Seeing Things in a New Light: Synchrotron Science and the Australian Synchrotron Project

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Introduction

Significant advances in scientific knowledge are often driven by the discovery of new techniques and new ways of examining the building blocks of the world around us. Chadwick's discovery of the neutron was predicated on Wilson's 1911 invention of the cloud chamber. In a similar manner the invention of the spectroscope which briefly became a party amusement,[1] became the vital tool in the study of everything from atomic structure to the composition of stars.

The spectroscopists dream is a radiation source which provides useful photon intensities across as wide a range of wavelengths as possible, and thus accesses many modes of interaction with atoms, molecules, and structures. Perhaps the closest thing we currently have to such an ideal source is the synchrotron. Since the early 60s it has provided increasingly powerful, broad spectrum sources across a huge part of the electromagnetic spectrum and has opened up a new range of techniques, and extended the capabilities of many laboratory-based spectroscopic methods, in addressing many areas of application. The extreme brightness, energy selectivity, time structure, and polarisation options provide powerful tools in materials and biological sciences, medical imaging, and fundamental spectroscopy. The synchrotron radiation source has developed to become the dominant method used in large molecule crystallography, the only technique which can readily access the far IR, which is the best hard X-ray source for investigating materials structure and increasingly a tool for medical imaging and potentially therapies. Indeed the *coming of age* of synchrotron science might be seen in the sharing of the 2003 Chemistry Nobel prize by Roderick MacKinnon largely based on his synchrotron based work on ion channels.[2] The formal participation of NZ research institutions in the Australian Synchrotron project will soon bring the power of these techniques to our doorstep. The nature of synchrotron radiation and several applications of synchrotron-based methods are outlined below.

In July 2004 an announcement was jointly made by the NZ and Victoria State Governments that NZ was to be part of the consortium which constructs the initial suite of beamlines on the Australian Synchrotron.[3] This prompted the question of the role of access to synchrotron-based techniques and how it would fit into the NZ science strategy, given that the costs involved - small in terms of the overall project - are significant in terms of the NZ research budget.

The June 2001 announcement on the construction of the Australian Synchrotron was in many ways a logical progression for a community that now numbers in excess of 140 principal investigators and 400 users. This community, covering fields from protein crystallography, materials, bio- and environmental sciences, medical imaging, and pure spectroscopy, has grown strongly over the past decade in particular, based on Australian investments in, and access to, beamlines at the Photon Factory in Tsukuba, the Advanced Photon Source (APS) in Chicago, and more recently a soft X-ray line at the NSSRC in Taiwan. They have provided a ready, low cost, mechanism for access to the facilities on the basis of peer reviewed merit access.[4] Importantly, the peer reviewed merit access is decided from a strategic perspective within the borders of Australia.

The arguments for an Australian synchrotron were based strongly around the impacts in research, technology, and economic activity, emphasising the desire to be (and stay) internationally competitive in science across a wide range of applications, especially in biotechnology and materials science.[5] Synchrotrons have been perceived as central to these goals in a number of countries; Canada and Taiwan provide interesting and very different examples of this philosophy. Establishment of the Canadian synchrotron was driven largely by a strong spectroscopy community, while the Taiwanese Government made the decision to build a synchrotron against much of the advice of its scientists, because of a commitment to a high technology future.[6] Thus an indigenous synchrotron has been a logical consequence of Australia's increasing use of and dependence on such facilities; there are also major practical advantages, *e.g.* in the handling of potential bio-hazard materials, and avoidance of shipping such materials internationally.

The Australian facility (Fig.1) is now under construction at a cost, in its initial configuration of ~11 beamlines, of $NZ240 M. Of this, the Government of Victoria has provided the $175 M for the storage ring itself, with a consortium of partners (including NZ) contributing to the beamline construction consortium. The building to house the synchrotron was formally handed over to the project team in March, and hand-over of the facility to the operators, with at least four operational beamlines, is targeted for April '07. Thus the synchrotron is well advanced and will provide a major frontline science facility for Australasia, whether NZ chooses to maximise this opportunity or not.

