# SYNCHROTRON RADIATION PROJECTS OF INDUSTRIAL INTEREST

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*Abstract*

The paper briefly reviews the nature and generation of synchrotron radiation. Its role in the investigation of the atomic, molecular and macroscopic structure of a wide range of materials is then presented, along with the significance of such work in industrial strategic research. Industrially related activities at four European synchrotron radiation laboratories are then discussed and details of a compact source, manufactured specifically for commercial use, are presented.

## 1 SYNCHROTRON RADIATION

The generation of synchrotron radiation (s.r.) by relativistic charged particles following curved trajectories in magnetic fields is well documented and the study and construction of dedicated sources, generating this radiation for experimental use, have been pursued for over the last three decades [1],[2],[3],[4]. The following brief description of the nature and generation of s.r. is provided for the benefit of the non-specialist; for a fuller, more scientifically based, survey the reader is referred to the citations and many other published papers.

### *1.1 Generation and Properties of Synchrotron Radiation.*

All charged particles emit electromagnetic radiation (e.m.r.) when experiencing acceleration and many conventional sources of e.m.r. work on this principle. However, when high energy, ultra-relativistic charged particles are subjected to extreme centripetal acceleration in the magnetic fields of a circular particle accelerator (of the order of $10^{15}$ gravities), the resulting radiation - 'Synchrotron Radiation' - has very unusual properties; these are:

- the radiation has a continuous spectrum over a broad range of frequencies - typically extending from microwave frequencies to the x-ray band;
- the radiation is of high intensity; in a typical s.r. source, the amplitude peaks in the x-ray region, with intensities $10^3$ to $10^4$ times greater than a conventional x-ray set;
- the radiation is highly collimated in the vertical plane, with a typical divergence of the order of 1 mrad in the x-ray region;
- the radiation is emitted over the full 360º horizontal plane; the emitting particles are not lost from the synchrotron and the radiation can be channelled continuously and simultaneously to many beam-lines;
- the radiation is polarised (linear on axis, elliptical off-axis) and has a precise, regular time structure.

### *1.2 Synchrotron Radiation Sources.*

The standard s.r. source is a storage ring in which a beam of high energy, relativistic leptons (usually electrons but, occasionally, positrons) circulates through an array of electro-magnets; these both steer the electron beam around the circular path and cause the emission of s.r. in a direction tangential to the electron orbit. The energy lost due to the emission of the energetic s.r. photons is made up by a radio-frequency power system. The charged particle beam travels in a vacuum envelope and the radiation which is to be used for experimental purposes passes through ports on the outside of this vessel.

The energy of the charged particle beam in the storage ring strongly determines the nature of the emitted s.r. To generate a spectrum which extends into the 'hard' x-ray region, electron energies of many GeV are needed - the national Japanese source 'SPRING8' [5] has an electron energy of 8 GeV. At the other extreme, many smaller sources have charged particle energies less than 1 GeV, serving experimenters using vacuum ultra-violet or soft x-ray radiation.

In addition to the bending magnets, it is now usual to incorporate a number of special 'Insertion Magnets', placed in the straight sections between the bending magnets; these generate additional beams of s.r. with specific characteristics. To avoid producing any net deviation of the charged particles, the insertion device must have a zero integral of magnetic field. They are therefore composed of regions of alternating field polarity, producing local (usually horizontal) deflections. These magnet systems fall into two main categories:

- undulators - usually permanent magnet assemblies, generating a large number of beam oscillations of small amplitude; strong interference effects occur and the radiation has a high intensity line spectrum over a very restricted frequency range;
- wigglers - higher field devices producing broad spectrum s.r. extending to higher photon energy and with amplitude enhancement due to the multiplicity of poles; in some cases the wiggler uses superconducting magnets to generate very high fields in a small number of poles; these 'wavelength shifters' produce photons of very high energy, for use in the most demanding experiments.

The photon spectrum emitted by bending and wiggler magnets is characterised by a parameter known as the 'critical energy' ($E_c$). This is the point in the spectrum which equally divides the total integrated spectral energy.

The critical energy is close to the peak of the s.r. spectral curve and experiments can usually be performed using radiation of energy up to a factor of five greater than $E_c$ but, because of reducing intensity, not beyond.

During the evolution of s.r. source design there have been a number of distinct phases. Modern sources are now designated as 'third generation' facilities. These are distinguished by very small transverse dimensions of the circulating beam (typically ~$10^{-3}$m horizontally, ~$10^{-4}$m vertically) and by the use of many wigglers and undulators to generate much of the required radiation.

