Overview of Synchrotron Soft X-ray Application

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Editors' Note: The author received his Ph.D. degree in 1981 from Stanford University, with a study of resonance and relaxation processes in photoemission spectroscopy on transition-metal and rare-earth compounds based on his work at Stanford Synchrotron Radiation Laboratory (SSRL). Recently he served as the beamline division director at Pohang Accelerator Laboratory, Korea, from July 1997 to June 1999. He is now a professor of physics and the director of the Center for Strongly Correlated Materials Research at Seoul National University, which is supported by Science Research Center program of Korean Science and Engineering Foundation. Dr. Oh's e-mail address is "sjoh@plaza.snu.ac.kr".

I. Introduction

Synchrotron Radiation (SR) has now become a major tool in many areas of research including physics, chemistry, biology, materials science, and environmental sciences. Since synchrotron radiation provides highly-focused high-intensity light of well-defined characteristics with wavelengths ranging from infrared to x-ray, it can benefit any research and development efforts utilizing electromagnetic radiation. And its impact has been truly far-reaching not only in the basic science but also in technological applications such as nano-lithography and microelectronic device fabrication. Obviously it would be impossible to review the whole field of synchrotron radiation research in a short article, and so in this paper I will limit myself to applications in the vacuum-ultraviolet and soft x-ray region. This wavelength region is where the Korean synchrotron radiation facility Pohang Light Source (PLS) is principally designed for and has world-class competitiveness.

Third generation synchrotron facilities such as PLS brought about a quantum jump in the quality of research using SR. Third generation SR facility is characterized by the low emittance of electron beam and extensive utilization of insertion devices such as undulators and wigglers. These made it possible to increase the photon brightness by several orders of magnitude, and many ``photon-hungry" experiments which had been only dreamed about now become feasible. In fact, new techniques are continuously developed, and the performance and scientific outcome from 3rd generation SR facilities such as European Synchrotron Radiation Facility (ESRF) in Grenoble, France, and Advanced Light Source (ALS) in Berkeley, USA, far exceed the expectations envisioned in the design stage [1,2].

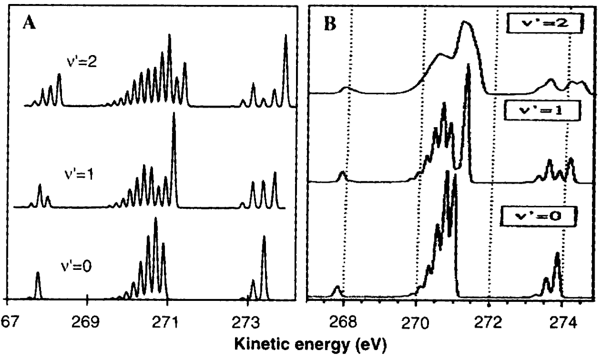

FIG. 1. Decay spectra of the carbon $1s \rightarrow \pi^*$ resonance in the CO molecule taken at ALS (panel A) and NSLS (panel B). (From Ref.3)

The high brightness photon beams provided by undulator beamlines are utilized in three major directions. The first one is the improvement of energy resolution. If we take an example of photoemission experiment, the typical energy resolution in the 2nd generation bending magnet beamline such as National Synchrotron Light Source (NSLS) in Brookhaven was around 100 - 300 meV. This resolution was too poor to study interesting physical properties such as superconducting gap or phonon structure, which typically has the energy scale of a few meV at most. However the 3rd generation undulator beamlines now routinely provide energy resolution better than a few meV, and many fine structures near the Fermi level can be investigated in detail. An example of this improved resolution can be seen in Fig.1. In the left panel A the decay spectra of the carbon 1s →π* resonance in the CO molecule measured by Auger resonant Raman experiments performed at the 3rd generation source ALS is shown, where the vibrational progressions for molecular Auger decay are completely resolved. The right panel B of that figure is the result of the same kind of measurements taken previously at the 2nd generation source NSLS. The difference of energy resolution in two spectra is truly remarkable.

The second direction of utilizing high brightness is the realization of small focal spot. It is now possible by various focus techniques such as zone plate and Kirkpatrick- Baez optics to obtain focal spot of the photon beam less than one micron. This improvement of spatial resolution is ideally suited to the study of nano-structures, which will be one of main areas of the research in the 21 century. The third direction is to perform low signal (cross-section) experiments. A good example is soft x-ray emission spectroscopy (SXE). SXE has been recognized for a long time as a powerful tool to study electronic properties at the interfaces and wet surfaces, but the low cross section of the radiative decay hindered the full utilization of this technique up to now. The powerful photon beam from 3rd generation SR sources removes this obstacle, and SXE may become almost as routine as photoelectron spectroscopy in the future.

