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Future probes in materials science

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Abstract

Advancements in condensed matter science have been primarily driven by the discovery and refinement of new materials and innovative approaches to characterization tools. There are many examples where advances in spectroscopic techniques including electron and magnetic resonance, new and more accessible approaches to phase space (pressure, magnetic fields and temperature), and the development of major facilities, specifically photon and neutron sources have profoundly impacted the development and accelerated the advancement of condensed matter sciences. The importance that nations attach to future probes for materials sciences is reflected worldwide in the major investments being made in both large facilities and researcher driven instrumentation development. Within this presentation, several instrument areas are reviewed and opportunities for the development of future probes for materials science are discussed. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Some of the most significant advances in condensed matter science have been driven through innovative approaches to the synthesis of new materials or the development of new probes. New probes and new materials feed the engine of discovery and furthering understanding. There are numerous examples where new materials, single crystals, or selective doping has led to new discoveries and many of the most significant discoveries, e.g., heavy fermions, have built on early studies where sample purity or crystal perfection constrained the research or confused the interpretation of the results. Likewise, imaginative approaches to measurement techniques have provided new insight into the complexity of

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nature. So often these new probes have impacted science well beyond early expectation. For example, the impact of synchrotron light sources in the biological sciences was not recognized during the early years of the development of these resources. The invention of the laser and the scanning tunneling microscope have opened new exploratory opportunities and led to new understanding beyond those anticipated by the inventors. Prestigious awards like the Nobel award and others have recognized the impact on science originating from new measurement approaches and the discovery of new phenomena through new materials.

Much of this symposium has centered on discovery through imaginative approaches to new materials. In this chapter, a brief survey is provided on a few select probes and their possible impact on future science. The chapter first focuses on probes that require a major investment in national facilities followed by a discussion of spectroscopies that have had a major impact on the evolution of condensed matter science along with a look into the "crystal ball" to speculate what new opportunities may be forthcoming.

2. Neutron scattering and neutron sources

Neutron scattering provides unique information about the condensed phase that is important throughout the materials sciences. The versatility of the probe can be traced to the nature of the neutron–matter interaction and the neutron mass and spin. These conspire to enable direct measurements of static and dynamic density and spin correlation functions for a wide range of materials.

While neutrons have provided essential information about magnetic structures, lattice structures of materials with light elements, mixed phases in superconductors, magnetic and buried interfaces, spin waves, and phonons, there are significant limitations associated with 20th century instrumentation. Neutrons are tightly bound in nuclei so their release for experiments requires dissipation of substantial thermal energy (190 MeV/n for fission, 30 MeV/n for spallation). In addition, neutron scattering cross-sections are typically smaller than X-ray cross-sections. These challenges have generally limited neutron scattering to cases where large samples are available or where limited information about strong scattering cross-sections is important.

A number of projects leading to improvements in source brightness, beam delivery, and detection efficiency will provide 2–3 orders of magnitude improvements in overall instrument efficiencies. On the source side, accelerator-based spallation neutron production promises pulsed neutron beams with greatly enhanced peak brightness as illustrated in Fig. 1 [1]. Dramatic improvements in flux on sample can also be achieved by enhancing beam delivery systems at both reactor and spallation sources. In particular, cooling the neutron gas by a cold moderator both increases the source brightness and allows the sample to accept neutrons from a greater solid angle at constant wave vector resolution. Finally, significant efficiency gains are possible through concurrent detection of scattering events associated with different resolution elements of the instrument.

Focusing on US facilities, upgrades along these lines have recently been completed or are underway at the NIST Center for Neutron Research (NCNR), the High Flux Isotope Reactor (HFIR) of Oak Ridge National Laboratory (ORNL), and Los Alamos Neutron Scattering Science Center (LANSCE). The greatest advances, however, can be expected from the 2 MW spallation neutron source (SNS) to be completed in Oak Ridge, Tennessee in 2006. Not only will the SNS provide 1–2 orders of magnitude increase in peak source brightness, but each instrument to be installed will bring additional performance gains through ambitious detection systems. Instruments that will be available in 2006 and that are of particular interest to condensed matter physicists are summarized in Table 1. The improved instrumentation for neutron scattering at reactor and spallation neutron sources should produce a dramatic expansion in the range of science that can be addressed with neutrons. One particularly interesting area is nanoscience and technology where the impact of neutron scattering has been limited so far. With orders of magnitude greater efficiency, however, 21st century neutron scattering instrumentation is poised to have a major impact in understanding

