Oak Ridge National Laboratory led by Cullie Sparks. The results (Sparks *et al.*, 1977) showed definitively that these elements could not be present in the concentrations reported, a result which, although negative, was of great significance since it stopped the expenditure of resources to follow up the spurious initial result using less sensitive methods. In the process the superb capability of synchrotron radiation for trace-element analysis was proven. Such studies are now routinely pursued at many facilities, including the SSRL where the technique is used to lower detection limits of contaminants on the surface of silicon wafers.

The many important experimental results from the successful initial utilization of synchrotron radiation over a broad spectral range at the SSRP led to strong user pressure for additional facilities in the US and abroad. In 1976 the US National Research Council formed a panel to 'Assess the National Need for Facilities Dedicated to the Production of Synchrotron Radiation'. As input to the deliberations of the panel, the SSRP produced a detailed report on the experience and prospects of using a multi-GeV storage ring for synchrotron radiation research (Hodgson, Winick & Chu, 1976).

Shortly after the report of the panel, the SSRP received \$6.7 million from the NSF for a major expansion of facilities, called Phase 2, including a new building to house the proposed three new bending-magnet beamlines plus one wiggler line, all to be constructed from November 1977 to October 1980. After the successful test of the first wiggler (see below) these plans were revised. The new plan reduced the number of bending-magnet lines to one so that the same funds could provide for a second wiggler line in an extension to the existing building housing the first two bending-magnet lines (see Fig. 2). The one bending-magnet line was beamline 3, which included a second grasshopper monochromator and the JUMBO monochromator which uniquely covered the photon energy range from 0.8 to

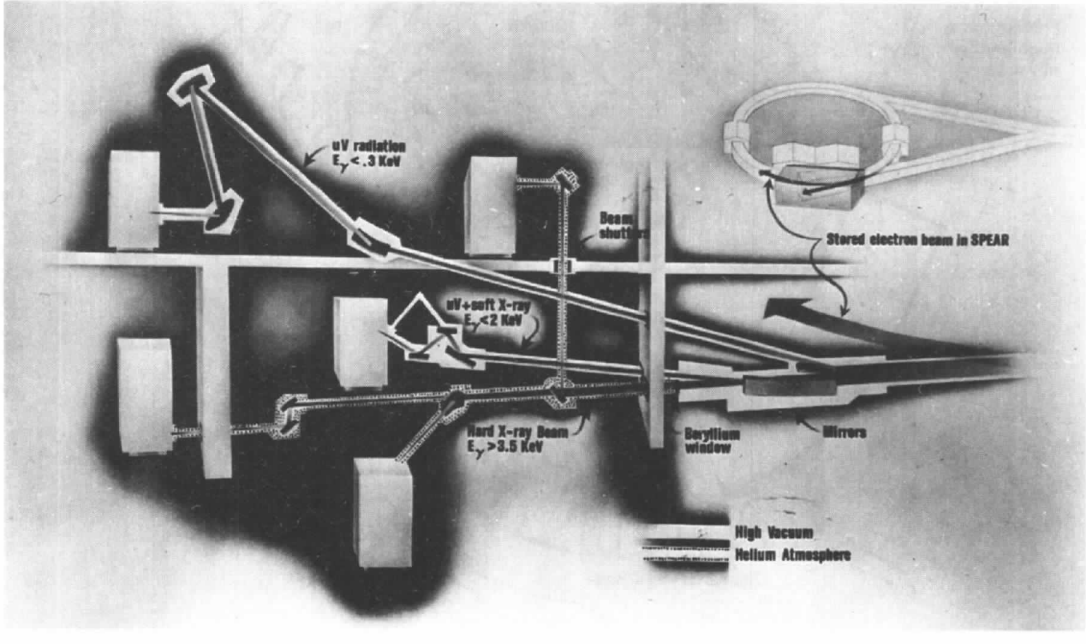


Figure 1
Drawing of the first SSRP beamline showing how 11.5 mrad of horizontal divergence from a SPEAR bending magnet was shared by five simultaneously operational experimental stations, each with a monochromator.

4.5 keV (Cerino *et al.*, 1980; Hussain *et al.*, 1982). Primarily used for surface EXAFS during its first ten years of service (Stohr *et al.*, 1982), JUMBO saw a resurgence of interest in its second decade as it became used for standing-wave studies in environmental and semiconductor research as well as EXAFS on environmental samples. The latter research was facilitated by the introduction of YB_{66} monochromator crystals which made the difficult Mg, Al and Si *K*-edge regions accessible (Wong *et al.*, 1990).

Also, in the mid-1970's, approval was given for the construction of new dedicated facilities, the so-called second-generation light sources, in the US (the Aladdin facility at the University of Wisconsin and the National Synchrotron Light Source at Brookhaven National Laboratory) and in Germany (the BESSY facility in Berlin), Japan (the Photon Factory at KEK in Tsukuba) and the UK (the SRS at Daresbury). The many source and beamline instrumentation developments in the early years of the SSRL were important input to the design of these new facilities.

2. Early source developments

The euphoria that came with the initial use of synchrotron radiation from SPEAR operating at electron energies from 2.4 to 3.7 GeV was dampened when SPEAR began extensive operation below 2 GeV to study new particles that were discovered starting in November 1974. For example, studies of the psi particle, for which Burton Richter shared the Nobel Prize in 1976, required that the ring operates at 1.5 GeV. At this low electron energy the magnetic field in the SPEAR bending magnets is 0.39 T, resulting in a critical energy of the synchrotron radiation spectrum of only 600 eV. Under these operating conditions VUV/soft X-ray experiments could continue on the two stations of beamline 1 designed for the use of photons below ~1 keV, but there was negligible flux of X-rays above ~3 keV for the three stations designed for hard X-rays on beamline 1 and for the three hard X-ray stations of beamline 2. Furthermore, the maximum current that could be used in the colliding-beam mode at this energy was ~3 mA. As a parasitic operation, the SSRP had no control over the electron energy.

Frustration over the lack of X-rays reinforced interest in high-field wiggler magnets to extend the radiation spectrum to higher photon energy. Thus, one of the beamlines planned for the phase 2 expansion of facilities was based on a high-field multipole wiggler source. After a wiggler workshop (Winick & Knight, 1977) in 1977 explored insertion devices in general and their possible impact on storage ring operation, the first wiggler (Berndt *et al.*, 1979) (a 1.8 T

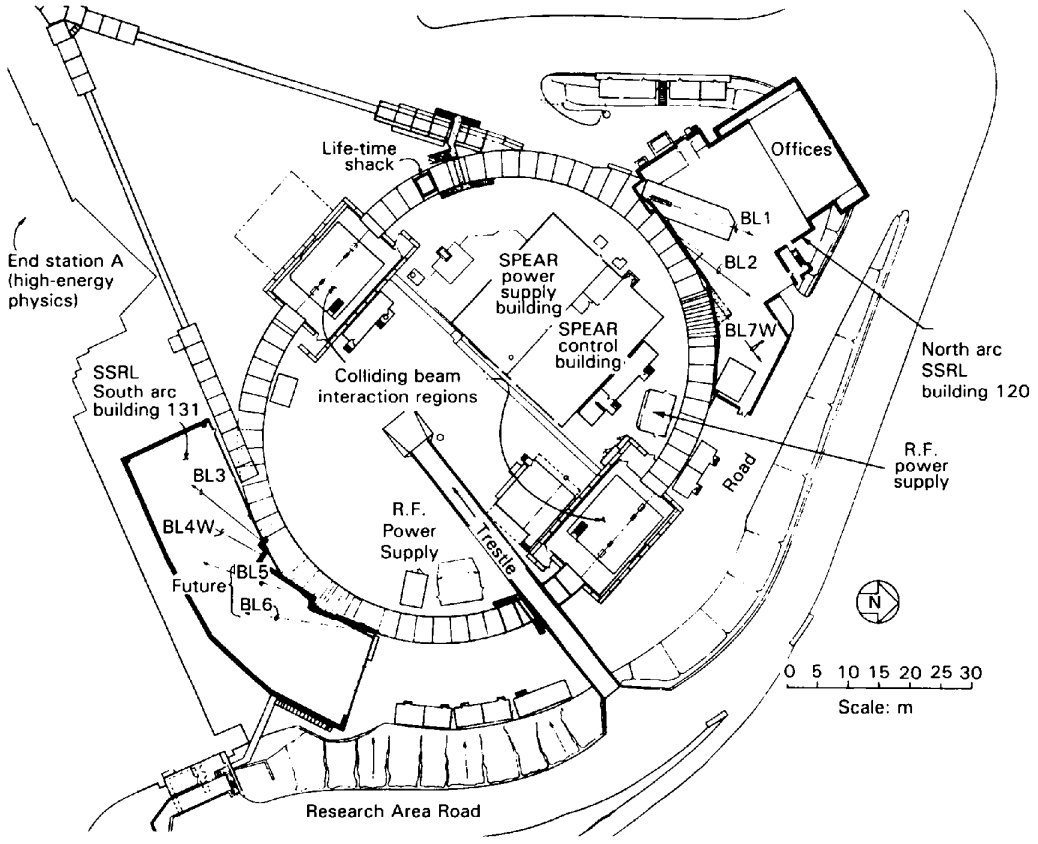


Figure 2
Layout of the SSRL after the phase 2 expansion showing the north arc building 120, with two operational bending-magnet beamlines plus an extension for a new wiggler line, and the new south arc building 131 for bending-magnet beamline 3 and wiggler beamline 4 and future beamlines.

three-period 1.2 m-long electromagnet, see Fig. 3) was designed, installed in SPEAR in 1978 and quickly shown to be compatible with stored-beam and colliding-beam operation. At 1.8 T the critical energy of SPEAR at 1.5 GeV was raised to 2.7 keV, a level at which considerable hard X-ray flux was produced. Furthermore, the six poles of the magnet enhanced the intensity by a factor of six. The beamline was completed in 1979 so that experiments could be carried out exploiting the increase in intensity and extension of spectral range. (The completion of the beamline had been delayed pending demonstration that the wiggler was compatible with ring operation.) This was the first such magnet used routinely as an X-ray source for experiments.