In the following I will review the current status and future direction of experimental techniques utilizing high-brightness vacuum-ultraviolet and soft x-ray photon beams provided by undulators in the 3rd generation SR facilities. The techniques to be reviewed are photoelectron spectroscopy, x-ray absorption spectroscopy, x-ray emission spectroscopy, resonant scattering, and soft x-ray microscopy. This list obviously does not exhaust all the interesting SR techniques in the soft x-ray region. However, they are probably most representative and most-widely-used current techniques. In addition to the technical developments of these experimental tools, the research topics that will be addressed using new capability of 3rd generation facilities will be discussed.

II. Development of Experimental Techniques

1. Photoelectron Spectroscopy (PES)

Photoelectron spectroscopy (PES) is a very powerful tool to probe electronic structures of atoms and solids. In this technique, photon beams are incident on the sample, and the energy and momentum of (photo)electrons ejected by photoelectric effect are analyzed to obtain information on the electronic structure of the sample. Thanks to the low emittance of the electron beam and the excellent performance of undulators, extremely high resolution both in energy and momentum $\Delta E < 5$ meV and $\Delta q \approx 0.02$ Å^{-1}) has now become possible. This high energy resolution gives a wealth of information on small energy scale properties such as superconducting gap, phonon contribution, and extremely fine structures of electronic density of states near the Fermi level. The best example is probably the determination of the superconducting order parameter by angle-resolved photoemission spectroscopy [4]. The dependence of the gap size on the wave-vector $\vec{k}$ confirmed d-wave character of the order parameter for cuprate high temperature superconductors.

Angle-resolved photoemission is often the only technique capable of measuring the Fermi contour for many strongly correlated materials. Hence it offers a direct test of the quasiparticle picture of solids, as illustrated in recent angle-resolved PES studies on one-dimensional system [5,6]. These studies clearly show the separation of spin and charge, a characteristic feature of the Luttinger liquid as opposed to the conventional Fermi liquid. Recent finding of the pseudo-gap phenomena in underdoped cuprates and colossal magnetoresistive (CMR) manganites is another example [7,8]. These pseudo-gaps are very hot topics in the condensed matter physics community these days, and will provide important clues to the origin of high temperature superconductivity and colossal magnetoresistance phenomena. We are probably witnessing only the beginning of new physics related to the strongly correlated materials. High-resolution angle-resolved photoemission will give more surprises in the future, and undoubtedly provide critical information on the electronic structure of these new classes of materials.

For magnetic materials, spin-resolved photoemission provides spin-dependent electronic structure information and a clue to the origin of interesting magnetic properties. A nice example is the confirmation of half-metallic nature of CMR manganites $La_{0.7}Sr_{0.3}MnO_3$ [9], as shown in Fig.2 here. Manganites undergo a phase transition from ferromagnetic metallic to paramagnetic insulating states as the temperature is raised, and attracted a lot of attention lately because of their huge change of resistivity in the magnetic field (hence the name colossal magneto-resistance). The PES spectra in Fig.2 shows clearly that the majority spin band is metallic while the minority band is an insulator in the low temperature ferromagnetic state, as predicted by the famous double-exchange model. Another example is the origin on the oscillatory coupling phenomena between magnetic layers in nanostructure revealed by the photoemission on the spin-polarized quantum-well states. Spin-resolved photoemission is one of the typical ``photon-hungry" techniques because the detection efficiency of electron spin is very low (~10^{-4}). Hence the bright 3rd generation SR facility would certainly help to make this technique widely used.

So far the development of photoemission beamlines in 3rd generation SR sources has been mostly directed to achieve the best resolution in energy and momentum, and there were few initiatives to utilize the small focal spot (spatial resolution). However, to study nanostructures we will certainly need better spatial resolution in the future. Furthermore sample homogeneity becomes a problem as we probe materials with better energy and momentum resolutions. Hence it is expected that the effort to obtain smallest focal spot in photoemission experiments will be forthcoming, and in fact in PLS such effort is already under way.