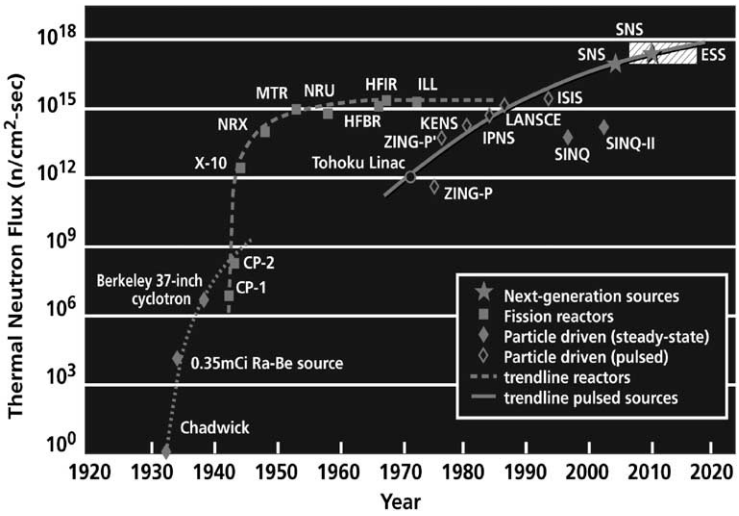

Fig. 1. History of peak fluxes for reactors and spallation neutron sources. Updated from Ref. [1].

Table 1
List of SNS instruments for condensed matter physics scheduled for completion in 2006

Instrument	Specification	Condensed matter science
Silicon backscattering	$\Delta E \in [2.2, 10]\,\mu\text{eV}$	Diffusion, tunneling, and solvent dynamics
Vertical reflectometer	$Q \in [0, 7]\text{Å}^{-1}$ $R > 10^{-10}$	Solid and magnetic interfaces
Horizontal reflectometer	$Q \in [0, 0.5]\text{Å}^{-1}$ $R > 10^{-10}$	Structure of liquid interfaces
Extended Q SANS	$Q \in [0.004, 12]\,\text{Å}^{-1}$	Nano-scale solid and solvent structure
Powder diffraction	$0.1\% < \delta Q/Q < 1.6\%$	High resolution structure
meV–eV spectrometer	$\Delta E \in [1, 10^3]$ meV	Lattice, spin, and liquid dynamics
μeV–meV spectrometer	$\Delta E \in [0, 20]$ meV	Lattice, spin, and liquid dynamics

structure and dynamics of condensed matter confined to the nanoscale and of interfaces in artificially structured materials and devices.

3. Synchrotron radiation—light on materials

X-rays have been one of the primary probes to characterize materials for almost 100 years. The advent of the first synchrotrons in the 1970s and then the dedicated second generation (e.g., NSLS at Brookhaven) in the 1980s greatly increased the intensity of the sources, and, most importantly, provided sources where the wavelength (energy) could be continuously tuned, rather than fixed at certain K-edge emission energies. These advancements led to a vast increase in characterization techniques, especially those based on absorption edges, e.g., EXAFS, SEFAFS, XANES, DAFS, etc., that have had a well documented influence on our understanding of materials. In the 1990s, third generation synchrotron machines began to come on line (e.g., the ESRF in Grenoble, APS at Argonne, and SPRING-8 in Japan). Again the intensities are increased from the earlier machines, the tunability is more accentuated with the undulator and wiggler insertion devices, but there are also some new features that are changing research in condensed matter science.

3.1. Brightness

This is related to the number of photons passing a certain cross-sectional area per second. The

ability to pack all the photons into an extremely small cross-section, say $50 \times 50\,\mu m^2$ has led to some striking advances. Among these we might list research on high pressure, surfaces, and microcrystals. In each case the experiments profit greatly from the fact that the beams are very small, but very intense. Experiments with diamond anvil cells at 100 GPa and beyond now use μg (or less) samples and image plates to collect the data in times normally <1 min per pressure point.

