

FEL Applications – Photoemission in Solids

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Synopsis: The FEL project will open up exciting scientific opportunities for the solid-state photoemission community. The advanced features of the FEL, including longitudinal and transverse coherence, ultrafast pulse structure, and extreme brilliance, will enable new applications and technical advances relevant to solving fundamental, outstanding, and emerging issues in condensed matter physics. The impact will be enormous and far-reaching.

A workshop was held in June this year to examine the scientific case and to develop a vision for the future of the photoemission field in connection with the FEL project. A number of experts participated in a brainstorming session aimed at identifying future directions in this area. The ideas and concepts were circulated after the workshop among a selected larger group for further discussions and comments. What has emerged from the process is a strong consensus that the proposal for a FEL facility is compelling, and the FEL will play a critical role in condensed matter research for the next several decades. The participants enthusiastically endorse a vigorous R&D program that will prepare the community for the utilization of the new, transformational capabilities offered by the FEL facility. The envisioned areas and topics where the FEL facility will have major impact include:

- Strongly correlated systems – competing order parameters; quantum critical behavior; pattern and domain formation; high-temperature superconductivity; magnetoresistive materials; ferroelectrics; f-electron and heavy Fermion systems; organic conductors and superconductors; ...
- Nanoscale systems – nanocrystals; intrinsic and extrinsic inhomogeneities; domain structures; pattern formation; self assembly; quantum size and confinement effects; dimensional, shape, size, and boundary effects; ...
- Excitation kinetics and dynamics – properties of elementary and collective excitations (magnetic, spin, electronic, lattice, ...); relaxation and lifetime effects; electron-lattice and spin-lattice coupling; lattice and atomic motion;...

Substantial developments in experimental techniques and endstation instrumentation are required for effective utilization of the advanced features of the FEL. Major areas of development include:

- Nano-focus angle-resolved photoemission and spectromicroscopy (Nano-ARPES) – utilizing the source coherence for diffraction-limited focusing, and utilizing the source brightness for parallel characterization of structural and chemical features at the nanoscale.
- Three dimensional angle-resolved-photoemission (3D-ARPES) – utilizing the ultrafast time structure of the FEL and time-of-flight (TOF) techniques for rapid high-resolution mapping of electronic properties $A(k_x, k_y, \omega)$ of novel materials.
- 3D-Nano-ARPES – combining the capabilities of 3D-ARPES and Nano-ARPES to yield a powerful tool for systematic exploration of complexity and nanoscale phenomena with simultaneous spatial

and momentum resolution (see Fig. 1 for a schematic illustration of some systems and problems well suited for 3D-Nano-ARPES investigation).

- Ultrafast pump-probe measurements of excitation dynamics, coupling, and relaxation.
- Time-resolved photoelectron diffraction and holography to follow atomic movements and bond rearrangements on surfaces, processes that are relevant to materials synthesis, self assembly and organization, and surface chemical reactions.

The discussion in the following will elaborate on the central issues, illustrated by a few selected examples.