## 2 USE OF SYNCHROTRON RADIATION

The properties of s.r. described above indicate that it has great potential for any application where intense e.m.r is required. Many such cases are in the areas of the analysis of materials and their structures; these are described in the next section, with an emphasis on the value of such investigations to commercial applications. There are, also, a smaller number of areas where s.r. is used as part of a manufacturing process and these applications are also briefly discussed.

### *2.1 Materials Investigation with S.R.*

The unique properties of s.r. allow investigators to 'probe' matter of widely differing nature and at very dissimilar levels of magnitude, from macroscopic assemblies to atomic structure. These investigations are usually academically oriented [6] and are relevant to many disciplines:

- surface science, studying work functions, boundary features, thin films, surface depositions, contamination, etc.;
- materials science, both steady state and dynamic phenomena, in substances ranging through metals, ceramics, polymers, semiconductors, etc.;
- life and medical sciences, particularly the quantitative identification of the atomic assembly of large bio-molecules (proteins, enzymes, viruses...) and the determination of the micro-structure of biological tissue (muscle, ligament, tendon) in dynamic situations;
- chemistry, particularly the study of catalytic and other complex processes not easily addressed by 'wet' chemistry;
- earth sciences, including the study of trace element concentration, etc. etc.

### *2.2 Industrial Use of Synchrotron Radiation.*

Much of the commercial work carried out by or for industry at s.r. laboratories is confidential and contracts usually guarantee such secrecy; this makes it difficult to survey the work comprehensively. However, there is sufficient evidence to indicate that whilst the industrial use of s.r. covers many different manufacturing sectors, using a range of techniques, most of these involve the use of the x-ray component of the s.r. spectrum [7],[8],[9],[10]. It is also clear that the work is concentrated into what could be classified as 'strategic research' - the investigation of products and processes - rather than fundamental research.

From the experimental stations that are requested, it is known that the most frequently used industrial techniques are:

- glancing angle x-ray reflection/diffraction, probing the surface of a material at variable depth;
- energy dispersive x-ray diffraction, a fast process which allows the identification and classification of phase transitions during dynamic changes (temperature, pressure, chemical reactions, etc.);
- high resolution powder diffraction, a technique allowing the identification of atomic structures of micro-crystalline materials; the technique is available in a conventional x-ray laboratory, but s.r. provides much enhanced speed and resolution;
- x-ray spectroscopy (EXAFS), a technique unique to s.r., which resolves atomic structures in non-crystalline/amorphous materials, sometimes with very low concentration of the 'target' element;
- small angle/wide angle x-ray diffraction, two separate techniques which, when combined, provide structural information of one and two dimensionally ordered systems from the molecular to the macroscopic level;
- protein crystallography, a major technique allowing the full identification of the atomic structure of large bio-molecules, but only if three dimensional fully ordered crystals of the material are available.

The techniques described above are all concerned with investigation and measurement. However, s.r. is also used as a manufacturing tool for x-ray lithography, as described below for two separate procedures.

### *2.3 Use of Synchrotron Radiation for Lithography*

The lithographic process used to manufacture micro-chips conventionally makes use of ultra-violet radiation and currently is able to produce structures with minimum line widths of the order of 0.25 μm. To obtain further reduction in size, achieving higher component densities with a corresponding increase in operating frequency, the use of x-rays for the exposure of the photo-resist is necessary; this appears to offer the possibility of resolving features of 0.07 μm or less [11]. The parallelism and intensity offered by s.r. sources makes them eminently suitable for this work and investigations have been carried out at a number of laboratories [12]. Whilst this technique has not yet matured to the stage of supporting routine manufacture, purpose built sources suitable for use in a manufacturing environment are now being designed and constructed; one such project is reviewed in the next main section.

## 2.4 LIGA

This technology was developed in Karlsruhe, Germany, to produce micro-mechanical components for isotope separation [13]. The required accuracy indicates that lithographic methods are necessary but the specified thickness of the components calls for a process able to penetrate photo-resists to a substantially deeper level than the thin-film lithography used for microelectronics. The resulting LIGA (**Li**thographie, **G**alvanoformung, **A**bformtechnik) process uses s.r. to penetrate to depths of 0.5 mm or greater in the photo-resist. After development, to remove the exposed material, deposition by electrolysis fills the resulting voids and either directly produces the required micro-structure or provides a mould for replication. The micro-components so produced can be of a variety of materials (metals, polymers, ceramics), have height to width aspect ratios of up to 100:1 and side wall accuracies usually better than 1 μm [14]. Unlike thin-film lithography, where soft x-rays provide the necessary penetration, the LIGA technique requires x-ray in the 5 keV range for optimum performance.