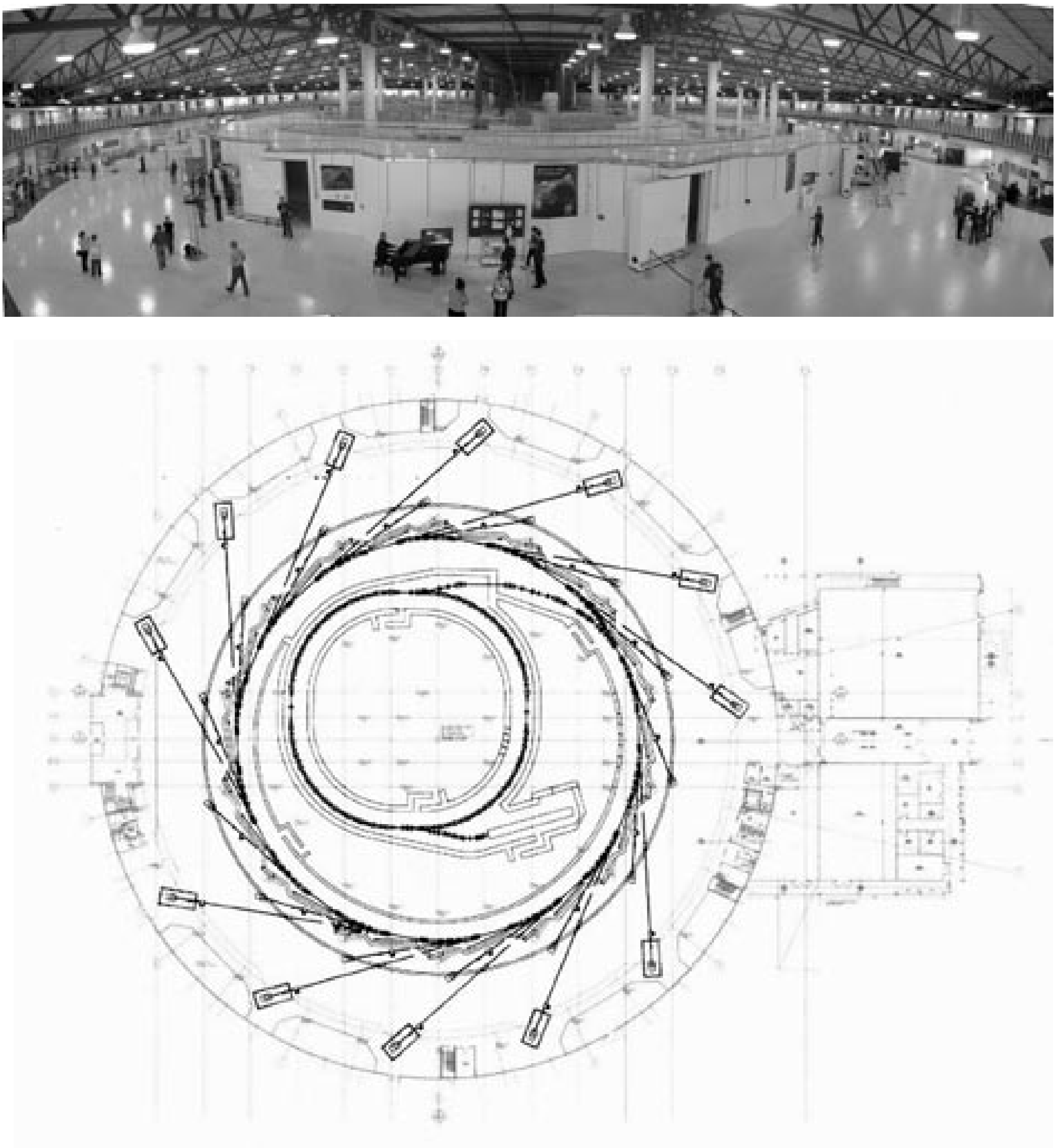

Fig. 1. (a) Wide-angle image (Mar. ’05) of the interior of the building for the Australian Synchrotron. The interior shield walls are visible while the open floor area will eventually contain the beamlines; (b) the floor plan showing the first suite of beamlines extending tangentially from the ring (Reproduced courtesy Australian Synchrotron Project).

Synchrotron Light

The acceleration of electrons produces electromagnetic radiation. Synchrotrons are electron storage rings that exploit this effect. Bunches of electrons orbit at near the speed of light (*c*); in the case of the 3 GeV (giga electron volts) Australian ring, >99.9999% c) and are accelerated or *bent* through a series of magnets that are separated by straight sections. The acceleration through the bend results in a flattened cone of radiation that is emitted tangentially to the bend and captured in a beamline extending along the tangent (Fig. 2). The radiation covers a continuous spectrum from the far IR to a cut-off energy determined by the energy of the orbiting electrons and the radius of

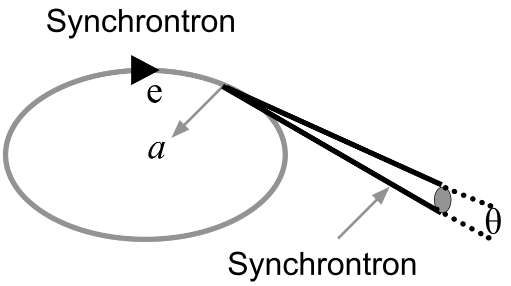

Fig. 2. Flattened radiation cone emitted tangentially to the bend when electrons are accelerated in the magnetic field of a bend magnet.