3.2. Tunability and intensity

The use of highly specialized monochromators and analyzers (piggybacking on the Si technology developed by the semiconductor industry) has led to higher energy resolution. In absorption experiments this has led to increased resolution, and such techniques as time-resolved (ns time scale) EXAFS, and in elastic scattering experiments the increased energy resolution has allowed many features at various absorption edges to be investigated. By using backscattering and nuclear resonant techniques, there has been a dramatic breakthrough in being able to measure phonons with a resolution of a few meV that will challenge neutron spectroscopies of phonons in the next decade.

3.3. Coherence

The more well defined incident energy of the incident photons has now led to increased coherence of the photon beams. This has allowed the development of techniques similar to time-correlated spectroscopy (speckle) used with lasers, although over length scales that are much shorter because of the smaller photon wavelength compared to those of lasers. Until now this technique has had its major impact in soft matter (e.g., colloids) but has been used also in hard condensed matter (e.g., phase transition in Cu_3Au) and even in magnetism. Coherence has allowed also phase contrast techniques to be developed in imaging and at microprobe beamlines. These are now rivaling the details of TEM, without the great difficulties of sample preparation of the latter technique. We can expect applications of coherence to increase in the future.

3.4. High energy

Clean photon beams of energies from say 60 to 100 keV are now been used for materials science applications. Such beams penetrate deep into materials (like neutrons) and the small size of the beams can be used to learn about the microstructure, residual strain, etc.

Synchrotrons have proven much more useful to magnetism than was predicted 20 years ago. Techniques like dichroism, resonant scattering, and others, especially at the lower energies, have given new information on electron correlations. What of the future? Many of the newest ideas focus on *coherence,* which has barely been exploited in present third generation machines. *Time structure* is another new window into condensed matter science, whether it is biology, chemistry, or physics. At present there are a number of experiments at the nanosecond (10^{-9} s) level, a few pushing into the picosecond (10^{-12} s) range. Most synchrotrons have bunch lengths in the picosecond range so any faster type experiments are not possible with circular machines. Free-electron lasers (FELs) will have brightness many times greater than present circular sources, and a time structure in the femtosecond (10^{-15} s) range (for information 1 eV = 4 fs, and the speed of sound of most materials ~ 1 Å/100 fs). Such machines, which are seriously being discussed at Stanford, Hamburg, and other places, will represent a totally new capability in condensed matter science. The future for photon-based research is indeed bright and (hopefully) coherent!

4. The extremes of parameter space: pressure and magnetic fields

Recent years have seen—and future years will continue to see—an unprecedented development of high field magnet facilities, e.g., the National High Magnetic Field Laboratory (NHMFL) in the United States, the High Magnetic Field Laboratory in The Netherlands, and numerous pulsed

field facilities across the world, focusing on condensed matter sciences and other areas of research. Powerful new magnets within these facilities include the newly commissioned 45 T Hybrid Magnet, a 14 ton superconducting coil cooled to 1.8 K surrounding a resistive magnet insert, and the new 60 T Long Pulse Magnet with a controlled-waveform achieving 60 T for 100 ms at the NHMFL. The future includes the development of a 100 T multi-shot magnet, which nests a small $\sim$10 ms pulse solenoid inside a 47 T long-pulse solenoid to achieve unprecedented non-destructive magnetic field intensities up to 100 T. Maximizing the scientific impact of these newly developed magnets depends on the simultaneous development of new experimental probes designed specifically for the unique environment of intense magnetic fields. The NHMFL and other laboratories are currently developing a wide range of experimental techniques to address the outstanding scientific questions at high magnetic fields. A few of these new approaches are outlined below.

Nuclear magnetic resonance (NMR) in resistive magnets to 45 T, using new pulse sequencing techniques and micro-coils, has obtained spectra in powered DC magnets at the very high fields and has helped reduce the negative impact of homogeneity and temporal stability [2]. For example, recent ^{17}O NMR studies have led to the imaging of magnetic vortices in the high-T_c superconductor $Yba_2Cu_3O_7$ at 37 T [3] and studies of Al NMR have clearly demonstrated the $\sim 1/B^2$ reduction in quadrupolar line broadening which will permit certain NMR studies on quadrupolar nuclei [4]. Pulse sequence development has demonstrated techniques to reduce the negative impact of temporal instabilities leading to the observation of spectra with line widths of 2 orders of magnitude lower than anticipated, i.e., approaching line widths in the 10's ppb with field homogeneity and stabilities of $\sim$1–10 ppm. These techniques coupled with the development of micro-coils and miniaturized magic angle spinning probes will open new opportunities to apply NMR to structure and spin dynamics problems in the future including developing approaches relevant to nanoscale sciences. This topic is discussed further at the end of this chapter.