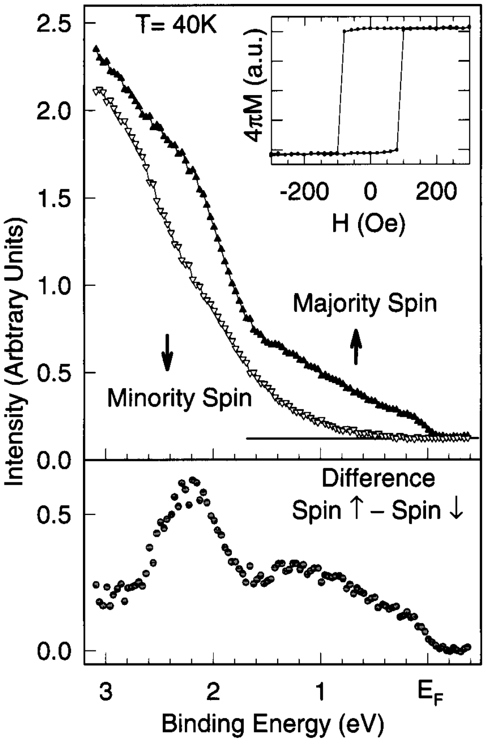

FIG. 2. Spin-polarized photoemission spectra of a 1900-Å thick film of $La_{0.7}Sr_{0.3}MnO_3$ taken at T=40K (T_C=350K). The inset shows the magnetization (M) vs. applied magnetic field (H) hysteresis loop. (From Ref.9)

2. Soft X-ray Emission Spectroscopy (SXE)

Although photoelectron spectroscopy has been a preeminent technique for the investigation of electronic structures of solids, it has some important drawbacks. Since it detects electrons, the experiments have to be done in vacuum. This makes it almost impossible to study the materials in some conditions such as under high pressure or solid-water interface, which is quite important in environmental sciences, biology and catalysis technology. Another drawback is the short escape depth of photoelectrons ejected from the solid. This is advantageous if we are interested in the property of surface, but less useful if we want information on the sample interior (bulk). These two drawbacks can be overcome if we use a *photon- in / photon-out* experimental technique. X-ray emission spectroscopy (XES) is exactly such a technique, which complements PES by giving bulk-sensitive information on samples in the natural condition.

Previously XES has not be used as extensively as PES because the cross-section of the radiative decay of the excited states in solids is usually very low. However, strong photon flux at 3rd generation SR facility can overcome this disadvantage. In fact, Soft x-ray emission spectroscopy now enjoys wide-spread use in many SR facilities in the world, and promises to become a major tool for the investigation of electronic structure of solids in the future.

3. X-ray Absorption Spectroscopy (XAS)

In contrast to x-ray emission spectroscopy, x-ray absorption spectroscopy (XAS) is not so much ``photon-hungry", and therefore many XAS techniques have been developed already in the 2nd generation SR facilities such as Stanford Synchrotron Radiation Laboratory (SSRL) and National Synchrotron Light Source (NSLS). In the 3rd generation facilities, XAS beamlines put much effort in developing micro-focus techniques to investigate position-dependent sample characteristics, which gave birth to the field of ``microspectroscopy". One example of the micro-focus techniques in soft x-ray region is shown in Fig.2. Using Fresnel zone plate, the soft x-ray beam from the SR undulator can be focused into the submicron spot. The scanning can be done by moving the sample stage.

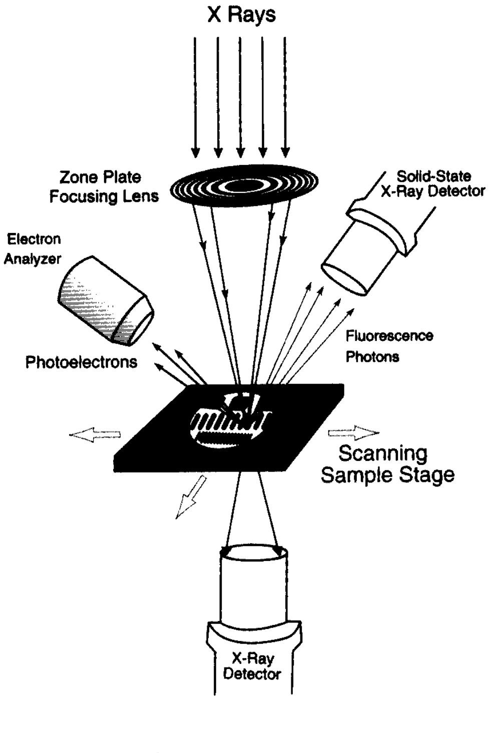

FIG. 3. Principle of scanning x-ray microscopy (also referred to as microspectroscopy). In this mode, a small x-ray spot is formed by a zone plate and the sample is scanned relative to the x-ray focal spot. The spatial resolution is determined by the spot size. The intensity of the transmitted x-ray or the fluorescence or electron yield from the sample, which is related to the x-ray absorption coefficient, are detected.