the bend. The power radiated by the accelerated electron is given by:[7]

$$P = \frac{2}{3}\frac{e^2\gamma^2}{m_0^2c^3}\left|\frac{dp}{dt}\right| \quad .... (1)$$

where m_o is the rest mass of the electron, e is the electron charge, and c the speed of light; $p = m_o v$ *is the momentum* and $(1/m_o).(dp/dt)$ is the acceleration; γ is the ratio of the mass of the relativistic electron to its rest mass m_o and is given by:

$$\gamma = \frac{E}{m_0c^2} = 1957\,E[\mathrm{Ge}V] \quad ....(2)$$

Thus for the 3 GeV Australian Synchrotron, γ is 5,871 while for the 7 GeV Chicago APS, $\gamma = 13{,}699$. For electrons circulating at a fixed radius, r, the energy lost (as synchrotron radiation) by the circulating electrons per orbit is given by:

$$\Delta E[ke\mathrm{V}] = 88.5\frac{E^4[GeV^4]}{r[m]} \quad ....(3)$$

Because the intensity of the emitted radiation follows the fourth power of the ring energy, higher energy gives significantly more synchrotron radiation. The frame of reference effect for these relativistic electrons means this radiation is forward projected more strongly, leading to higher effective brightness of the source. The loss of this energy requires the positioning of an RF cavity in the ring to provide an energy kick to the orbiting electrons, thus restoring their orbital energy. In typical operation the ring current (200 mA in the case of the Australian ring) decays steadily due to scattering and other losses, and the beam current is topped up, sometimes continuously, but generally by injection of *electron bunches* at several scheduled points in an operating day.

The ring energy and bend radius also determine a *critical* energy above which, by definition, half the radiated power is given off. In practice this leads to a relatively rapid drop in flux above this threshold:

$$\varepsilon_c = \frac{2.218E^3}{\rho} = 0.665BE^2 \quad ....(4)$$

ρ is the radius of the bend at the magnet in metres, E the ring energy in GeV, and B is the magnetic field in Tesla. The intensity curve from a bend magnet calculated for the Australian 3 GeV ring (216 m circumference) is shown in Fig. 3. The shape of the curve implies that useful intensity is generally obtained up to ca. 4 x ε_c. The use of *wigglers* and *undulators* positioned in the straight sections of the synchrotron improves performance, both in brightness and by extending the energy range, as discussed below. The calculated flux from a 30 pole 1.9 Tesla wiggler on a straight of the Australian ring is shown in Fig. 4.

In the so called *third generation rings* as is the Australian facility, increasing emphasis is placed on radiation obtained by the wiggling of the electron beam by lines of magnets placed along the straight sections of the ring. If the period of this wiggle is short, the radiation is again a continuous spectrum (although usually extends to higher energy due to tighter radius of the oscillation) and is multiplied in intensity by the number of magnet pairs (and thus oscillations induced) – so called *wiggler radiation*. Longer oscillation periods produce an interference pattern with a characteristic series of *harmonics* producing very high intensities at specific energies. These energies are tuned usually by adjusting the magnet separation and thus the tightness of the oscillation. These undulators are an increasingly favoured source, *e.g.* in protein crystallography.

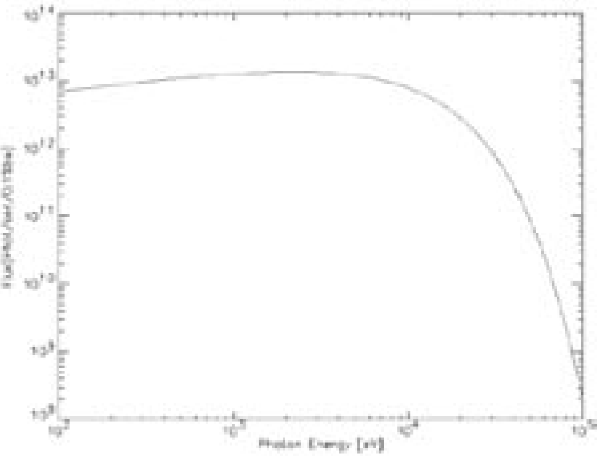

Fig. 3. Intensity curve from a bend magnet calculated for the Australian 3 GeV ring of 216 m circumference.