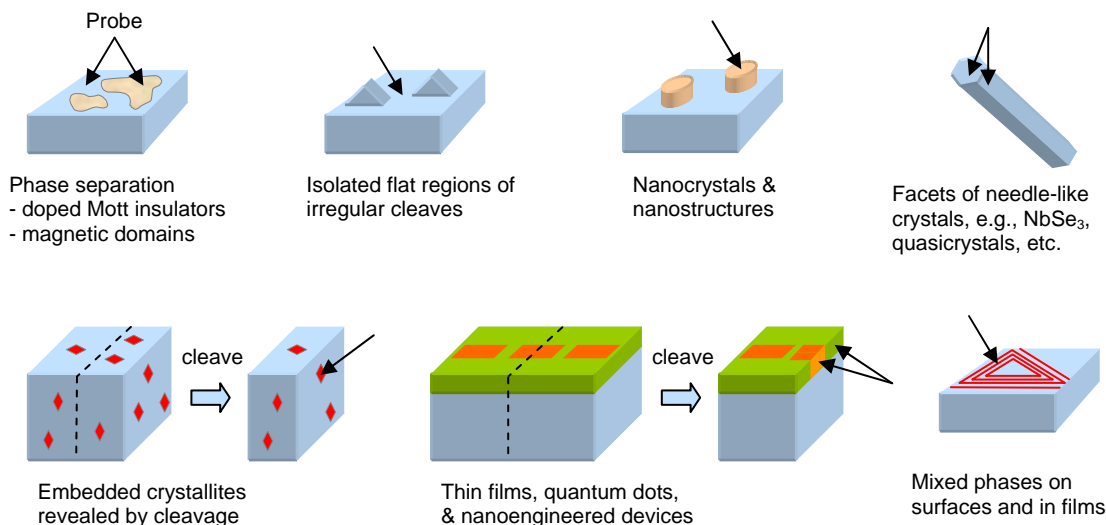


Fig. 1. Examples of systems and problems well suited for 3D-Nano-ARPES investigation.

Scientific Case: The physics of strongly correlated materials and nanoscale systems has been at the forefront of condensed matter research and will remain so in the foreseeable future [1,2]. Angle-resolved photoemission, or ARPES, has made substantial inroads in these areas. It is a powerful technique for systematic mapping of the electronic structure of solids and surfaces. Electronic interactions in solids determine the bonding among atoms and the resulting atomic structure and lattice vibrations; they also determine the electronic, electrical, thermal, optical, mechanical, magnetic, and chemical properties. Mapping of the quasiparticle spectral function or band structure is a fundamental requirement for a detailed, basic understanding of the electronic interactions and the resulting material properties. This is especially important for strongly correlated and nanoscale systems where intricate electronic interactions and geometrical constraints give rise to novel quantum effects and functionality including complexity, competing order parameters, quantum critical behavior, high-temperature superconductivity, magnetoresistance, heavy-Fermion behavior, oscillatory variations in thermal stability and superconductivity in thin films, etc. While ARPES has played a pivotal role in the recent progress in these areas, its applications have nevertheless been severely hampered by three issues: probe size, data acquisition rate, and time resolution, because of limitations of present generation of light sources.

Modern materials of interest, including complex oxides and f-electron compounds, do not usually come in the form of large single crystals. Even for the cases where such crystals are readily available, sample

inhomogeneity can complicate measurements and obscure fundamental properties. As an example, Fig. 2 presents a scanning electron micrograph of a cleaved $\text{YBa}_2\text{Cu}_3\text{O}_8$ high-temperature superconductor [3]. The image reveals a relatively flat, seemingly homogeneous area. However, ARPES taken from two selected spots in this area as indicated in the figure reveals vastly different spectral features that can be related to different cleavage planes of the material. The results illustrate the critical need for characterization at the nanoscale. Other types of spatial variations can arise in complex oxides such as high-temperature superconductors, colossal magnetoresistive materials, and ferroelectrics because of dopant or alloy distribution fluctuation, or spontaneous quantum phase separation related to energy minimization involving competing order parameters and strong electron-lattice coupling. These spatial variations can be key features of the functionality of the materials. The length scales of interest can vary from nanometers to microns, and a tightly controlled probe size is essential for uncovering the spatial modulation and its consequences. The proposed FEL, with an output that is fully laterally coherent, allows diffraction limited focusing at high intensity, and is thus ideally suited for spatially-resolved ARPES measurements.

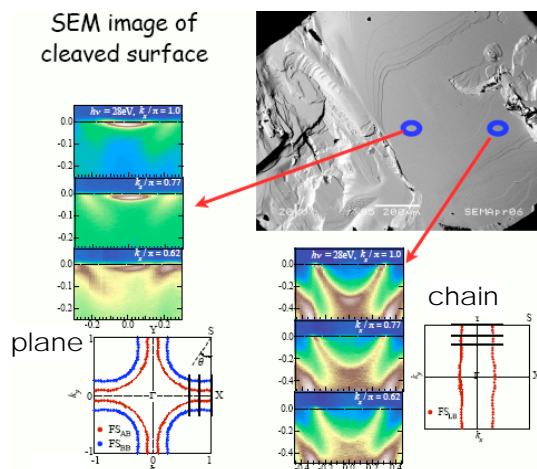


Fig. 2. A SEM image of a cleaved $\text{YBa}_2\text{Cu}_3\text{O}_8$ superconductor. Two spots within a seemingly homogeneous area are selected for ARPES measurements with different results that can be attributed to different cleavage planes.