Faster electronics and innovative approaches to measurement have opened new opportunities at high field that were formerly deemed to be impossible. For example, specific heat measurements have been extended to 60 T pulsed fields in a recent experiment with the sample, thermometer, and heater adiabatically isolated on a stage with a very rapid internal thermal response. By using the controlled-waveform capabilities of the 60 T Long Pulse Magnet to fix the magnetic field near the peak of the pulse, researchers were able to measure specific heat to observe the closing of the collective Kondo insulator gap in magnetic fields above 40 T and the carrier mass in the high-field metallic state [5].

High magnetic fields are uniquely suited for the most difficult deHaas-van Alphen (dHvA) experiments, those involving heavy carrier masses or disordered samples. In these measurements, the quantum oscillations of magnetization are enhanced by low temperatures and high magnetic fields. The quantum oscillations saturate below the experimental Dingle temperature, however, they continue to grow with higher magnetic fields. High field measurements of dHvA oscillations in $Ce_xLa_{1-x}B_6$ show the oscillatory magnetization of a heavy-mass in a highly disordered alloy [6]. From this experiment, the carrier mass enhancement and Fermi surface distortion upon substituting the f-electron Ce element on the La site in LaB_6 could be observed across the whole series. The high magnetic fields and low temperature permitted these measurement to be extended into regions of disorder that had previously been unattainable. In addition, contactless radio-frequency magnetotransport, suitable for small samples and pulsed magnetic fields, were used recently in measurements of the quantum oscillations in the resistivity, metallic skin depth, and superconducting penetration length for both organic and high-T_c superconductors. This technique measures the change in resonant frequency of a highly stable 10–100 MHz tank circuit in response to the changing shielding current in the sample. Also, dramatic improvements are being seen in the development of new custom-made electronics for sensitive magnetotransport measurements using sufficiently high frequencies to extend these techniques to pulse

magnets. New digital synthesizers and commercial digitizers have been used at the NHMFL to develop a new generation of four-terminal magneto-transport measurements in pulsed magnetic fields. These approaches applied to pulse magnets allow the data to be collected and phasing between detection signal and reference signals adjusted as part of the analysis of the data thus not losing critical data that typically occurs in other approaches to measurements of transport in hostile environments, i.e., in the background of rapidly changing magnetic fields. Extending transport measurements to the gigahertz and terahertz spectroscopies are now beginning to allow researchers to measure both the amplitude and phase of the complex conductivity in this little studied range of the electromagnetic spectrum. This is a particularly exciting development because the 10–3000 GHz regime corresponds to the same temperature range (0.4–140 K) over which many correlated electron phenomena are observed. Equally important, is that this frequency range covers the same energy range (40 μeV–12 meV) typically imposed by today's powerful DC and pulsed field magnets.

High pressures and the marriage of high pressures and low temperatures with high magnetic fields have long been linked to key advances in the exploration of all types of strongly correlated electron materials. As these materials generically have multiple and competing energy scales, often closely balanced, as well as narrow bands near the Fermi surface, even modest pressures are often sufficient to make qualitative changes in both ground and finite temperature instabilities. The most dramatic use of high pressure is in the discovery of new superconductors [7]. In many cases, the broadening of conduction bands is sufficient to raise a superconducting transition into the experimentally accessible range in relatively simple metallic elements such as Ba or Sb. In other cases, such as Si and Ge, it is first necessary to metallize the element before superconductivity is enabled. However, the recent observation of superconductivity in elemental B, at pressures exceeding 150 GPa shows that superconductivity can also occur in an element that is insulating in the normal state [8]. It is especially exciting when superconductivity is observed in proximity to magnetic order, for here there is a possibility of unconventional superconducting order parameters and pairing mechanisms. The recent observation of superconductivity in elemental Fe relies on high pressures to suppress ferromagnetism and to drive the $\alpha-\varepsilon$ structural transition [9]. Even more striking is the observation of simultaneous ferromagnetic order and superconductivity in two intermetallic compounds, UGe_2 [10] and $ZrZn_2$ [11], under pressure.