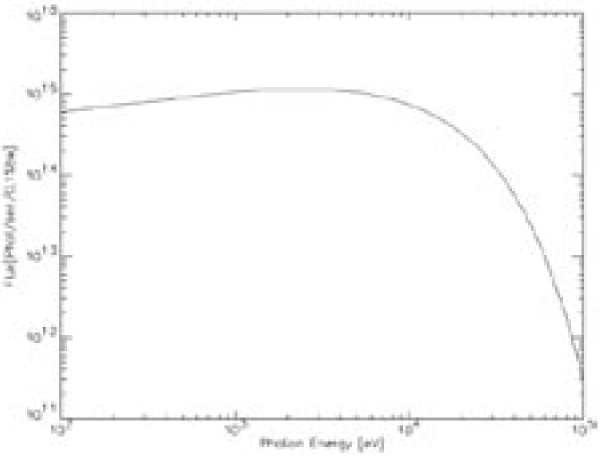

Fig. 4. Calculated flux from a 30 pole 1.9 Tesla wiggler on a straight of the Australian ring.

Synchrotron radiation was first observed in 1947 by scientists at the GE laboratories,[8] but it took time before the utility of this light source was appreciated. Second generation synchrotron sources were constructed from the early 80s specifically to use bending magnet radiation rather than the parasitic radiation from particle accelerators; a major step in utility and accessibility. Third generation rings date from the early 90s and have exploited increasingly the very intense radiation from the insertion devices – the wigglers and undulators described above – on the straight sections of the ring.

Two key attributes have driven the development and exploitation of these radiation sources. The first is the extreme brightness where a figure of a billion times the brightness of the sun is widely quoted, but this is some-what energy dependent; certainly practical intensities of a million times conventional laboratory X-ray sources are realistic. The second is the very broad span of energies which are accessible at most facilities by construction of appropriate beamlines to capture selected windows across this energy spectrum. There are other additional characteristics that can be usefully exploited, such as the variable polarisation and time resolved nature of the beam.[7] However, the synchrotron itself is simply a light source from which dedicated beamlines capture a window of this radiation. Very few experiments (notably in lithography and imaging work) use the *white light beam*. A beam transport system is required to select the requisite wavelength(s), and transport (and perhaps focus) it to a position in an experimental station that may consist of a conventional IR spectrometer, a PE microscope, a single crystal diffractometer, or many other devices. Thus a huge range of quite distinct experiments, in different energy regimes, are operating at any point in time in a mature synchrotron facility.

A very reasonable and frequently asked question, particularly in light of the NZ participation in the Australian ring, is what will the synchrotron do for these experiments beyond that which a laboratory-based diffractometer can do for a fraction of the cost? There are two key considerations. Firstly, there exist a variety of techniques that are only possible using synchrotrons, such as the X-ray absorption spectroscopies in which the primary beam energy is scanned. Secondly, many experiments are either prohibitively time consuming, or too difficult to be carried out in any other way. Typical examples of the first case are Extended X-ray Absorption Fine Structure (EXAFS) and Diffraction Enhanced medical imaging, while the second case is best exemplified by large molecule crystallography and far IR spectroscopy. In the latter case, the comparative flux of a synchrotron source in this region is shown in Fig. 5.

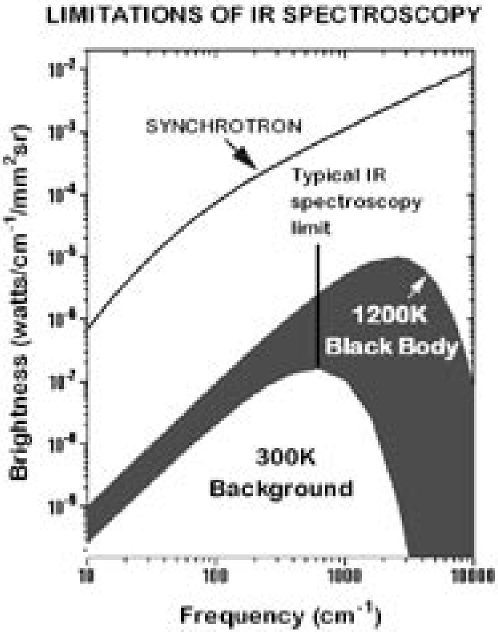

Fig. 5. Comparison of photon intensity in the IR region for a synchrotron and a conventional source. The several orders of magnitude more intensity from the synchrotron make it the only viable source in the far infrared (Reproduced courtesy Richard Garrett, ASRP)

In protein crystallography, the primary advantage is the order of magnitude reduction in time and the far greater number of reflections that can be collected – a function of the photon intensity. However, even more fundamental is the phase information available in the experiment as this allows exploitation of the so called *Multiple Anomalous Dispersion* (MAD);[9] *ca.* 98% of structures currently being registered on the protein crystallography database are collected on synchrotrons.[10]

The Australian ring is a 3rd generation synchrotron, the design of which is detailed on the synchrotron website,[11] and is one of about 18 such facilities built or under construction. It has an evolutionary design based on previous experience with 3 GeV rings, *e.g.* the CLS currently being commissioned in Saskatoon.[12] Comparison with the CLS or the UK Diamond ring (Table 1) shows that individual machines with a similar energy range may be optimised for different applications and capacities within the usual constraint of overall cost. However, use of 3 GeV is emerging internationally as a useful intermediate energy which, when coupled with increasingly powerful insertion devices in the straight sections, provides access to all but a few specialist high energy (≥ 70 keV) applications. Similar energy facilities are also planned for rings under construction in Shanghai (3.5 GeV) and Barcelona (3 GeV).