A second example, shown in Fig. 3, is Pb islands or nanocrystals self-assembled on a $\text{Si}(111)$ surface [4]. The assembly process, partly driven by quantum size effects [5], leads to fairly uniform island heights (magic heights) and radial ordering in the surface plane, but the islands can show significant lateral size variations. A detailed understanding of the island size and shape development and evolution as well as the ordering kinetics requires a mapping of the quantized electronic structure in each island over a wide range of processing conditions. This has not been feasible up to now because the available beam size is too large and covers many islands, resulting in a smeared signal. 3D-Nano-ARPES would be ideal for such studies. The amount of data for different island shapes and sizes and for island evolution under processing conditions can be enormous; a high data acquisition rate is essential.

In addition to being a model system for "electronic growth," Pb islands or nanocrystals are of special interest in connection with superconductivity in reduced dimensions. While scanning tunneling spectroscopy (STS) can be employed to measure the superconducting gap of individual islands, detailed information from a complete electronic structure mapping would be indispensable for advancing the quantum theory of superconductivity in confined geometries. Figure 4 shows a related case [6,7]. The scanning tunneling microscopy (STM) picture is taken from a Pb film of precisely 24 atomic layers in thickness everywhere on a $\text{Si}(111)$ surface. Films as such exhibit superconducting transition temperatures that vary as a function of film thickness with a bi-atomic-layer period,

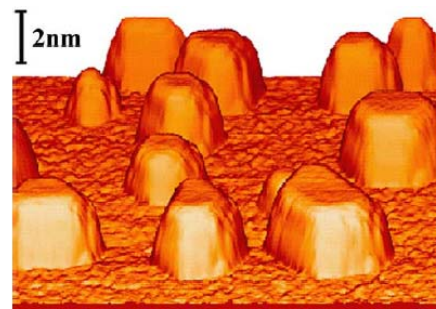


Fig. 3. A STM image of Pb nanocrystals on a $\text{Si}(111)$ surface that tend to adopt certain magic heights because of quantum confinement of electrons.

modulated by an envelope function with a ~ 9 -atomic-layer period, due to quantum confinement. Questions abound concerning the effects of the atomic steps on the substrate. For instance, do the steps affect the superconducting gap, and if so, how does the gap vary as a function of distance from a nearby step? Is the gap the same for all subbands that cross the Fermi level? This is a case where quantum size effects and electron correlation effects can be both important and possibly competing.

Strong electronic correlation effects associated with f electrons is another frontier area of condensed matter physics. Standard density functional theory has so far failed to account for many of the basic physical properties of such systems. A prototypical case is Pu, which is generally regarded the most complex metallic element in the periodic table [8]. As its 5f electrons are on the verge of being either localized or itinerant, Pu undergoes a number of phase transitions under moderate temperature and pressure variations. Its lack of thermal and mechanical stability is a key engineering concern and poses fundamental questions about the interatomic bonding forces. Most applications of Pu employ alloying to shift the phase boundaries in order to stabilize the phases of interest, but exactly how the alloying works is not yet known on the quantum mechanics level. A thorough understanding of these issues including the phase transitions and critical behavior requires a mapping of the electronic structure as a function of temperature through the many different phases (α , β , γ , δ , δ' , and ϵ). The phase instability in Pu makes the preparation of large single crystals impractical – the structure self-destructs due to the large volume changes and the resulting stress buildup across phase boundaries during thermal processing. A practical solution is to prepare nanocrystals self-assembled on a substrate, where they can remain single crystalline through the phase transitions. Competition between quantum size effects and electron correlation and possible cooperative effects would be of interest in such nanocrystals. 3D-Nano-ARPES will be an ideal tool for collecting the large quantities of data, with crystallite shape and size, temperature, and alloy composition as independent variables, that are needed for an in-depth understanding of these systems. Although Pu research presents some technical challenges, other strongly correlated f-electron materials containing Ce, Yb, and U also provide the opportunity to explore the localized/itinerant and metal/insulator transitions by means of manipulating crystal structure and/or ligand components. This is an area ripe for exploration using Nano-ARPES and taking advantage of reduced dimensionality with nanocrystals. Recently discovered f-electron superconductors are another area of strong interest. These include PuCoGa₅ [9], which has a surprisingly high superconducting transition temperature of 18.5 K, and the Ce 115 compounds, namely, CeMIn₅, where M = Co, Rh, and Ir. The connection among f-electronic structure, superconductivity, and magnetism in these materials is not well understood.