Around mid-1979 Klaus Halbach of the LBNL pointed out that short-period undulators could be constructed using permanent magnets. Prior to this, only superconducting magnets were used to achieve the required performance and these posed complications in a facility that was still primarily used for high-energy-physics colliding-beam experiments. In collaboration with Halbach, the first undulator (Halbach *et al.*, 1981) (a 2 m-long pure permanent-magnet device with a period length of 6.1 cm and a maximum K value of 1.4, see Fig. 4) was designed in 1979. It was installed in SPEAR and the first spectra taken in 1980. The first experiment using the quasi-monochromatic undulator radiation was carried out in 1981 (Winick, Boyce *et al.*, 1983).

Insertion-device development at the SSRL continued with the design and construction, in collaboration with the LBNL and EXXON, of the 54-pole hybrid wiggler with variable-gap vacuum chamber (Hoyer *et al.*, 1983) and subsequent wigglers and undulators, including the multiple undulator system that could select from four undulators with different periods on the same beamline (Bachrach *et al.*, 1985), the adjustable phase undulator (Carr, 1991) and the elliptical polarizing undulator (Lidia & Carr, 1994).

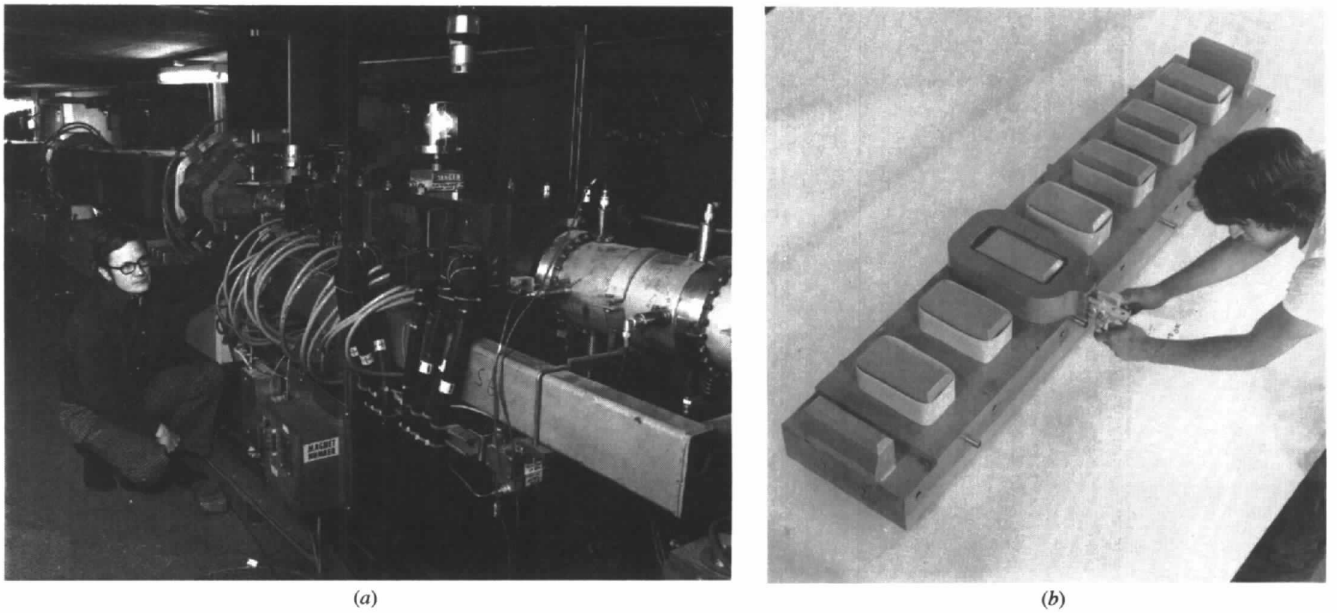
The early experience with insertion devices at the SSRL led directly to the widespread perception of the need for third-generation sources; storage rings with lower electron beam emittance and with many straight sections for insertion devices. A design for such a source at the SLAC was published in 1983 (Winick, Wiedemann *et al.*, 1983). Since then, about ten such sources have been built around the world and several more are in the design/proposal stage.

The perception of the need for third-generation sources was further reinforced when undulators and associated beamlines were installed into the 15 GeV PEP storage ring at the SLAC in 1986 and extremely high-brightness undulator spectra produced when PEP was operated at 7.1 GeV in a low-emittance (~4 nm rad) mode (Brown *et al.*, 1987; Bienenstock *et al.*, 1989).

After the first electromagnet wiggler and first permanent-magnet undulator were replaced by more powerful devices at the SSRL, these insertion devices were loaned to other laboratories; the wiggler to CHESS at Cornell University where it served as their most powerful source for many years, and the undulator to the SRC at the University of Wisconsin, where it is still in use.

3. Activities prior to the NSF funding for the SSRP in July 1973

Early in the planning for the SPEAR storage ring for electron–positron colliding-beam experiments, the possibility of using synchrotron radiation surfaced. In 1968 William E. Spicer contacted the SLAC staff and its director, Wolfgang K. H. Panofsky, about the usefulness of synchrotron radiation. In 1970 he was joined by Sebastian

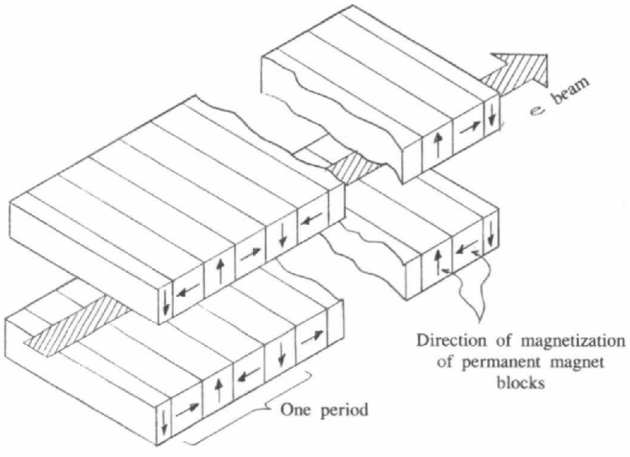


(*a*) (*b*)

Figure 3
(*a*) Photograph of the first wiggler installed in SPEAR in 1978 with James Spencer, the designer. (*b*) Photograph of the lower half of the eight-pole wiggler installed in SPEAR in 1980.

Doniach to initiate discussions among Stanford faculty members including J. Baldeschwieler, A. Bienenstock, who became SSRL director in 1977, W. Marshall and H. Taube. After some encouragement from the NSF, work on a proposal started in March 1971 and a formal proposal was submitted on 2 December 1971.