Table 1. Comparison of synchrotrons currently under construction.

Parameter	**Australian**	**Diamond (UK)**	**CLS (Canada)**	**SPEAR III (USA)**
Lattice Energy (GeV)	3.0	3.0	2.9	3.0
Periodicity	14	24	12	18
Useable Straights[a]	12	22	10	16
Circumference (m)	216.0	561.6	170	234
Current (mA)[b]	200	300	200	500
Emittance (nm-rad)[c]	7	2.7d	18.1	18
Lifetime (h) at max. current	>20	10 – 20	~50	
Beam Size in straights[d] (height/ width; µm)	389/20	123/6.4 (5 m)[d] 178/12.7 (8 m)[d]		

[a] The number of useable straights determines how many high performance insertion devices can be installed.

[b] Facilities generally start up with 200 mA but some plan to increase current after several years of operation; this option is available for the Australian synchrotron.

[c] The emittance specifies the size of the electron beam in the straight sections. The smaller the number the higher the brightness of the photon beams.

[d] Diamond has straights with two different lengths – 5 m and 8 m.

Beamlines

The beamlines and end-stations provide the experimental devices where the power of the synchrotron is harnessed. Initially, the experience with and preponderance of crystal monochromators meant that energies above 3-5 kV dominated synchrotron applications. For example, X-ray crystallography and X-ray absorption spectroscopy - particularly the use of the EXAFS - matured rapidly in geochemistry and materials science.[13,14] The advantages of tuneable energy and extreme brightness soon found application in large molecule crystallography and this field has now emerged to dominate demand for beamtime in many facilities (Fig. 6).

The chemical richness in the near edge structure of the X-ray Absorption spectrum (XANES), especially of the softer X-ray lines (below 2 kV) has also become more widely appreciated with the development of the spherical and plane grating monochromator beamlines now available at most facilities. This variant of classical PE spectroscopy makes the utility of the synchrotron apparent. In addition to a monochromatic source of tuneable energy, and perhaps 50 meV resolution, *cf.* monochromatised Al K_α at 1486.6 eV and 0.4 eV resolution of a laboratory instrument at best, which can be selected to control depth resolution, the source energy can be scanned across the absorption edge to reveal the fine structure in the Near Edge Spectrum. Thus in resolution, speed, control of analysis depth, access to bound states above the ionisation threshold, the advantages of synchrotron radiation are enormous.

Over the past decade, one of the fastest developing areas of application of synchrotron radiation has been medical imaging and therapy. At a workshop in Auckland (Aug. '04) Dr. F. Arfelli, who leads a group based at the Italian Synchrotron in Trieste, discussed clinical applications in mammography, where the enhanced resolution at lower dose accessible on the synchrotron beamline can be utilised in difficult cases associated with dense tissue imaging.[15,16] Several characteristics of the synchrotron radiation make it very useful in this respect. Firstly, the beam is highly collimated, thus the optical advantages are considerable, *e.g.* in increasing beamline lengths (and thus demagnification factors) often to greater than 100 m. Secondly, phase information is retained giving the potential for applications such as phase-contrast imaging that is simply not accessible with other approaches.[15] In the therapy area, energy tunability becomes a huge advantage, *e.g.* in radiotherapy where the beam energy can be tuned specifically to the absorption edge of, say, platinum contained in anticancer drugs; the bulk of the radiation