The need to characterize and define the properties of these novel high-pressure phases has led to the evolution of new experimental techniques, and a few examples will be discussed here. As indicated above, high-pressure diffraction measurements took a major leap forward with the increase in brightness characterized by the second and third generation synchrotrons. The development of synchrotron sources has also led to a renaissance in high-pressure infrared transmission and absorption measurements, due to their huge brilliance relative to conventional infrared sources [12]. Extending this technique to strongly correlated electron systems should be very exciting, given the large transfers of spectral weight and strong temperature dependences that have been documented in these systems at ambient pressure. Spectroscopic information is critically important for the theoretical interpretation of many strongly correlated electron systems, and the recent development of inelastic X-ray scattering using nuclear resonant techniques provides energy resolution similar to that found in medium resolution neutron time-of-flight spectrometers. In an experimental tour de force, the phonon density of states of Fe has recently been measured to pressures as large as 150 GPa. Even though there have been numerous advancements in applications of high pressure to synchrotron sources, neutron diffraction techniques have been largely limited to pressures below several GPa, due to the requirement of large sample sizes. The development of the Paris–Edinburgh pressure cell at the ISIS neutron source provides a unique capability of magnetic structure determinations at high pressures [13].

New sample environments also challenge the limits of high-pressure technology, as has been

demonstrated in pulsed magnetic fields. Eddy current heating of the pressure cell, typically made of high strength metals, has limited the use of either liquid clamp type cells or diamond anvil cells in the pulsed field environment. The development of a diamond anvil cell with a plastic support assembly has enabled both resistance and optical measurements to pressures as large as 8 GPa, in pulsed fields as large as 60 T [14].

To conclude, the study of strongly correlated systems under high pressure and high magnetic fields remains a very fruitful area of materials research. Our past experience has shown that high pressures and high magnetic fields can be used very powerfully as part of the materials synthesis process, allowing more continuous and disorder-free tuning of electronic and structural parameters than is generally possible with compositional variation alone.

5. Optical probes in materials physics

The physics of complex materials is governed by several key features, including: (1) strong interactions among several important degrees-of-freedom, i.e., charge, spin, lattice, and/or orbital; and (2) the spontaneous formation of (dynamical) meso-scale structures (e.g., magnetic polarons, charge- and orbital-ordering, and coexisting metallic and insulating domains), which strongly influence the dramatic phenomena observed in these systems, including colossal magnetoresistivity, field- and pressure-sensitive metal-insulator transitions, field- and pressure-induced disordering of charges and orbitals, and perhaps even pseudogap behavior and high T_c superconductivity. These features define some essential elements required of future optical probes of complex materials: (1) The ability to probe charge-, spin-, lattice-, and orbital-configurations on a range of length scales (from nanometer to micron); (2) the ability to probe relevant excitations on varying time scales, in order to provide important dynamical information regarding different meso-scale structures in these systems; (3) the ability to explore complex materials under extreme conditions, such as high magnetic fields and ultra-high pressures, using spectroscopic as well as static probes. These requirements suggest several key directions for future optical studies of complex materials which are briefly discussed below.

5.1. Time-resolved optical spectroscopy

Time-resolved (pump-probe) optical spectroscopies, such as terahertz time-domain spectroscopy [15], pump-probe absorption spectroscopy [16], and polarization-sensitive pump-probe spectroscopy [17], are becoming increasingly important as a means of probing spin- [18] and charge-dynamics [15,16] in complex materials, and also as a means of separating dynamical contributions that are not spectroscopically well-separated, such as orbital- and lattice-relaxation contributions [17]. Future applications of time-resolved optical spectroscopy to complex materials should involve extending to the fast time-domain other powerful photon-based probes, including time-resolved Raman spectroscopy [19], to exploit the great ability of Raman scattering to convey simultaneous dynamical information regarding charge-, spin-, lattice- and orbital-excitations [20], and time-resolved synchrotron X-ray scattering, to provide dynamical information regarding lattice distortions with nanometer-scale spatial resolution.