Among XAS techniques, Near-Edge X-ray Absorption Fine-structure Spectroscopy (NEXAFS) and Extended X-ray Absorption Fine-structure Spectroscopy (EXAFS) are simplest to perform and most widely used. These techniques measure x-ray absorption coefficient as a function of photon energy near the absorption edge of the element of interest. By analyzing these spectra, we can get information on the chemical environment of the element (chemical shift), its valency and spin state (low-spin vs. high-spin), distance to the nearest neighbor, and so on. Since soft x-ray region covers 2p edges (L edges) of most 3d transition metals and 3d edges (M edges) of 4f rare-earth metals, it is ideally suited for the study of magnetic materials. In addition, carbon, nitrogen and oxygen 1s edge (K edge) can also be covered, so that many interesting processes in biology, chemical dynamics, polymers, and catalysis can be investigated. Recently Scanning Transmission X-ray Microscopy (STXM) and micro-EXAFS techniques are developed to utilize focused x-ray beam and understand spatial dependence of the material properties.

Magnetic Circular Dichroism (MCD) technique is very powerful to study magnetism. In MCD, the difference of the x-ray absorption coefficient depending on the helicity (right/left circular polarization) of the incident photon beam (x-ray Faraday-Kerr effect) is measured. Soft x-ray MCD data can be analyzed to give the element-specific spin and orbital magnetic moments separately via powerful sum rules. This is very important information on the origin of the magnetic anisotropy, which is one of the frontier research areas in magnetism and magnetic recording industry. In addition, MCD together with appropriate scattering experiments can provide informations on (i) three dimensional element-specific magnetic hysteresis curves (ii) local magnetic ordering of disorder and dilute systems, and (iii) magnetic interlayer coupling in the multilayer systems, among others.

The use of circularly polarized light has other interesting effects such as spin polarization in the photoemission spectra of both core-levels and valence bands. Since the helicity of the synchrotron beam is another degree of freedom to play with very usefully to our advantage, various undulators are proposed to produce photon beams of arbitrary polarization following a pioneering work of Dr. Kwang-Je Kim [7]. Collectively called as the ``Elliptically Polarized Undulator (EPU)'', they are now built in many SR facilities around the world including ALS, ESRF, SPring-8 in Japan, and PLS (under construction).

4. Soft X-ray Resonant Scattering

Soft x-ray scattering is a *photon-in / photon-out* experiment, and hence is bulk sensitive and can be performed in extreme conditions such as under high pressure and high magnetic field. If we use the resonant photon energy at an absorption edge of a given element, it also becomes element-specific. In particular, resonant soft x-ray scattering is an excellent probe of the charge and spin order and dynamics as well as the elementary excitation of systems that undergo coupled spin and orbital ordering. Soft x-rays are ideal for probing the excitation of coupled spin and orbital order in 3d transition metal and 4f rare-earth compounds because of their ability to couple directly to the orbital moments.

In addition, because of the elemental specificity and strong spin-orbit sensitivity, soft x-rays are ideal for studying the static order and local density of states. It is the high-energy probe of electronic, vibrational, and magnetic properties of materials, but with sufficiently high resolution in terms of energy and momentum transfer it can give important information on the low-energy excitations of the system with element specificity. A particularly interesting recent development is the magnetic resonant scattering technique by using circularly polarized incident photon, either from the EPU undulator or off-plane bending magnet. This will give element-specific magnetic response of the system, and as mentioned before soft x-ray region covers most of magnetic elements of practical interest.

5. Soft X-ray Microscopy

Soft x-ray microscope is expected to provide the spatial resolution more than five to ten times better than that of visible-light microscope due to its short wavelength. However, x-ray microscopy is still in its infancy, and a lot of technological developments will still be necessary to realize its full potential. For example, in the field of bioscience, protein crystallography is a method of choice presently to understand its structure, while in materials science x-ray diffraction is routinely used to analyze crystal structures. However there are cases where x-ray microscopy is more preferable to diffraction-based techniques, such as the study of defects in crystals and behavior of biological cells *in vivo*.

High brightness photon beams from undulators have made possible a big advance in soft x-ray microscopy. The resolution has been improved substantially, and it is now possible to obtain 10 to 20 nm resolution with zone-plate lenses in the scanning soft x-ray microscopy mode. The possibility of polarization change for the incident photon beam also gives another dimension, which can be utilized for the study of domain structure and its motion in magnetic materials.

III. Conclusion

The advent of 3rd generation synchrotron facilities and their undulator based beamlines offer new scientific opportunities by providing high brightness photon beams which had not been available before. Many areas of research such as physics, chemistry, life science and materials and environmental sciences are now profoundly influenced by its impact. It may well be said that it is the scarcity of ideas, not technological innovations, that fundamentally limits the progress in this field.

It is fortunate that Korea has built the 3rd generation synchrotron facility in Pohang in a timely fashion, which is ideally suited for vacuum-ultraviolet and soft x-ray applications. Much of the new science and technology discussed in this article will play a central role in the 21st century, and will be dearly needed for the competitiveness of Korea in the future. I sincerely hope that the creativity of Korean scientists and engineers thrives on this golden opportunity.

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