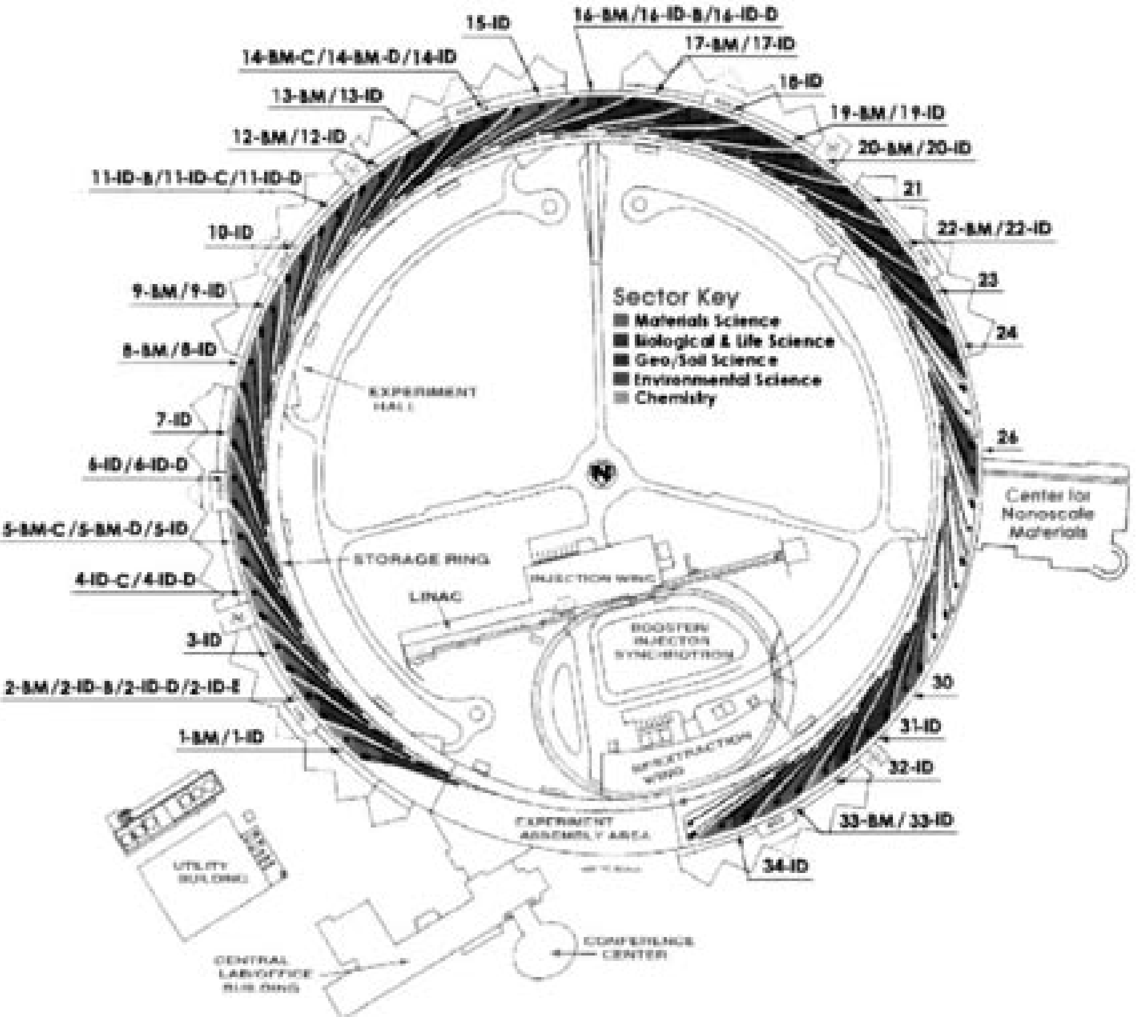

Fig. 6. Distribution of beamlines at APS Chicago; the website version of this diagram identifies the biological-life sciences (mostly protein crystallography) beamlines in blue. These now constitute around one third of the beamlines. (Taken from the APS website).

dose is then delivered only in the location of the drug.[16]

The Australian ring has the capacity to support more than 30 beamlines but cost constraints will limit the first phase of construction to perhaps 10 or 11. The current, ambitious plan is to have at least four of these lines operational by April '07 when the facility is handed over to its operator. The selection of the initial tranche of beamlines was addressed following extensive consultation with the user community, including that in NZ. It seeks to balance established need, *e.g.* in protein crystallography, EXAFS, X-ray microprobe, lithography, soft X-ray and IR spectroscopies, *etc.*, with the capacity to push beamline performance and enable quite novel science. For example, as indicated above, major interest is emerging in the area of medical imaging, but beamlines of 100 m of more in length are needed to best exploit the advantages of the synchrotron source. The technical difficulties are considerable but the results emerging in this area is stunning (see below), and extend into the potential use of the beam in medical therapy. A more complete discussion of individual beamline design and capability is available from the National Science Case for the Australian Synchrotron.[5]

Applications

To date, synchrotron use in NZ has been dominated by crystallography, and surface and materials science. Much of our own work has utilised soft X-ray lines in the 70 eV to 5 keV range at the Canadian Synchrotron Radiation Facility in Madison. The most useful of these has been the 200-800 eV spherical grating monochromator (SGM) line for the characterisation of amorphous GaN thin films,[17-19] with a stunning demonstration being the resolution of the XANES spectrum to observe the vibrational structure of the nitrogen molecule trapped in interstitial sites within the films (Fig. 7). However, the complete story emerges when studies of the photoemission spectra of these samples are also included to allow examination of the band structure below the band gap.[19] A combination of synchrotron experiments in the US and Germany are routinely used to characterise these materials.