5.2. High spatial-resolution scanning optical microscopies

High resolution scanning optical microscopies, such as near-field scanning optical microscopy (NSOM) [21] and confocal microscopy [22], are extremely promising optical techniques for providing imaging, spectroscopic, and polarization and spin-sensitive information in complex materials with sub-micron spatial resolution [23]. Of particular interest would be to use sub-micron optical spectroscopic or magneto-optic (e.g., Kerr-effect, Faraday-effect, spin-flip Raman) probes to explore the charge-, lattice-, and spin-dynamics of meso-scale structures in different phases of complex materials. Furthermore, marrying such nanometer scale optical probes to fast time-domain optical techniques [23] to study complex materials would enable one to explore the dynamics of local

charge-, orbital-, and spin-structures in these systems. Ultimately, however, the limited resolution of these optical techniques (>20 nm) demand the use of probes such as scanning tunneling microscopy [24] and electron diffraction [25] for studying mesoscale structures in complex materials with ultra-high resolution.

5.3. Phase-sensitive optical spectroscopies

Optical reflectivity and absorption measurements have long been favorite techniques for studying complex materials [26], because of the relative simplicity of this technique and its direct coupling to fundamental quantities such as the lattice and carrier dynamics. A key limitation of this technique is the need to perform a Kramers–Kronig analysis on the measured response to determine the complex optical functions of a material, a process that can introduce errors into the results. Recently, phase-sensitive techniques, enabling simultaneous study of both real- and imaginary-parts of optical functions, e.g., far-infrared ellipsometry [27] and terahertz time-domain optical spectroscopy [15,28], have enabled highly sensitive studies of charge and vortex dynamics in the important microwave/far-infrared frequency ranges of complex materials. These studies are likely to become increasingly important in future studies of complex materials, particularly as they are extended to time-resolved investigations [15] and to studies under "extreme" conditions such as at ultra-high magnetic fields and pressures.

5.4. Inelastic X-ray scattering

One limitation of conventional optical spectroscopic techniques (e.g., Raman) is that these methods are generally constrained to probing excitations essentially at the Brillouin zone center, $\mathbf{q}\approx 0$. Recent advances in synchrotron sources have opened up dramatic new possibilities for exploring the full $\mathbf{q}$- and ω-dependence of excitations in complex materials, and for probing excitations to which other photon probes are less sensitive (e.g., orbital excitations, using inelastic X-ray scattering) [29].

5.5. Optical studies under "extreme" conditions

A hugely promising future area of study lies in combining machines and devices capable of pushing complex materials into extreme phase regimes, e.g., at ultra-high magnetic fields and pressures, with optical probes that are capable of effectively probing excitations in these materials under the often complicated conditions imposed by large magnets, high pressure diamond anvil cells, etc., e.g., terahertz time-domain spectroscopy, and Raman spectroscopy. Of particular interest is finding probes that can convey time-resolved information and/or spectroscopic (ω-dependence) information under various extreme conditions.

6. Photoemission spectroscopy

Photoemission spectroscopy (PES) is by now well established as the method whereby the spectral function for single particle electron removal can be measured, under the assumptions that the photoemission event can be described within the sudden approximation and that the photoemission matrix element can be adequately disentangled from the measured spectrum. Angle resolved PES (ARPES) and PES yield the $\mathbf{k}$-resolved and $\mathbf{k}$-summed spectral functions, respectively. Recent technical advances have brought the spectroscopy to a new level of sophistication that is just now being explored. Strongly correlated electron materials pose particularly severe challenges for ARPES and PES and thereby provide an excellent context in which to describe and appreciate the newly ambitious efforts.

Difficulties that can be viewed as purely experimental are the $\mathbf{k}$ (angle) and energy resolutions, and the sample temperature. For a system with an enhanced mass, say $m^* = 50\,m_e$, and, say, Fermi wave vector $k_F = 0.5\,\text{Å}^{-1}$, the Fermi velocity $v_F = \delta E/\delta k$ can be estimated as $8\,\text{meV}/0.1\,\text{Å}^{-1}$, which gives a measure of the energy and $\mathbf{k}$-resolutions needed in ARPES to directly observe the heavy mass dispersion at the Fermi level. These enhanced resolutions then impose additional sample temperature requirements beyond simply accessing phase transitions of interest. The Fermi function

broadening of $4k_BT$ implies that the temperature T should be <14 K if the resolution is as good as, say, 5 meV, a great challenge for a spectroscopy in which the sample must be open to the (uncooled) electron analyzer and must have photons incident on the sample.