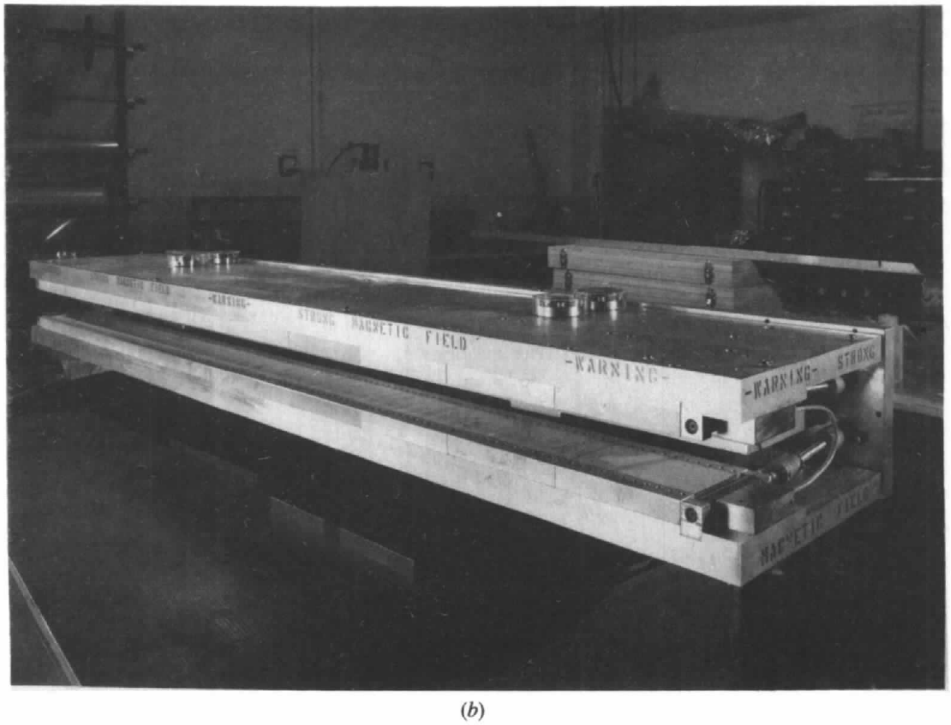
The construction of SPEAR proceeded rapidly from its official start in August 1970 to the first stored beam in April 1972. Included in this construction, and critical to the later utilization of synchrotron radiation from SPEAR, was a single bending-magnet vacuum chamber with a tangential port to allow synchrotron radiation with 11.5 mrad of horizontal divergence to leave the ring into a small alcove within the shielding wall which provided about two square meters for instrumentation. These features were included by Burton Richter, SPEAR project leader, at the strong urging of the SLAC staff scientists Gerhard Fischer and Edward Garwin, who appreciated the potential scientific and technological uses of synchrotron radiation from SPEAR. The existence of this port and the continued support of the SLAC in the implementation of the original front end was critical for the rapid exploitation of synchrotron radiation from SPEAR.



(*a*)

In January 1972 the Center for Materials Research (CMR) at Stanford provided the necessary funds ($5500) to install an ultra-high vacuum valve on this tangential port. This made it possible to later add a beryllium window assembly and other front-end components to this tangential port without venting the storage-ring vacuum system. The CMR also provided $5100 for the design and cost estimate for a one-port three-station facility at SPEAR.

Early in 1972 a decision was made to start a pilot project to use the synchrotron radiation. The design and construction of a beryllium window system (Hoyt & Pianetta, 1973) to extract the radiation started in July 1972 with funds again provided by the CMR and also the Dean of Engineering at Stanford. As a result of discussions with NSF officials a supplementary proposal was submitted in November 1972 to cover the costs for the pilot project, which was focused on high-resolution X-ray photoemission spectroscopy. The NSF authorized funding ($59 000) with a starting date of 1 January 1973. At the first NSF site visit to Stanford on 24 January 1973 it could be reported that the pilot project was



(*b*)

Figure 4
(*a*) Schematic diagram of the first permanent-magnet undulator showing the orientation of the four blocks per period. (*b*) The completed undulator.

well underway and that long-term expansion capabilities for a synchrotron radiation facility at SPEAR were excellent. The site visit also included presentations on the scientific opportunities with synchrotron radiation from Stanford faculty members, outside universities (Caltech and the University of Washington), government laboratories (the Naval Weapons Center at China Lake California), national laboratories (Lawrence Berkeley Laboratory) and industry (Xerox Corporation).

The first synchrotron radiation beam was successfully extracted from the SPEAR storage ring on 7 July 1973. Fig. 5 is a photograph of the beamline inside the SPEAR shielding. Most notable is the highly corroded copper surrounding the beryllium window. The environmental conditions were not the very best ones! In fact, the assembly consisted of two beryllium windows with pumping in between. The first important step had been taken, namely that X-rays could be extracted from the storage ring. From a seemingly endless number of Polaroid pictures of the X-ray beam exiting the beryllium window it was learned that the beam moved around quite a lot, leading to the first thoughts and discussions with the SPEAR machine physics group regarding beam steering.

Notwithstanding serious questions about beam stability, the design and construction of a double-crystal monochromator for 8 keV photons went ahead. It was successfully tested with a conventional X-ray tube and installed immediately behind the beryllium window in the small alcove inside the radiation shielding of the storage ring. The monochromatic 8 keV X-rays then passed through a hole in the radiation shielding into a hutch placed on the parking lot outside the storage ring. The monochromatic X-rays passed through a thin beryllium window into a UHV chamber housing the sample and the electron energy analyzer (cylindrical mirror). A trailer served as the data-acquisition room and sleeping quarters.

With this equipment the first X-ray photoemission spectra of the 4*f* levels of gold were obtained in November 1973 (Fig. 6). These very first scientific results, based on synchrotron radiation from SPEAR, were submitted to *Nature* on 1 March 1974, and appeared in the 19 July 1974 issue (Lindau *et al.*, 1974). The experimental resolution was high enough that it was possible for the first time to obtain an estimate of the inherent linewidth of the 4*f* states. This aspect was elaborated on in a later publication (Lindau *et al.*, 1975). After the NSF funding of the first general user beamline with five experimental stations and associated building in July 1973, construction proceeded quickly and the original hutch had to be removed (see Fig. 7).

4. Early VUV/soft X-ray results

The first beamline had two branch lines dedicated to the VUV and soft X-ray spectral regions: the 4 and 8° beamlines, so-called because they employed grazing-incidence mirrors which deflected part of the 11.5 mrad beam by these angles. The implementation of these beamlines goes back to initiatives taken in late 1972 by a group from the Naval Weapons Center in China Lake California, and the Xerox Research Labs in Palo Alto.

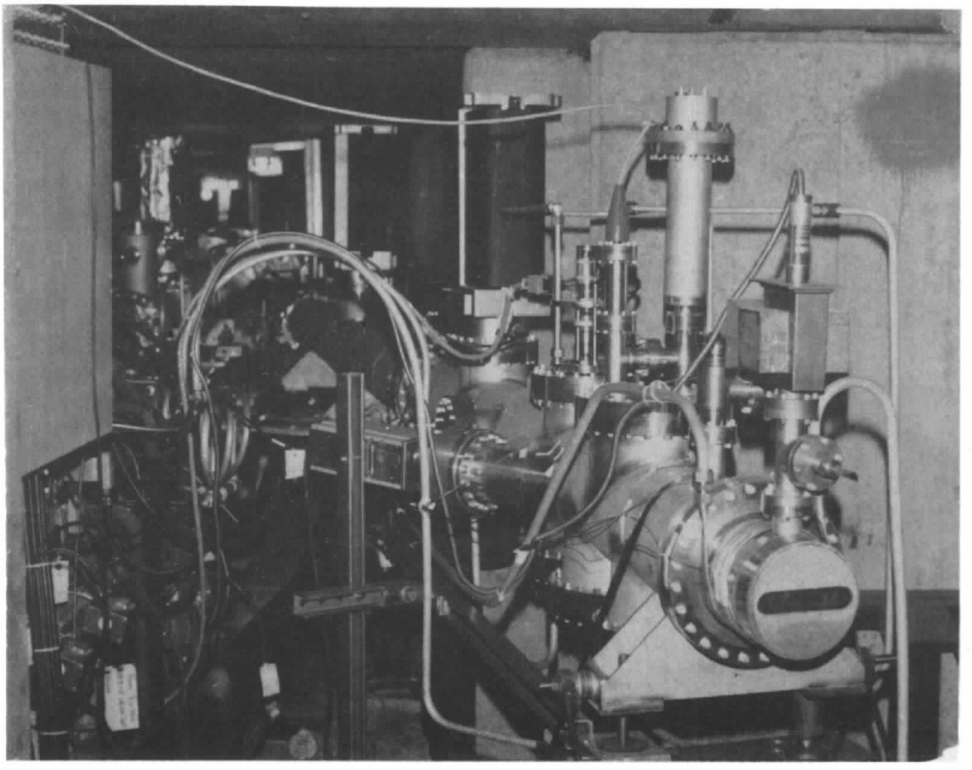


Figure 5
Photograph of the pilot project beamline inside the SPEAR storage ring where the first X-ray beam was extracted on 7 July 1973.

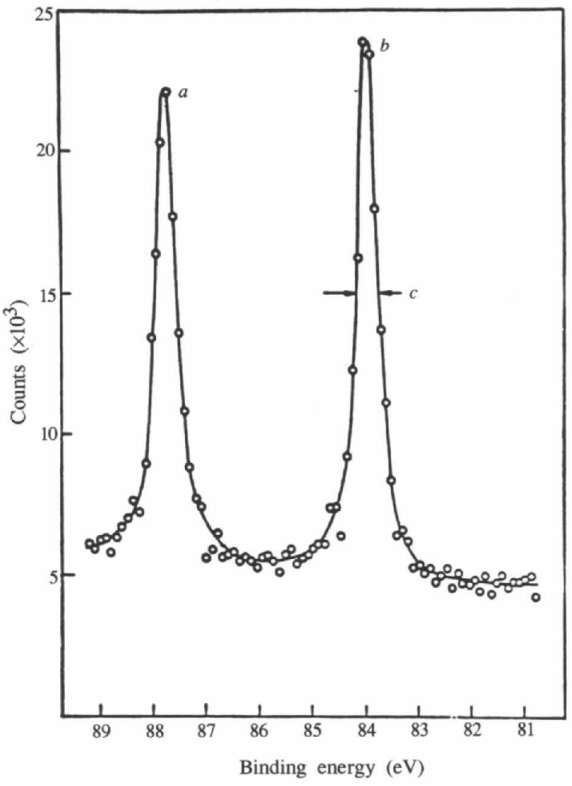


Figure 6
The first scientific result obtained from the pilot project was this electron distribution curve of the 4*f* doublet of gold taken with an 8 keV X-ray beam at a resolution of 0.25 eV which made possible an estimate of the inherent linewidth of the 4*f* states.