Spectra collected at the sulfur L edge (≈ 164 eV) from a series of model compounds used as standards in a recent study of sulfur speciation in aluminium smelting anodes[20] are shown in Fig. 8. The spectra allow differentiation of the 5-membered heterocycle from the 6-membered ring, and comparison with model compounds has been successfully in examining S speciation in carbon anodes containing ~1% sulfur.[20] This speciation information is critical in understanding the mechanism by which O=C=S is generated at the face of the anode during electrolysis.[21] This has environmental implications because the gas is sufficiently stable kinetically to allow a small proportion to be released into the duct gases at aluminium smelters, and eventually to the atmosphere. Soft X-ray XANES has also been used in the development of new cathode materials for Li ion batteries,[22-24] and is being applied to the characterisation of a range of semiconductor materials and refractories.

The growing power and diversity of these methods is illustrated in several international examples, firstly in the

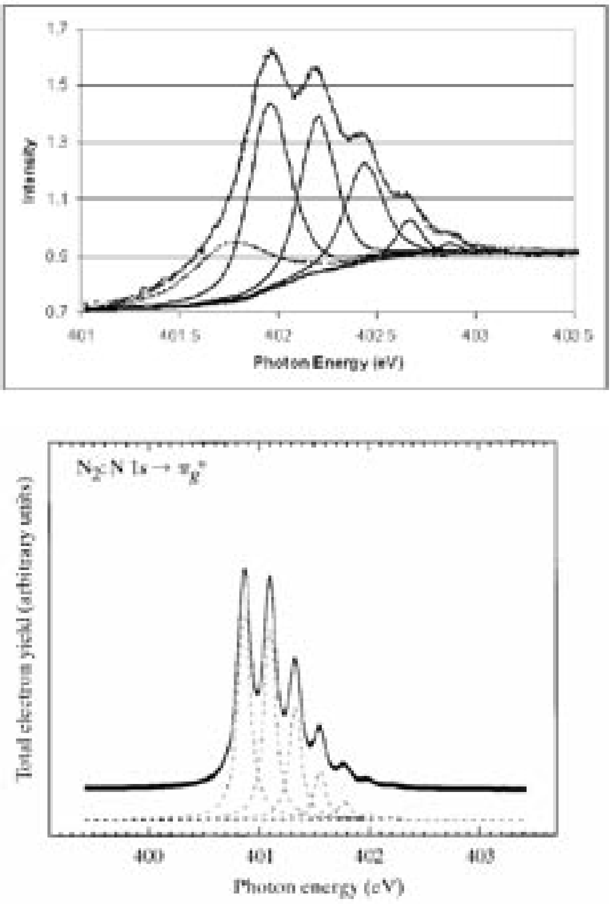

Fig. 7. (a) The X-ray Absorption Near Edge spectrum at the nitrogen K edge from an IAD-deposited amorphous GaN thin film showing gas phase N_2 trapped in interstitial sites within GaN – see refs. 17-19.; (b) the XANES spectrum from gas phase N_2.

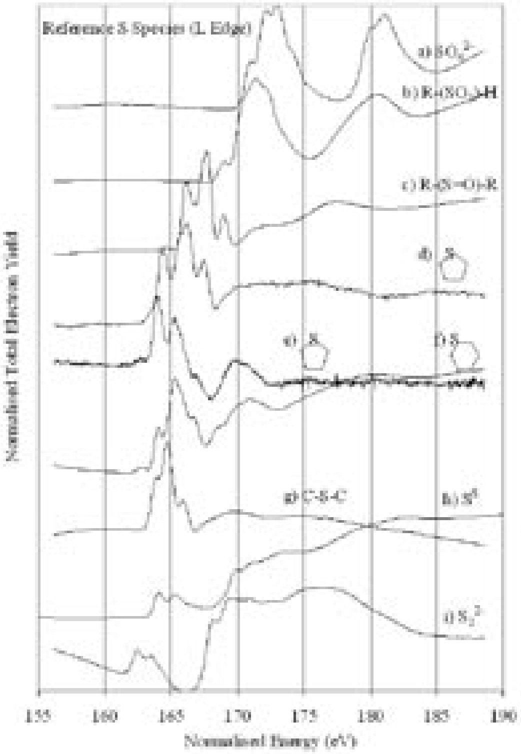

Fig. 8. Spectra collected on the Canadian SGM line at the sulfur L edge (≈ 164 eV) from a series of model compounds used as standards in a study of sulfur speciation in aluminium smelting anodes – see refs. 20 and 21.