There are also certain intrinsic difficulties that cannot be forgotten or minimized. First, many highly correlated electron systems are challenging simply because they are three-dimensional. As the electron detector angles are varied for fixed photon energy, a spherical **k**-space surface is traversed. To access the full three-dimensional Brillouin zone requires tuning the photon energy to change the radius of the spherical surface. Further, $k_\perp$, the component of **k** perpendicular to the sample surface, is not conserved in the photoemission process so that relating the value of $k_\perp$ measured outside the sample to its value inside the sample requires modeling the surface potential, e.g., by an "inner potential step" V_0. Determining V_0 and thus being accurately oriented in **k**-space entails measuring over a wide photon energy range to find repeating spectral patterns that can be registered correctly with repeating Brillouin zones for a suitable value of V_0. This process and indeed the spectra themselves can be compromised by the photoelectron lifetime, which causes $k_\perp$ broadening. The photoelectron lifetime also makes a contribution to the photo-hole line width that is additional to that of the intrinsic spectral function one seeks to measure. This contribution is proportional to the perpendicular hole velocity and so is again problematic for three-dimensional materials.

Second, the small electron elastic escape depths cause the technique to be surface sensitive. This fact limits the time over which a prepared surface remains free of contaminants even in excellent vacuums and imposes the need to distinguish electronic structure that is peculiar to the surface and not characteristic of the bulk. The latter need is met by tuning the probe depth through changes in detection angle and photon energy, or by testing a spectral feature for extreme sensitivity to deliberate surface contamination. Third, it is often desirable to distinguish the character of states, e.g., their angular momentum or their association with certain atoms. This task is accomplished by exploiting the photon energy dependences of the photoemission cross-sections for various kinds of states, e.g., cross-section resonances associated with core level absorption edges.

From the preceding discussion an inescapable conclusion is that the available experimental variables of angle and photon energy are badly overworked. Similarly, as the photon energy is varied to exploit a cross-section resonance, the position in **k**-space also changes. For serious PES or ARPES studies, it is a matter of both skill and luck to choose a material for study that embodies the physics of interest and does not manifest simultaneously all the possible challenges that must be overcome.

Set against the various difficulties and challenges are recent advances in instrumentation. Laboratory gas discharge lamps, e.g., the Gammadata He lamp, and undulator-based synchrotron beamlines offer much higher photon intensities than before and thus enable photon energy resolutions ranging from <2 meV for 20 eV photons to <100 meV for 1000 eV photons. The great importance of an extended photon energy range with good resolution is implicit in the discussion above, especially for three-dimensional materials, for materials with cross-section resonances at particular absorption edges, and for minimizing surface contributions to the spectra. Particularly notable for high resolution at high photon energy is the twin-helical undulator beamline BL255SU of the SPring-8 synchrotron in Japan. New electron detectors and energy analyzers, as exemplified by the Scienta SES200, offer an order of magnitude improvement in energy and angle resolutions, e.g., to ≈ 2 meV and $\approx 0.2^\circ$, respectively. Equally important is the use of multichannel energy and angle detection, causing the new ARPES data quantum to be an entire slice of **k** and binding energy space rather than a single spectrum for a fixed **k**-value. At the same time, more elaborate sample cooling schemes are enabling sample temperatures ≈ 10 K or less to be achieved. A recent advance in technique that exploits multi-channel angle detection particularly well is that of making Fermi surface intensity maps, in which the electron detector is fixed at a

kinetic energy corresponding to the Fermi energy for the photon energy being used, and the detector angles are then varied. The result can be interpreted as the intersection of the spherical **k**-space surface traversed with the Fermi surface. It is also possible to make such a map perpendicular to the sample surface by varying the photon energy and one detector angle.