# 3 INDUSTRIAL WORK BY EUROPEAN S.R. SOURCES.

To illustrate the range of work being performed, a brief survey of five European s.r. sources is presented; two are high energy storage rings serving a substantial x-ray community, two are medium energy sources and the fifth is a purpose built compact source of 700 MeV, intended principally for lithography.

## 3.1 The ESRF, Grenoble

The European Synchrotron Radiation Facility (ESRF) is Europe's largest purpose-built, dedicated s.r. source [15], supported by international funding and providing facilities for European researchers requiring high intensity hard x-rays. ESRF parameters are given in Table 1.

Table 1: ESRF parameters.

| | | |
|---|---|---|
| Energy | 6 | GeV |
| Circumference | 844 | m |
| Typical beam currents | 160 | mA |
| $E_c$ in bending magnets | 19.2 | keV |
| Beam-lines: bend. magnets | 10 | |
| Beam-lines: insertions | 16 | |

Commercial beam time at the ESRF is about 1 % of the total but, if collaboration between industries and academics entering through the peer reviewed route is included, this figures rises to 5%.

There are three main fields of industrial research:

- pharmaceuticals - with a dozen companies mainly using the protein crystallography technique;
- materials - fifteen companies working in areas such as chemistry, cements, cosmetics, glass, polymers, petroleum, metallurgy, etc.;
- microelectronics - ten companies performing trace element detection on Si wafers, using the x-ray florescence technique.

This last technique is proving so valuable that a joint ESRF/industry initiative is now funding a new experimental station dedicated to these investigations.

Further examples of commercially important industrial work at ESRF are:

- high resolution strain scanning in Al alloy for turbines in aero-engines;
- microanalysis of trace elements in wood by diffraction and fluorescence techniques;
- EXAFS investigation of metallic nano-particle catalysts;
- crystallinity of plastic containers using micro-focus x-ray diffraction.

## 3.2 HASYLAB at DESY, Hamburg.

This German high energy physics laboratory also supports a major s.r. programme, which obtains s.r. principally from the positron accelerator 'DORIS'; the parameters of this storage ring are given in Table 2.

Table 2: DORIS (DESY) parameters.

| | | |
|---|---|---|
| Energy | 4.5 | GeV |
| Circumference | 289 | m |
| $E_c$ in bending magnets | 16 | keV |
| Beam-lines: bend. magnets | 30 | |
| Beam-lines: insertions | 10 | |

Currently, industrial beam time at HASYLAB accounts for 1.5% of total. The Laboratory has long-term (three year) contracts with five commercial companies, three of whom are using EXAFS for catalyst research. These companies provide funding for post-doc positions and, in return, obtain rapid access to beam, help and advice with experiments, etc. However, the companies make additional payments for beam-time and any further support they may require.

Cited highlights of industrial and commercial work performed at HASYLAB are:

- the EXAFS study of Ni/Au catalyst used for the industrial synthesis of hydrogen from methane and water;
- the fast EXAFS of $Cu/ZnO/Al_2O_3$ catalyst during temperature variation;
- the small angle diffraction study of block-copolymers, used as an energy absorber in running shoes and other sports products;
- the power diffraction study of the phases of Fe/Zn alloy as a function of temperature;
- the protein crystallography study of rattle-snake and viper venom.

### *3.3 LURE*

LURE is the French National Laboratory for s.r research. Radiation is obtained from 2 rings: SuperACO, a purpose built, third generation U.V./soft x-ray source, and DCI, an earlier ring originally built for high energy physics. The Laboratory therefore has the advantage of operating the two rings, providing optimum performance in two different parts of the s.r. spectrum. Parameters of the two rings are given in Table 3.

Table 3: SuperACO and DCI Parameters.

| | SuperACO | DCI | |
|---|---|---|---|
| Energy | 0.8 | 1.85 | GeV |
| $E_c$ in bend. magnets | 0.67 | 3.4 | keV |
| $E_c$ in wiggler | | 9.6 | keV |
| Beam-lines: bend mags | 11 | 5 | |
| Beam-lines: insertions | 4 | 6 | |

Direct commercial work accounts for 5% of beam-time but a more accurate indication of industrial use would be 15%, if academic/industry collaborations were included.

LURE has provided statistics relating to the nature of the industries using the facility and the techniques employed; these data are given in Tables 4 and 5.

Table 4: Industries using the LURE facilities.

| Industry | % use |
|---|---|
| Petroleum | 24 |
| Chemicals | 15 |
| Military | 17 |
| Electronics | 13 |
| Pharmaceutical/cosmetics | 11 |
| Metallurgy | 8 |
| Automobile | 6 |
| Small companies | 6 |

Table 5: Techniques favoured by Industry at LURE

| Technique | % use |
|---|---|
| EXAFS | 44 |
| Diffraction | 27 |
| Surfaces | 8 |
| Biology | 14 |
| Infra-red | 7 |

Industrial ‘highlights’ include:

- the structure of skin and hair for cosmetics development;
- the study of catalysts for automobile exhaust systems;
- fluorescence detection for environmental studies.