reading of ancient manuscripts and secondly from cutting edge studies of bone development in animals. The Stanford website[25] recently featured an epic detective story in which Stanford synchrotron (SSRL) X-ray fluorescence was used to completely read the Archimedes Palimpsest, the only source of at least two previously unknown treatises thought out by Archimedes in the 3rd century BC. The palimpsest is a 1,000-year old parchment made of goat skin containing Archimedes' work as laboriously copied down by a 10th century scribe. Due to the value of the parchment, two centuries later the documents were erased, the parchment scrapped down with pumice and written over to make a prayer book. Parts of the document were even painted over some centuries later (as ancient parchments became increasingly valuable to art forgers). However, the residue from the original iron gall inks gave a sufficient signal in the XRF spectrum than when the parchment was scanned across the micro-focused synchrotron beam, the characters could be read! The second example, at the cutting edge of medical imaging, is taken from the work of Whitley and Lewis at the Victorian Department of Primary Industries and Monash University, respectively. Here interest is in the early development of lungs in mammals and the images shown in Fig. 9 follow the calcification of bones in the chest of wallaby from 1 to 22 days of growth.[26]

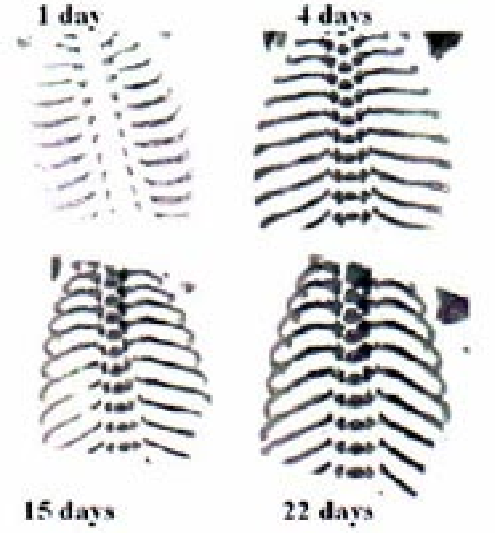

Fig. 9. Clacification of bones in the chest of a wallaby during early stages of development from data collected on the largest synchrotron, Spring8 (Japan) [Reproduced courtesy of Dr. J. Whitley (Victorian Department of Primary Industry) and Prof. R. Lewis, (Monash University].

The NZ Situation

The RSNZ was commissioned by MoRST in 2003 to prepare a detailed report on the case for formal NZ involvement in the Australian Synchrotron. Much of this was released[27] in Dec. '03 providing a review of then current and anticipated use of synchrotrons by NZ-based researchers and examines the nature of the opportunity presented by the Australian initiative. What is perhaps surprising is that NZ has activity across most spheres of mainstream synchrotron application, especially in protein crystallography, materials science, and IR spectroscopy. However, the regular community of about 12 regular users compares to 400 or so users across some 140 groups in Australia.

The vehicle for the growth and increasing sophistication of the Australian user community has been the Australian Synchrotron Research Programme (ASRP), a scheme mirrored in most developed countries, *e.g.* by the Canadian Synchrotron Radiation Facility (CSRF) initially based at the Madison synchrotron *Aladdin*, and supported by a Canadian *Major Facilities Access Fund*. The difficulty for NZ is that our fully costed research funding regime provides a poor fit with the way international science is carried out, particularly in the operation of very large science facilities, *e.g.* the APS in Chicago (Fig. 6) provides Australians access to four beamlines. These are billion dollar facilities for which the fully costed access regime is clearly inappropriate.

The local funding regime has in the past prevented any *as of right* synchrotron access for NZ users through an ASRP-type arrangement. Thus use has been restricted to relatively experienced scientists with international contacts through whom beamtime can be secured, typically by competitive, peer-assessed application. There is no doubt that this is highly cost effective since the international operational model is invariably that where *photons are free*. However, favourable costs must be balanced against the strategic limitations of relatively scarce access, and the external selection of NZ science to gain access to such frontline facilities. A further consideration is a perception of poor citizenship of our users who, in terms of the development and operation of such facilities, are able to contribute very little. Nevertheless, there is strongly growing use and awareness of the power of these techniques within NZ science. The Royal Society report identifies a number of notable examples of recent applications from the Baker group (Auckland), Jameson (Massey), Gainsford (IRL), and from our own work.

An industry-based example lies the development of new cathode materials for Li ion batteries by Pacific Lithium. This is an excellent case study of the evolution of materials from the initial Al- and Cr-doped Li manganate spinels, into much superior materials in battery performance, especially in cycle life. This systematic development has been based heavily on hard X-ray, EXAFS spectroscopy, and soft X-ray Absorption Near Edge Spectroscopy (XANES), using synchrotrons in France, the US and Taiwan.[22]

There is a wide, but currently very small, synchrotron user community in NZ. The challenge over the next few years is to develop the funding initiatives that will allow for rapid growth of a much stronger and more diverse user community; something of a catch-up on other nations. This is essential in order to make best use of the opportunities the Australian facility will provide and, more importantly, to ensure that this access has the maximum impact in enhancing NZ science and technology.

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