At the time of the IV International Conference on Vacuum Ultraviolet Radiation Physics (Koch *et al.*, 1974) in Hamburg on 22–28 July 1974, there were impressive progress reports on both the 8 and 4° beamlines (Rehn *et al.*, 1974; Stanford *et al.*, 1974; Brown *et al.*, 1974; Bachrach *et al.*, 1974). At the first SSRP Users Group Meeting on 24–25 October 1974 there was a report on the first photoemission data on metallic niobium from the 8° beamline. In early December 1974 the first photoemission spectra were obtained on the 4° beamline. Again, gold was the victim of the studies. Many of the advantageous attributes of synchrotron radiation were exploited: the tunability was used to achieve high surface sensitivity (Lindau & Spicer, 1974; Lindau *et al.*, 1976*a*) and to study the energy dependence of the photoionization cross sections from threshold and upwards (Lindau *et al.*, 1976*b*). The extended photon energy region that was now available made it possible to study both valence bands and inner core levels. One such example is shown in Fig. 8, where electron energy distribution curves from gold for excitation energies between 80 and 180 eV are displayed (Lindau *et al.*, 1976*b*). The high resolution and extreme surface sensitivity (one to two atomic layers) made it possible to study surface chemical shifts and surface phenomena in unprecedented detail. One such study is the oxidation of GaAs which was performed on the 4° beamline in early 1975 and published later that year (Pianetta *et al.*, 1975). Fig. 9 shows energy distribution curves, taken at a photon energy of 100 eV to achieve optimal surface sensitivity, for the Ga and As 3*d* core levels as a function of increasing oxygen exposures.

Figure 7
Photograph taken on 20 September 1973 showing the SPEAR ring, pilot project alcove and outdoor hutch which housed the UHV photoemission chamber. Data collection continued as the construction of the first SSRP building proceeded with the experimenters negotiating around the concrete forms and relying on plastic sheets to protect the hutch and UHV chamber from rain.

Early on, angle-resolved photoemission was applied to studies of single crystals of copper and gold (Stohr, McFeely *et al.*, 1976; Stohr, Apai *et al.*, 1976). It was discovered, with some surprise, that the angle-resolved spectra had not converged to the so-called XPS limit even at photon energies as high as 200 eV. A wealth of information could be retrieved on the valence-band electronic structure from these measurements. One such example is shown for copper, where photoemission spectra are taken along the [001] and [111] directions (see Fig. 10).

The advantageous properties of polarized synchrotron radiation were also realised early at the SSRP and applied to absorption measurements at the *K*-edge of boron in boron nitride (Brown *et al.*, 1976). The effects of crystalline

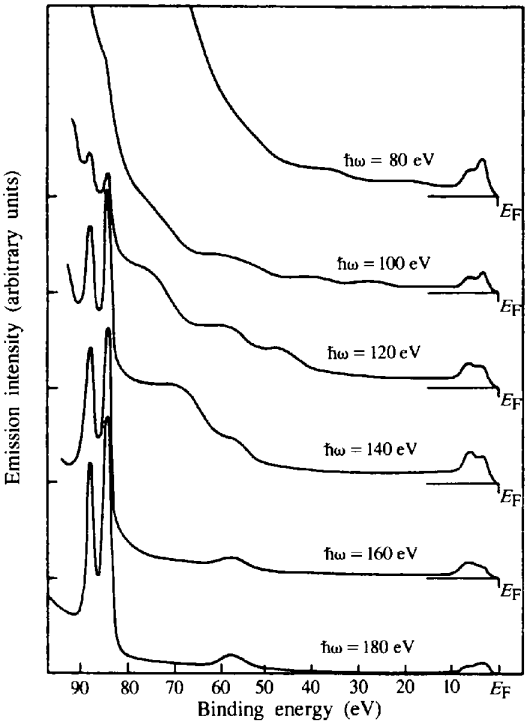


Figure 8
Electron energy distributions from gold for excitation energies between 80 and 180 eV. The horizontal scale gives the binding energies referred to the Fermi level.

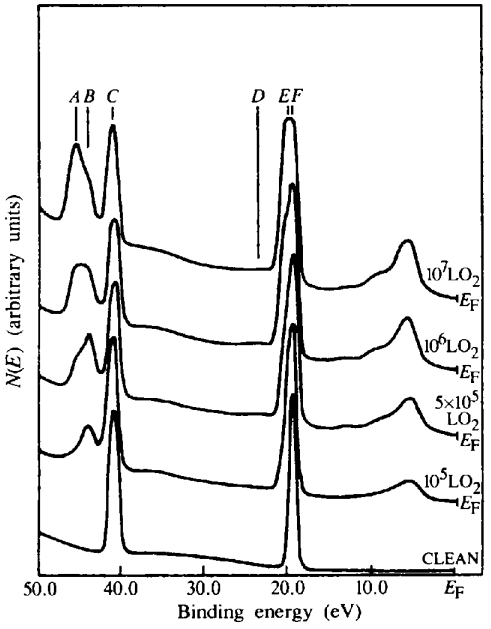


Figure 9
Photomission spectra of clean and oxidized GaAs(110) for 100 eV photon energy.

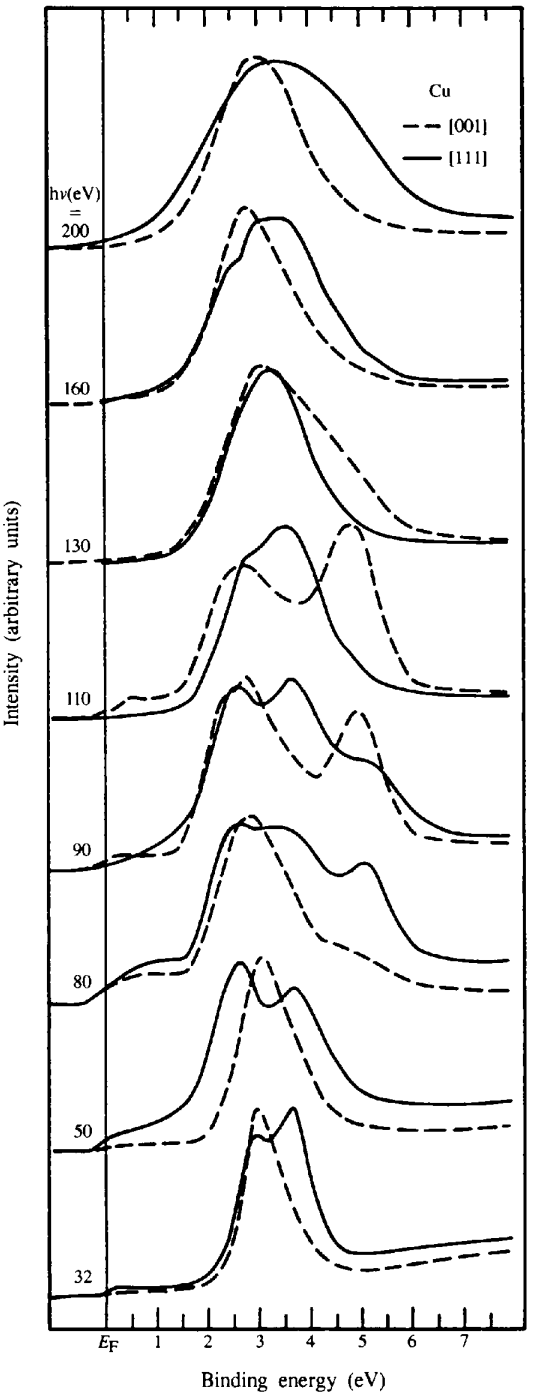


Figure 10
Comparison of photoemission spectra taken along the Cu [001] and [111] directions (dashed and solid lines, respectively) for various photon energies.

anisotropy on the core excitations were clearly revealed, as shown in Fig. 11.

The SSRP came into operation as a US National Facility in May 1974 and a year later a number of significant scientific accomplishments had already been reported, as illustrated above and summarized by Doniach *et al.* (1975). In 1976 the floodgates opened completely and both the 4 and 8° beamlines entered an era of extremely high productivity with the involvement of many research groups. Since then, more than 1000 peer-reviewed papers have been published and over 100 graduate students have based their PhD work on the 4 and 8° beamlines and subsequent beamlines covering the VUV and soft X-ray spectral regions at the SSRL.