At the present time, the data acquisition rate of ARPES is mostly source limited, which presents a severe limitation on the amount of data available and thus the level of understanding achievable for a given system. For most of the cases of interest as discussed above, a full mapping of the quasiparticle spectral function or band structure is needed as a function of possibly several variables: shape and size (for systems with nanoscale features), reduced temperature $(T - T_c)/T_c$, and material composition or doping concentration. 3D-ARPES, with TOF detection utilizing the ultrafast pulse structure of the FEL, would be an excellent solution. Some of the technical issues will be addressed in the next section.

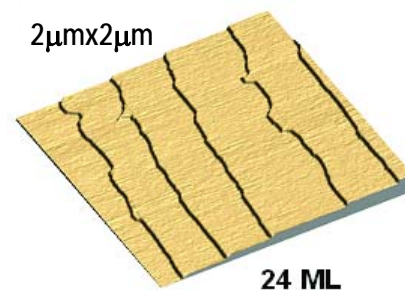


Fig. 4. A STM image of a Pb film of a uniform thickness of 24 atomic layers prepared on a Si(111) substrate, with a few atomic steps in the field of view.

The ultrafast time structure of the FEL also opens up exciting opportunities for studies of time-dependent phenomena including excitation dynamics, coupling, relaxation, and atomic motion [10]. Limited by space, we will just mention a couple of examples here to illustrate the basic ideas. The spin dynamics in magnetic systems is of great scientific interest and possibly of technological importance to magnetic storage and spintronics. Figure 5 presents time resolved photoemission data taken from a film of seven Ni atomic layers deposited on W(110) [11]. A 1.5-eV, 85-fs pump pulse excited the system at time $t = 0$, and a 6-eV, 180-fs probe pulse was used to record the photoemission data. The equilibrium exchange splitting (-1 ps spectrum) was largely suppressed after the pump excitation (1 ps spectrum), but recovered after a few ps (4 ps spectrum). The spin dynamics in magnetic films is often characterized by time scales on the order of ~ 1 ps or longer, which are well matched to the time resolution available with the proposed FEL. This pump-probe approach, with spin manipulation using polarized light, can be applied to magnetic films, multilayers, quantum dots, and artificial three-dimensional structures of interest to electronics applications. Dichroism measurements with ultrafast pulses can yield additional, complementary information [12].

The structure and motion of atoms on surfaces is another research area where the FEL pulsed time structure would be of great value. Of special interest are time-resolved photoelectron diffraction and holography measurements of surface atomic structure following excitation by a pump laser that triggers surface atomic motion, bond rearrangement, chemical reaction, and/or desorption. These issues are relevant to energy transfer and relaxation, and are of interest to laser processing of surfaces and photochemical processes.

Photoelectron holography and diffraction are well established techniques for determination of surface atomic structures [13]. In these measurements, core levels of surface atoms are excited, and the photoemission intensity is recorded as a function of emission angles to yield a diffraction pattern. In essence, the direct wave from the surface emitter interferes with back-scattered waves (Fig. 6), yielding a pattern that encodes the position of the emitter. Diffraction patterns recorded at a number of different photon energies are combined to yield a photoelectron hologram, which can be inverted mathematically to yield three-dimensional images of the atoms near the emitter. The analysis can be carried out for core levels of different atoms or the same kind of atoms but in different chemical bonding states, provided that the chemical shift is sufficiently large. The result is a set of site specific local images or Patterson functions. The data may contain additional information about the surface dynamics through time-dependent core level

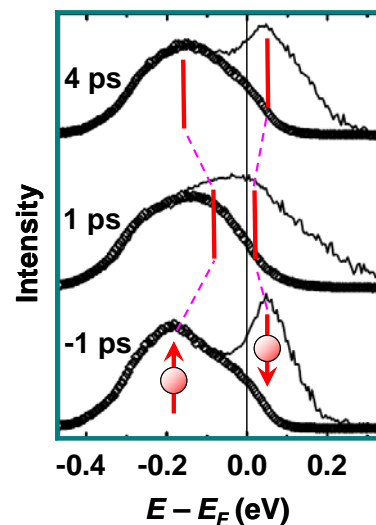


Fig. 5. Time-resolved photoemission spectra from a Ni film of seven atomic layers deposited on W(110). The results illustrate the collapse of exchange splitting after a pump pulse and recovery at a later time.