### *3.4 The SRS at CCLRC, Daresbury Laboratory.*

The SRS is a fifteen year old, medium energy source which supports a large academic programme extending from the infra-red to the x-ray band. This early facility was the first purpose built, dedicated, x-ray source but a major upgrade has enhanced the radiation brightness to meet the needs of the present experimental programme. The source parameters are given in Table 6.

Table 6: Parameters of the Daresbury SRS.

| | | |
|---|---|---|
| Energy | 2 | GeV |
| Circumference | 96 | m. |
| Typical beam current | 250 | mA |
| $E_c$ in bending magnets | 3.2 | keV |
| $E_c$ in super-conduct. wigglers (2) | 13, 16 | keV |
| No. of exp. stations | 40 | |

The Daresbury SRS has been used for industrial work for well over ten years. During this time the percentage of beam-time directly scheduled for commercial applications has varied but is typically between 2% and 3% of the total time available. However, as with the other sources, its is known that many industrial users obtain access through collaboration with academics.

A number of major companies, including ICI, Unilever, Glaxo and Zeneca, have long term contracts, whilst others, including some major pharmaceutical and petro-chemical companies, obtain s.r. and staff effort through shorter term arrangements. The analysis of the work according to technique is similar to the LURE data, with EXAFS, powder diffraction and protein crystallography featuring strongly. The analysis according to industrial sector is given in Table 7.

Table 7: Industrial Sectors using the SRS.

| Industrial Sector | % use |
|---|---|
| General chemicals | 40 |
| Petro-chemicals | 34 |
| Health care | 10 |
| Pharmaceuticals | 9 |
| LIGA | 4 |
| Others | 3 |

LIGA work has also been promoted, with a group of four interested industrial companies forming a ‘club’ to support the work and obtain micro-structures. These included representatives from the automobile engineering, nuclear material processing, and micro-electronics sectors.

Recently, CCLRC has launched a new initiative, named ‘DARTS’. This is intended to make s.r. more easily available to small companies by offering a sample analysis service with a quoted price per sample and a fast turn-round time. DARTS is proving to be popular with companies which have never used s.r. in the past and the service has examined samples as diverse as foam rubber, bladder stones, solar cells, paint, deodorants and toothpaste. The DARTS service is expected to continue to expand and could, in the future, represent greater commercial use of s.r. than the earlier core activity of beam-time use by industry’s own experts.

### *3.5 HELIOS, Oxford Instruments, UK.*

Helios is a ‘compact’ superconducting storage ring, intended for both the development and manufacture of micro-chips by x-ray lithography [11]. The design of the accelerator was carried out through a joint Oxford Instruments (O.I.)/Daresbury Laboratory initiative and O.I. are now offering the source for sale to laboratories and manufacturers; the compact source is sufficiently small to allow delivery of the complete instrument by commercial aircraft and/or road transport. Helios 1 was made to order for IBM, USA and is currently being used for x-ray lithography research. Helios 2 is now commissioned and will shortly be delivered to the National University of Singapore. Parameters relating to Helios 2 are given in Table 8.

Table 8: Parameters of Helios 2.

| | | |
|---|---|---|
| Energy | 700 | MeV |
| Dipole bending field | 4.5 | T |
| Max. beam current | 600 | mA |
| Beam 1/e lifetime | ~ 10 | hours |
| $E_c$ | 1.5 | keV |
| No. of beam-ports | 20 | |

Whilst Helios is designed principally for thin-film x-ray lithography, the emitted radiation is sufficiently energetic to support a programme of LIGA work, though the critical energy is not optimum for this technique. Conventional s.r. sources located at large laboratories require users to travel to the site of the source to make use of the facilities. The availability of Helios now overcomes this problem for lithography work and makes it possible for a manufacturer to use s.r. from a factory based facility.

## 4 CONCLUSION

The data presented for the commercial activities at four laboratories shows that s.r. has the potential for contributing to the understanding of processes and the structure of products in a wide range of manufacturing industries. It is clear from the examples quoted that much of this activity lies in the x-ray part of the spectrum, x-ray spectroscopy and diffraction being the favoured techniques. Hence, industrialists will, most likely, need to use the facilities of medium or high energy laboratory based s.r. sources for this work in the future. In the area of lithography however, soft x-rays are required, and it is expected that purpose-built compact sources, based at manufacturing premises, will be available for this work.

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