The scientific progress was, of course, strongly coupled to improvements in storage ring operation and beamline optics. The following episode can serve as one illustration. Led by Vic Rehn, the China Lake group took on the main responsibility for the beamline optics for both the 4 and 8° beamlines. The first collecting mirror (M_0, receiving the total synchrotron radiation flux) on the 4° beamline was made of copper, thermally stabilized, polished and coated with platinum. In the rush to get the beamline ready for the May 1974 start of operation and because of the special vacuum requirements for components located in the SPEAR vacuum system, the mirror did not have the smoothness according to the high standards set by the China Lake group. Before installation, the measured roughness was 63.9 ± 2 Å and, when it was removed about two years later, it had worsened to 186 ± 14 Å. The replacement mirror, installed in April 1976, had a roughness of 38.9 ± 1.6 Å and spectacular improvements (Bachrach *et al.*, 1976; Rehn & Jones, 1978) in the performance of the beamline followed (see Fig. 12).

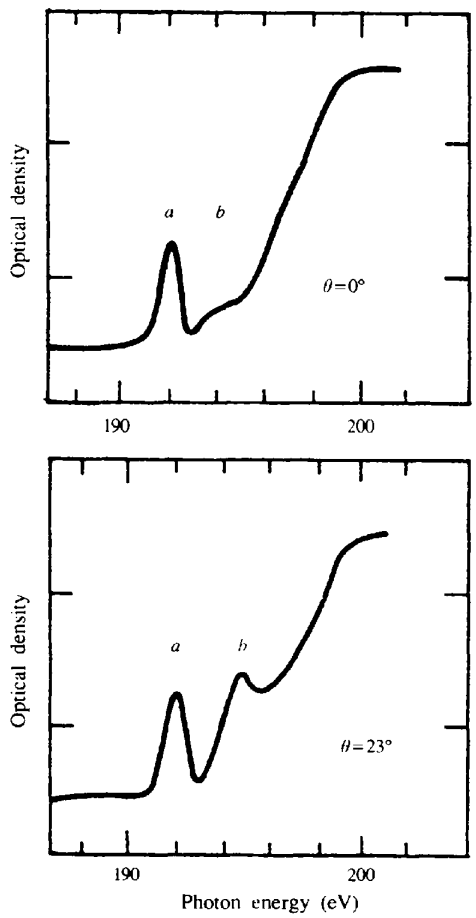


Figure 11
Optical density *versus* photon energy for a thin sample of hexagonal BN. Line *a* is at the beginning of the *K* threshold. The upper curve was taken for $E \perp c$, whereas the lower curve, $\theta = 23°$, had a substantial component of $E \parallel c$.

5. Early results in X-ray absorption spectroscopy

The original proposal to the National Science Foundation for funding to exploit the synchrotron radiation from the SPEAR ring highlighted X-ray absorption spectroscopy as one of the important applications based on the pioneering work of the Seattle group of Sayers, Lytle and Stern. When it became clear that the project would be funded, Seb Doniach, Principal Investigator and Project Director, talked with Peter Eisenberger of Bell Laboratories about the correct kind of technology for producing a tunable monochromatic beam. Eisenberger pointed out the usefulness of a channel-cut silicon crystal which had been developed by Bob Batterman at Cornell, since this could cover a large range of X-ray wavelengths with a very simple mechanical mechanism, namely a one-circle goniometer together with a stepping-motor control. The outgoing monochromatic beam from a channel-cut crystal is fixed in direction but varies slightly in elevation as the wavelength is scanned. A table also under stepping-motor control would be able to keep the sample at the correct height relative to the outgoing beam during the scan.

In 1974 the first tunable X-ray monochromator on the beamline 1–5 end station was constructed in cooperation with the Bell Laboratory and Seattle groups. The other

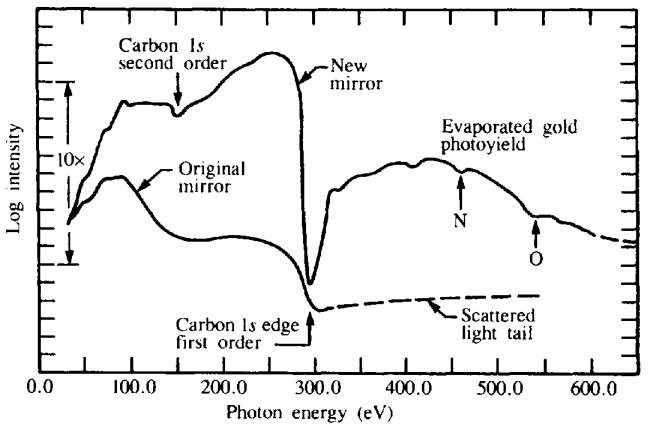


Figure 12
Evaporated gold photoyield spectral distribution for the 4° beamline optical system before and after installation of a new M_0 ultra-smooth platinum-coated mirror. The original mirror had a roughness of 186 Å while that of the new mirror is 39 Å. Note the significant improvement in flux with the new mirror and the strong dispersive loss due to carbon.

important practical issue was the development of the personnel protection system, and the 'hutch' system was evolved whereby an experimenter could change samples without needing supervision by radiation protection staff members (as was the usual case for large-scale particle physics experiments at the SLAC). The first EXAFS hutch was a steel box, about 2.5 feet long and about 1 foot in each transverse dimension. It was adequate to hold a pair of ion chambers and the sample to be studied and was called a hutch since it was about the size of a rabbit hutch. Redundant interlocks assured that the hutch door could only be opened when both of a pair of thick lead shutters were closed. Safety was assured because the hutch was too small for a person to be inside with the door closed.

As soon as the beam was turned on, the enormous advantage of using synchrotron radiation from a stable storage ring beam became immediately evident. Previously, X-ray experiments had been performed at cyclic accelerators such as the 50 Hz DESY synchrotron, with cycle-to-cycle intensity variations as well as variations in intensity, spectral distribution, and source position within each cycle. By contrast, even though SPEAR was being used for synchrotron radiation research in parasitic mode, the spectral distribution was constant and the intensity and source position were relatively stable over periods on the scale of hours. The slow drift in source position and its changes from fill to fill led to the development of the first beam-steering system, initially under manual control and later in a closed loop using a photon beam position monitor.

As a result of the roughly 10^4–10^5 increase in counting rate relative to tunable radiation from X-ray tubes, it was possible to look at X-ray absorption fine structure in very simple systems. This was immediately evident upon seeing the dramatic difference in time to measure a spectrum of a copper foil using station 1–5 compared with a rotating-anode source. Fig. 13 shows spectra taken in 20 min at the

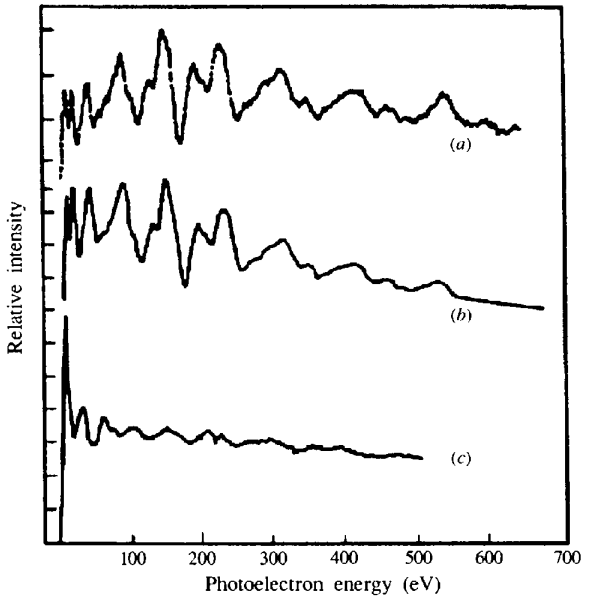


Figure 13
Synchrotron radiation revolutionized the capability of obtaining EXAFS spectra. This is dramatically illustrated by comparing the Cu foil spectrum recorded with a 60 kW rotating-anode source [curve (*a*), top] with that obtained from SSRL station 1–5 [curve (*b*), middle]. The synchrotron data were recorded in 20 min and extend to higher energy with better signal-to-noise than that recorded in two weeks with the conventional source.

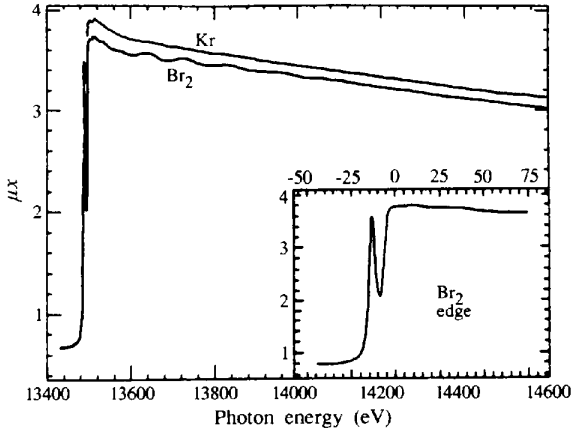


Figure 14
Among the first X-ray absorption spectra taken at the SSRP: *K*-edge X-ray absorption spectra for Kr and Br_2 gases. The Kr energy scale has been shifted and the curve displaced for comparison with Br_2. Near-edge data from Br_2 are given in the inset. (From Kincaid & Eisenberger, 1975*a*.)