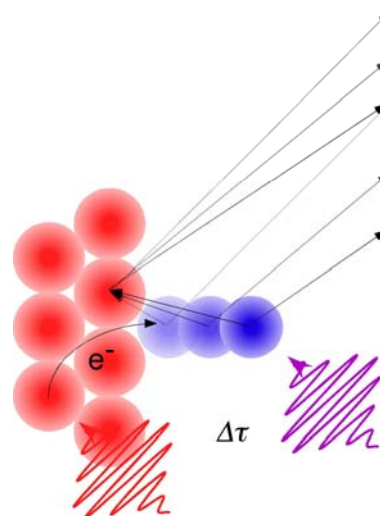


Fig. 6. A schematic illustrating time-resolved photoelectron holography. A pump pulse induces surface processes, and a delayed pulse probes the core levels at a later time.

shifts. Efficient diffraction pattern recording is important for this type of work, where a large number of time-resolved images are required to track the atomic motions. TOF measurements would fit the needs well.

Technical Issues and Development Projects: The proposed FEL output is longitudinally coherent. A 30 fs pulse length translates into an energy band width of 60 meV. This is a fine resolution for most core level measurements, but generally inadequate for high resolution ARPES from valence electrons. Subtle electronic correlation effects and nanoscale interactions may give rise to energy shifts or spectral features with energy scales of the order of 0.1-10 meV ($\sim k_B T_C$). For high-resolution work, a grating monochromator will be employed to both compress the energy resolution and to stretch the pulse length. Energy resolution to ~ 0.06 meV and pulse length up to 30 ps can be generated this way. A variable mask on the grating allows optimization of the pulse length and energy resolution for a best match to the experiments. For studies of ultrafast dynamics, very short pulses will be employed. For ultrahigh energy resolution ARPES, stretched pulses will be employed.

An important consideration with ultrafast pulse excitation for photoemission is space charge effects, which can negatively impact the energy resolution [14]. With current sources, either based on storage rings or table-top UV lasers, there have been few cases where space charge causes noticeable problems. Experience has shown that a 7 eV laser (6th harmonic of a mode-locked Nd:YVO₄ laser) with a photon flux of $\sim 2 \times 10^{15}$ photons/second and a focused spot size down to the submicron range yields negligible energy broadening at the sub-meV level in ceramics [15,16,17,18,19]. This result suggests that space charge effects with a stretched pulse from the FEL might be quite tolerable in the majority cases of interest to the users. However, space charge effects could become significant for the shortest pulses at higher energies. In many of the planned studies of ultrafast dynamics, a high energy resolution may not be needed (core level excitation, for example). The energy resolution of the shortest pulses is limited by the natural band width of 60 meV of the FEL in any case. While it appears that space charge effects are not necessarily a problem in many cases, further studies, both experimental and modeling, are needed during the R&D phase of the FEL project in order to establish general rules and guidelines for the experimenters. A possible solution for extreme cases is to apply a strong electric field on the sample using an immersion lens to quickly extract the photoelectrons and thus to minimize the Coulomb interactions among the electrons. A related issue is sample damage. This can depend on the sample materials. Experience has shown that most hard materials (metals, semiconductors, ceramics) are fairly robust against a table top laser with a photon flux level similar to that of the FEL [18,19]. Soft materials can be much more sensitive to radiation damage, but maintaining the samples at low temperatures may help. For delicate systems, one might be limited to wavelength ranges where sample absorption is relatively low, or it may be necessary to detune the monochromator or use slits to reduce the incident beam intensity. Again, R&D will be needed for a better understanding of this issue during the FEL developmental phase.