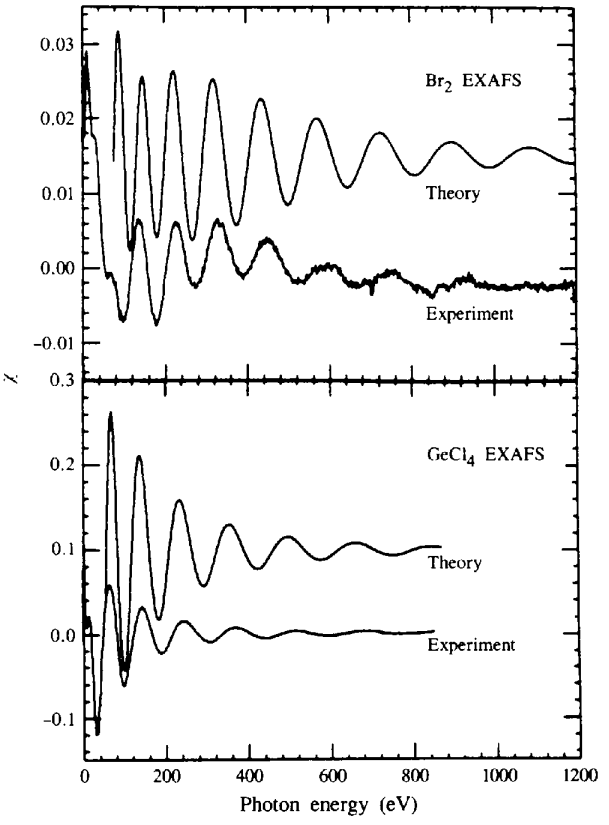


Figure 15
Comparison of theory and experiment for EXAFS oscillations seen in Br_2 and $GeCl_4$. The theoretical curves have been displaced for clarity. (From Kincaid & Eisenberger, 1975*a*.)

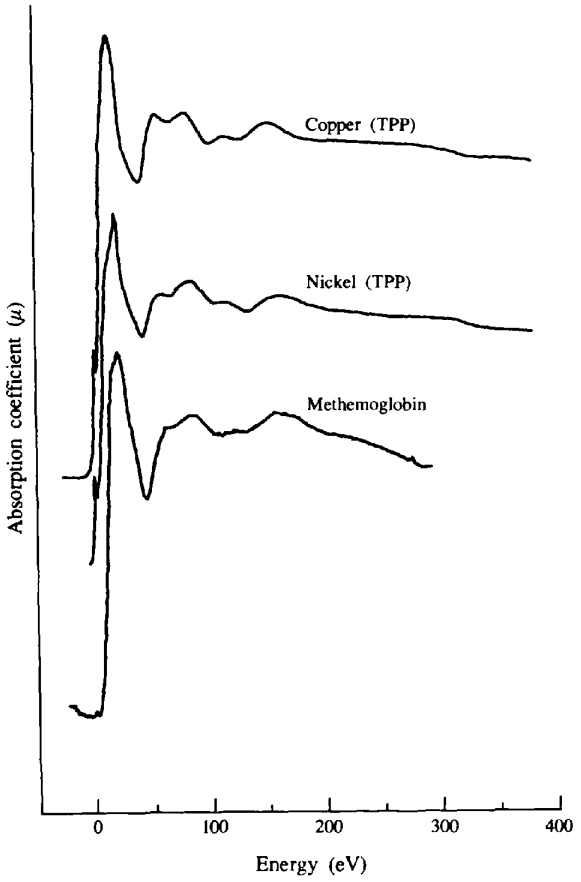


Figure 16
X-ray absorption plotted as a function of energy measured relative to the *K*-edge for copper and nickel tetraphenylporphyrin (TPP) and methemoglobin. The characteristic interference pattern for photoelectrons scattered from the first shell of N atoms and pyrrole C atoms is clearly visible in all these spectra. (From Kincaid *et al.*, 1975.)

SSRL *versus* about two weeks on a 60 kW rotating-anode source. In one of the first quantitative measurements, Kincaid & Eisenberger (1975*a*) looked at the extended X-ray absorption fine structure (EXAFS) oscillations above the *K*-shell absorption edge of bromine in the gaseous dibromine molecule at 13.5 keV and compared it with the absorption edge of krypton at 14.3 keV, for which no such oscillations occur (Fig. 14). The single sinusoidal interference pattern was very evident and allowed a direct measurement of the backscattering phase shift for the outgoing electron from one Br atom when reflected off the second Br atom. A numerical calculation by Kincaid of the backscattering phase shift using a self-consistent Hartree–Fock potential for the bromine gave reasonable agreement with the measured *d* value (Fig. 15). This was the first measurement in which a quantitative theory could be applied to the EXAFS spectra, since earlier measurements using X-ray tube sources had been on dense materials such as crystals and glasses which yielded quite complex spectra, and which at that time were not possible to study theoretically.

Soon after these first measurements, theoretical work by Ashley & Doniach (1975) and independently by Lee & Pendry (1975) showed that backscattering phase shifts for electrons in the few hundred eV range, as computed from electron–atom scattering theory for LEED experiments, could be successfully used to make a quantitative fit to EXAFS data on crystalline solids.

The use of X-ray absorption spectroscopy to study the structure of chemically complex systems was then developed by several groups. Among the first measurements of the X-ray absorption spectra of metal ions in molecules of biological relevance was that published by Kincaid *et al.* (1975) (Figs. 16, 17). This paper described results on Cu and Ni in porphyrin ligands as well as Fe in methemoglobin,

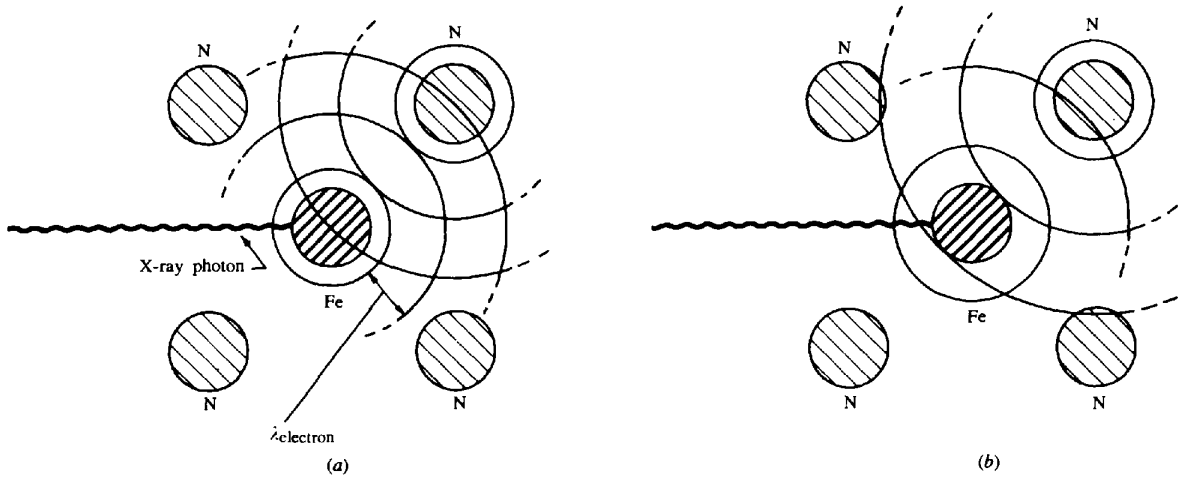


Figure 17
The mechanism of extended X-ray absorption fine structure (EXAFS). The circles denote peaks of the photoelectron wave ejected from the Fe atom in a porphyrin ring and backscattered from the neighboring N atoms. In (*a*) the amplitude of the outgoing and backscattered waves add at the Fe site, leading to a maximum in the X-ray absorption probability. In (*b*) the X-ray energy has been decreased, leading to a longer photoelectron-wavelength electron for which the outgoing and backscattered waves interfere destructively at the Fe site with a resulting minimum in the absorption.

and postulated for the first time that small changes such as the movement of the Fe relative to the porphyrin plane could be detectable and quantified by EXAFS analysis based on solution measurements. A paper on EXAFS of rubredoxin by a group from Bell Laboratories appeared at roughly the same time in which the Fe–S distances were shown to be equal in length, in contrast to the then available crystal structure results (Schulman *et al.*, 1975). Further work on rubredoxin was also published by Sayers *et al.* (1976). Another advance was in the first use of XAS to study local structure in liquids by Kincaid & Eisenberger (1975*b*). Similarly, Hunter *et al.* (1976) characterized the changes of coordination with composition in Cu–As–Se glasses. A wide energy range scan showing the As and Se *K*-edges in $CuAsSe_2$ is shown in Fig. 18.