We envision two approaches to implement Nano-ARPES. One involves the focusing of the FEL beam by either reflective optics (Schwarzschild mirrors or KB mirrors) or diffractive optics (zone plates). Since the laser beam is fully transversely coherent, the final focus spot size can be on the order of the wavelength of the photon beam. Each focusing scheme has its advantages and challenges; the considerations include spot size, working distance, alignment difficulty, wavelength tuning range, and cost. It is likely that we will adopt all available methods to accommodate the various experimental needs. For example, SiC coated reflective optics can be used for broadband applications up to about 22 eV. Beyond that, grazing-incidence optics may be used, but the geometry tends to disallow a tight focus. Or, multilayer coatings could be used at the expense of wavelength tunability. Likewise, diffractive optical elements are generally limited to narrow wavelength ranges.

Pulses in the ~ 50 ps range or shorter (depending on the kinetic energy range of interest) are ideally suited for high resolution TOF measurements [20]. A simple but very effective scheme for 3D-Nano-ARPES is to use a focused beam to excite a nanoscale feature of interest. A drift tube followed by a TOF detector is used to collect the angular pattern of emission intensity as a function of delay time, which is a measure of the kinetic energy (see Fig. 7 for a schematic illustration). Each laser shot yields a complete spectrum $E(k_x, k_y)$ that involves three variables (thus the name "3D"). The signal to noise ratio can be improved by integrating over many laser shots. To improve the performance and to increase the collection solid angle, an electrostatic lens system can be used in lieu of a drift tube to control the trajectories of the emitted electrons [21]. A magnetic field can also be employed to further increase the collection angle [22].

A second approach to 3D-Nano-ARPES is to use a photoemission microscope (PEEM) to image an illuminated area on the sample that can be several microns in diameter. Spreading the beam over several microns has the advantage of minimizing space charge and damage effects. Modern PEEM designs often allow the acquisition of either real space images or diffraction patterns. In a microscopy mode, a PEEM, in conjunction with an energy filter or a TOF detector, can be used to collect photoemission spectra, in parallel, over all of the nanoscale features of interest within the illuminated area. Thus a set of nanocrystals on surfaces with different shapes and sizes can be simultaneously analyzed. Alternatively, the PEEM can be operated to form a diffraction pattern on the detector. An aperture in an intermediate image plane can be used to select a given nanoscale feature within the illuminated area for detailed ARPES analysis. Some commercial instruments currently available on the market already possess most of these capabilities [23,24], but the resolution, dynamic range, and flexibility still have much room for improvement. This is an area where R&D work is needed during the FEL development phase.

The greatest hurdle to efficient 3D-Nano-ARPES at the present time is the TOF detector efficiency and resolution. Present commercial instruments using delay lines have a maximum count rate of about 1 MHz. This is too low for efficient use of the FEL output. We envision a vigorous R&D effort, perhaps with vendor participation, for a vastly improved efficiency for the detector and associated electronics that may involve multiple parallel channels for data readout, transfer, and storage.

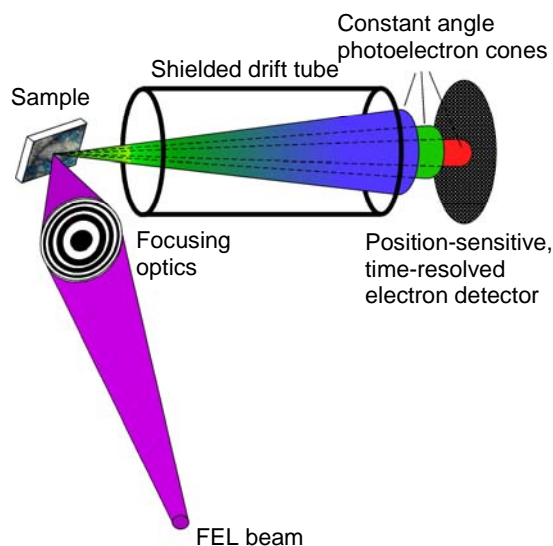


Fig. 7. A schematic diagram illustrating 3D-Nano-ARPES. A nano-focused beam of short pulses excites a region of interest on the sample. The emitted electrons are collected and analyzed by a TOF detector.

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