After the initial experiments a period of consolidation followed in which the use of EXAFS for analyzing the atomic environment of a given chemical element in a complex material was developed as a quantitative tool. As had been originally pointed out by Stern *et al.* (1975), the use of Fourier analysis to obtain a rough estimate of near-neighbor and second-neighbor positions relative to an absorber proved to be very useful. Further refinements in the analysis involved nonlinear least-squares fits to the EXAFS data in terms of the energy-dependent back-scattering phase shift expressed as a sum of individual electron–atom scattering phase shifts. These could be estimated both from first-principles calculations and, as proved important in practice, by measuring the back-scattering phase shifts in model compounds. The first description of the least-squares approach with applications to chemical complexes was by Cramer, Eccles, Kutzler, Hodgson & Doniach (1976). This was elaborated in a more detailed study of Mo complexes, where accuracy and error limits were carefully examined (Cramer, Hodgson, Stiefel & Newton, 1978). Another important step was the development of the use of X-ray fluorescence detection for measuring XAS in very dilute samples (Jaklevic *et al.*, 1977).

The promise of EXAFS as an important new tool to investigate the structure and function in biological and chemical systems was quickly realised. The first application of EXAFS to determine *de novo* a metal site in a metalloprotein was the remarkable discovery of an unprecedented polynuclear Mo–Fe–S cluster in the nitrogenase enzyme from the EXAFS data analysis (Fig. 19) (Cramer, Hodgson, Gillum & Mortenson, 1978; Cramer, Gillum *et al.*, 1978). Applications to cytochrome P-450 (Cramer, Dawson *et al.*, 1978) quantified the presence of an axial sulfur ligand. The 'blue copper protein' azurin was found to have an unusually short Cu–S ligand which defined the electronic structure and function of the active site (Tullius *et al.*, 1978).

As the ability to produce quantitative measurements for distances and chemical composition of the near-neighbor environment of a scatterer improved, applications were made to a variety of fields, including metalloproteins, supported catalysts (Sinfelt *et al.*, 1978), materials under pressure (Ingalls *et al.*, 1978) and surface science (Citrin *et al.*, 1978).

The near-edge structure in X-ray absorption spectra is also of considerable interest to chemists. In particular, the

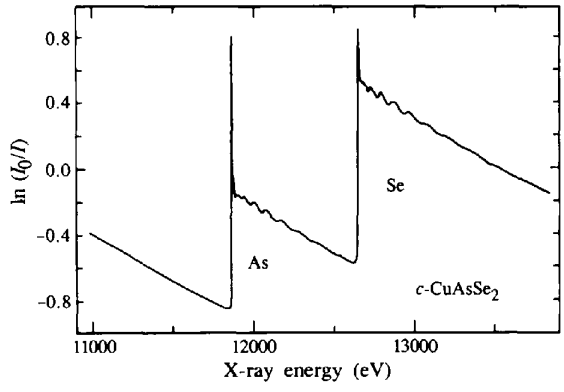


Figure 18
A wide energy range X-ray absorption scan showing the As and Se *K*-edges in $CuAsSe_2$. Although As and Se are adjacent in the Periodic Table, the energy separation is sufficient that Hunter *et al.* (1976) were able to determine the changes of As and Se coordination in amorphous Cu–As_2Se_3 glasses with Cu concentration.

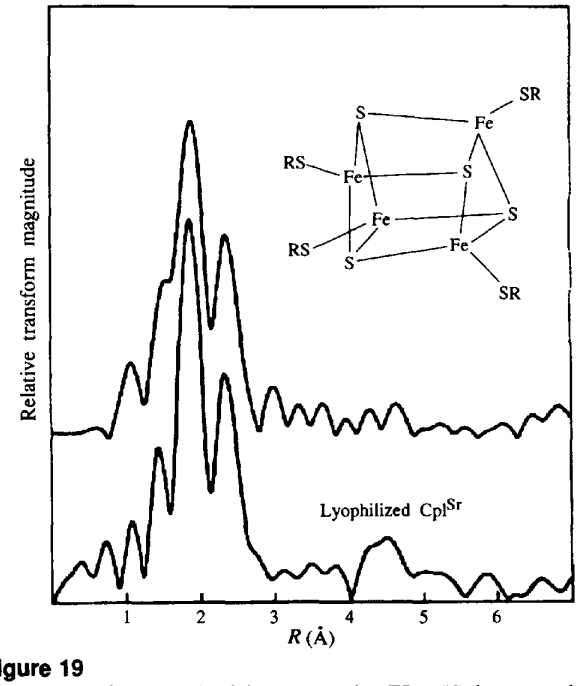


Figure 19
Fourier transforms (FT) of the Mo *K*-edge EXAFS data recorded at the SSRL for the nitrogenase MoFe protein (bottom) compared with the FT of the EXAFS from the Fe *K*-edge of a synthetic model 'cubane' Fe_4–S_4 cluster (top) (from Cramer, Eccles, Kutzler, Hodgson & Doniach, 1976). The FT of the protein exhibited strong first and second shells that had striking similarity to the known model structure which contained metal–sulfur and metal–metal distances in the ordered cube. Quantitative analysis based on the least-squares approach described by Stern *et al.* (1975) gave rise to the details of the previously unknown Mo polynuclear cluster containing Fe and S.

fact that the threshold for absorption depends on the oxidation state of a metallic ion in a compound was found early on to be a very useful analytic tool (Cramer, Eccles, Kutzler, Hodgson & Mortenson, 1976). Detailed structure of the absorption edge (so-called X-ray absorption near-edge structure, or XANES) also proved to be a fruitful source of information about the atomic environment of an absorber when coupled with detailed multiple-scattering calculations of resonant states close to threshold (Natoli *et al.*, 1980).

Now that more than 20 years have passed, X-ray absorption spectroscopy has become an analytic tool of increasingly broad application to many fields of science and technology, including environmental science where it can provide unique information on the chemical state of contaminants in the environment, and help to understand interfacial phenomena.

6. Early crystallography results

The SSRL pioneered many of the early developments and applications of synchrotron radiation in protein crystallography. The primary contributions were made in demonstrating that monochromatic data collection was possible for protein crystals that were difficult or impossible to study with conventional sources, and in contributing to the development of a completely new approach to solving the classic 'phase problem' for protein structures using synchrotron radiation. Highlights of the SSRL's contributions in the early-to-late 1970's are described below as well as the evolution of multiple-wavelength phasing based on synchrotron data into the 1980's.

The first published single-crystal diffraction studies on proteins using synchrotron radiation were performed at the SSRL on station 1–4 (Webb *et al.*, 1976) and reported in the *Proceedings of the National Academy of Sciences of the USA* (Phillips *et al.*, 1976). This first report addressed questions about the actual gain in diffracted intensities and the ability of biological molecules to handle the high radiation flux from the storage ring. The SSRL was operating in a parasitic mode at the time and the source was only a bending magnet, but the studies on crystals of rubredoxin, azurin and nerve growth factor (NGF) clearly demonstrated dramatically shorter exposure times (3–60-fold), even with stored currents of a few milliamperes, compared with conventional sources (Fig. 20). At non-characteristic wavelengths the intensity gains were much greater. Perhaps most striking was the observation that radiation damage was not nearly as great as had been anticipated and that a decay mechanism was operative which was not linear with dose. Crystals diffracted longer and to higher resolution than could be obtained with rotating-anode sources. Also reported was the observation of enhanced differences in Friedel pairs as a function of wavelength near the *K*-absorption edge of Fe in rubredoxin. Using NGF the effects of low angular divergence were demonstrated to result in improved spatial resolution for large unit cells. Taken together, it was convincingly demonstrated that synchrotron radiation enabled rapid data collection from smaller crystals to higher resolution than possible with any conventional X-ray source. Later, in 1976, more details about the magnitude of anomalous-scattering effects were published, including difference Fourier maps which demonstrated the wavelength-dependence of the Fe signal for rubredoxin (Hodgson, Phillips & Wlodawer, 1976).

More extensive analysis of the results of protein diffraction studies using synchrotron radiation were published in *Acta Crystallographica* (Phillips *et al.*, 1977). This paper described quantitative measurement of beam flux on the sample and the use of f' and f'' differences to locate the Fe atom in rubredoxin. The results pointed toward the

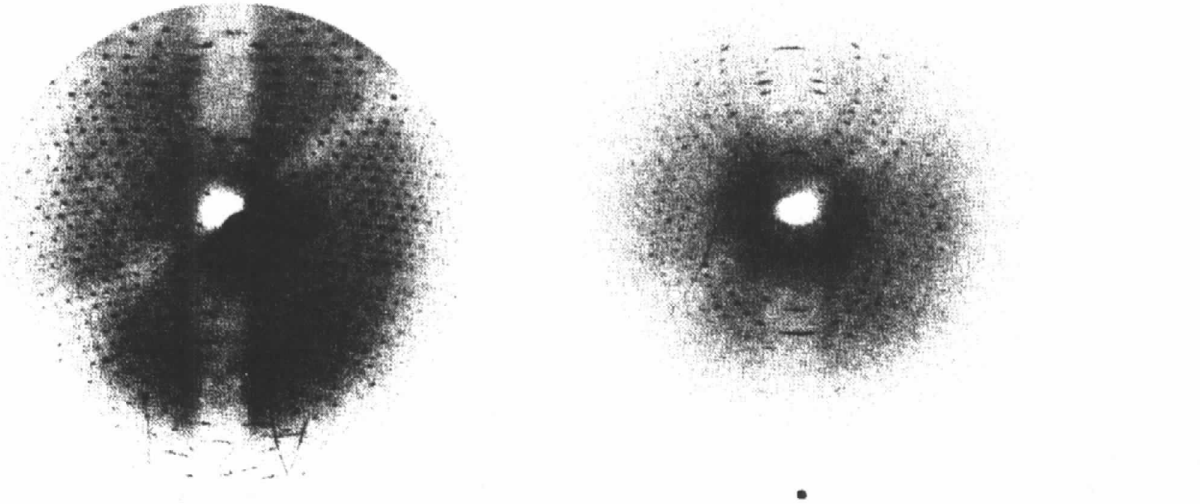


Figure 20
One of the first cone-axis oscillation photographs of protein crystals recorded using synchrotron radiation. The measurements were made at the SSRP. Shown are the synchrotron image (left) and the image taken using a copper-anode sealed tube (right) as described by Phillips *et al.* (1976). The image recorded with synchrotron radiation required much less time (10 min *versus* 6 h) and extended to higher resolution. The crystal sample was azurin.

effective use of anomalous scattering as a means of solving the phase problem in protein crystallography. After the successful isolation and crystallization of a protein, indeed the greatest obstacle to solving the crystal structure is the determination of the crystallographic phases. Traditionally, the phases of the individual reflections have been determined by the multiple isomorphous replacement (MIR) method. However, this method relies on the ability to successfully produce (by binding heavy atoms) a series of independent isomorphous heavy-atom derivatives, which involves a certain element of luck, is often time consuming, and usually significantly reduces the resolution of the diffraction pattern. It was realised many years ago, before synchrotron radiation became available to the research community, that the phase problem could be solved by anomalous-scattering methods using data collected at different wavelengths (Okaya & Pepinsky, 1956; Herzenberg & Lau, 1967; Hoppe & Jakubowski, 1975). As described in the *Acta Crystallographica* paper (Phillips *et al.*, 1977), data collected at three wavelengths were used to calculate phases based on anomalous-scattering data measured with synchrotron radiation where the magnitudes of the anomalous effects could be significantly strengthened by measurements made near to absorption edges.

Interest in the use of anomalous scattering led to the development of a program at the SSRL, in close collaboration with David and Lieselotte Templeton from the University of California at Berkeley, to investigate fundamental aspects of this interesting phenomenon that could be effectively exploited with synchrotron radiation. The first accurate measurements of the anomalous-scattering terms for the caesium L_{III}-edge were reported in *Science* (Phillips *et al.*, 1978). These measurements were carried out using an Enraf–Nonius CAD-4 diffractometer which had been specially modified to have the diffracted beam detector move in the vertical plane because of the horizontal plane polarization of the synchrotron radiation. Using the known crystal structure of caesium hydrogen tartrate and data sets measured at multiple wavelengths, values of f' and f'' were derived by a least-squares refinement approach. The scattering power of caesium was observed to change by as much as 25 electrons, the largest such value measured at that time. A full description of the CAD-4 diffractometer hardware and software as adapted to the synchrotron beamline was published (Phillips *et al.*, 1979), including a comparison of the system performance using synchrotron radiation and a conventional source, and a discussion of applications to fundamental anomalous-scattering studies.

A more complete analysis for results on caesium and extensions to study the *K*-edge of cobalt were published in *Acta Crystallographica* (Templeton *et al.*, 1980). In this study a Kramers–Kronig transform was used to calculate f'' data from measured absorption curves (which are proportional to f'') and the results were compared with values calculated independently from diffraction measurements. The overall very good agreement provided additional validation for the diffraction measurement approach and illustrated that accurate values of the anomalous-scattering terms could be determined from simple absorption measurements. This approach would eventually become a standard means of determining the values from a specific sample in a multiple-wavelength anomalous-dispersion phasing experiment.

It was recognized that the larger the anomalous-scattering effects were, the stronger the phasing power that could be derived. Because of their orbital vacancies in higher lying atomic orbitals, it was expected that there would be very large anomalous-scattering terms for the lanthanide and other heavy-metal *L*-edges (such effects had been noted in X-ray absorption measurements by a number of others). These effects were systematically investigated and quantified in a *Proceedings of the National Academy of Sciences of the USA* paper (Lye *et al.*, 1980). The prominent 'white lines' of these elements occur as narrow transitions within 5–10 eV of their absorption thresholds. The resulting changes in the imaginary (f'') and real (f') components of the anomalous terms are correspondingly very large. Europium was observed, for example, to have f' values as negative as *ca* −30 electrons (Fig. 21). Applications of these effects to protein crystallography and to solution and membrane scattering were described. More quantitative studies using the diffraction approach developed with Cs and Co were made with Sm and even larger effects were observed (Templeton *et al.*, 1982).

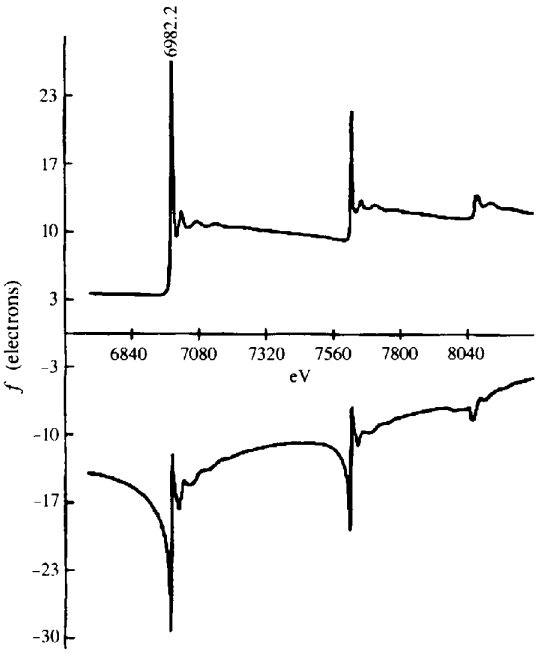


Figure 21
An example of the very large values of the anomalous-scattering terms f' and f'' observed near the *L*-edges for heavy elements such as the lanthanides. The sharp 'white line' absorption near threshold for the europium ion is seen to give values of f'' of nearly 25 electrons as discussed in detail by Templeton *et al.* (1980). The accompanying changes in the real scattering power, f', decrease to almost −30 electrons. The wavelength dependence of such effects can be used to solve the phase problem as described in the text.

Throughout this time it became increasingly apparent that measurements of data sets at multiple wavelengths chosen to make optimum use of changes in anomalous-dispersion terms could indeed provide a powerful approach to solving the phase problem. A theoretical and practical analysis as to the best strategy for such experiments was published in *Acta Crystallographica* (Phillips & Hodgson, 1980). In this paper the very large effects observed at the lanthanide and other heavy-metal *L*-edges were specifically considered and were observed to be very powerful contributors in phasing diffraction patterns from macromolecules.

During the early 1980's instrumentation developments, especially at the SSRL and LURE, contributed to the practical use of synchrotron radiation for MAD phasing experiments. Most notable was the adaptation of area detectors at the SSRL (Phizackerley *et al.*, 1986) and LURE (Kahn *et al.*, 1985). Measurements by Hendrickson and collaborators at the SSRL illustrated the power of MAD phasing on a known structure (Hendrickson *et al.*, 1988) while similar studies were being performed at LURE (Kahn *et al.*, 1985). Ultimately, one of the first *de novo* MAD structure determinations was based on data recorded on SSRL station 1–5 (Guss *et al.*, 1988). In this study, which made use of anomalous scattering from the single Cu atom intrinsic in the native 'basic blue cucumber' metalloprotein, a single polypeptide of molecular weight 10 100 was solved using data collected at four wavelengths around the Cu *K*-absorption edge. Since that time many structures have been solved using the MAD phasing approach at the SSRL and other synchrotrons around the world. Numerous other advances, most notably the utilization of selenomethionine incorporated into proteins for MAD phasing (Hendrickson, 1991), have contributed to a very large growth in the use of this method in solving protein structures. This technique has subsequently evolved as an important complement to the more conventional multiple isomorphous approach to solving the phase problem for protein crystallography.

The very successful initial operation of the SSRP was due in large measure to the contributions of many at the SLAC and Stanford University. In particular, G. Fischer of the SLAC provided critical contributions to the development of the original concepts for the facility. The initial scientific results were due to the capabilities of those visionary first users who persevered through the frustrations of parasitic operation, with its frequent changes in the operational energy and schedule. Special thanks go to the National Science Foundation for the initial funding of the pilot project and the SSRP, and to J. Budnick and H. Etzel, who played important roles at the NSF in providing support during these early days. The SSRL is funded by the Department of Energy, Office of Basic Energy Sciences, under contract DE-AC03-76SF00515. The Biotechnology Program is supported by the NIH, Biomedical Research Technology Program, National Center for Research Resources. Further support is provided by the Department of Energy, Office of Health and Environmental Research.

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