There is not space here to describe specific recent results that illustrate the new possibilities, but an excellent introduction and overview can be obtained by consulting a recent collection of articles focusing on many aspects and applications of photoemission for highly correlated electron systems, including Fermi surface mapping of both low dimensional and three dimensional materials; detailed line shape studies of high-temperature superconductors, of a Luttinger liquid material, and of other non-Fermi liquid systems; and high photon energy studies to maximize bulk sensitivity for various materials [30]. These new results encourage the belief that it will be possible to resolve and identify the details of the bulk electronic structure and Fermi surfaces of numerous highly correlated electron systems, even three dimensional ones, on all relevant energy scales and to track changes in their spectra through phase transitions of interest. Such studies will enable detailed testing of the results of modern many-body theories of the electronic structure of highly correlated electron systems and of course to novel materials generally.

7. Nuclear magnetic resonance studies of solids

Magnetic resonance is a powerful probe of condensed matter systems; one that has particularly influenced our understanding of correlated electron systems. A local probe, NMR is able to distinguish behavior at various atomic sites in a material. At the same time, even in good conductors, NMR is able to probe bulk properties of materials.

NMR measurements are able to determine both the static uniform spin susceptibility and a weighted average over wave vectors on the Fermi surface of the low energy dynamical susceptibility. These capabilities nicely complement neutron scattering techniques. For example, by comparing ^{17}O and ^{63}Cu, NMR measurements demonstrated antiferromagnetic spin fluctuations in optimally and underdoped $YBa_2Cu_3O_{7-\delta}$ [31]. The exact character of the spin fluctuations continues to be refined by neutron scattering measurements and continues to provide one of the most fruitful avenues for understanding the superconducting cuprates.

Another strength of NMR that has been exploited in the cuprates is its ability to characterize and study variations in crystal structure or electronic properties regardless of their degree of spatial order. For instance NMR has shown the existence of static modulations in local charge and magnetic environment that vary on length scales of a couple of lattice spacings [32]. Additionally, it was shown that the modulations of charge and magnetic properties are correlated, that is, an increase in one is accompanied by an increase in another. In the absence of spatial ordering, such modulations can be very difficult to detect by other means.

The primary weakness of magnetic resonance techniques is their relative insensitivity. Typically 10^{16}–10^{18} nuclear spins are required to obtain acceptable signal-to-noise ratios in NMR experiments. This is an unfortunate limitation that hinders application of these techniques to systems containing few spins (e.g., thin films, surface species or micro-fabricated materials). This is due in part to the smallness of the nuclear magneton that induces only a weak voltage when precessing in a coil, and in part to the very small net polarizations of the spins, typically of order 10^{-5} at room temperature in typical laboratory field.

One approach to enhancing sensitivity in magnetic resonance experiments is to increase the spin polarization above thermal equilibrium values. In situations where they can be used, high fields and low temperatures increase the spin polarization. Another powerful and widely used approach employs circularly polarized light to generate an excess population of one electronic spin species [33]. Through the hyperfine coupling between nuclear and electronic moments, this excess electron spin polarization can be transferred

to the nuclear spins. Tycko et al. [34] have demonstrated the value of this approach in obtaining selective sensitivity to Ga nuclear moments located in the two dimensional electron gas confined in a quantum well in a GaAs heterostructure enabling powerful studies of the quantum Hall state.

The hyperfine coupling between nuclear and electron spins also allows one to use optical techniques to detect the nuclear resonance signal. This approach has recently been exploited to perform all optical magnetic resonance in GaAs semiconductors [35]. Such techniques can achieve very high sensitivity, possibly single spin [35].

A very general approach to high sensitivity magnetic resonance is to employ very high sensitivity detection techniques. Mechanical detection by means of sensitive high Q mechanical resonators is one such approach. First proposed a decade ago [36], the magnetic resonance force microscope (MRFM) is based on this concept and is proving to be a versatile instrument that has been demonstrated in a variety of magnetic resonance experiments: electron spin resonance [37,38], nuclear magnetic resonance [39], and ferromagnetic resonance [40,41]. Presently, the MRFM has demonstrated resolution in NMR at the μm length scale.

The MRFM detects magnetic resonance signals mechanically by sensitively measuring the force between a permanent magnet (which generates $\nabla\mathbf{B}$) and the spin

$$\mathbf{F} = (\mathbf{m}\cdot\nabla)\mathbf{B}$$

magnetization $\mathbf{m}$. This force is detected by a high Q, low spring-constant micro-mechanical resonator (cantilever or bridge) such as is used presently in atomic force microscope. Advances in surface micro-machining and the use of low-loss (equivalently, high quality factor Q) single crystalline materials have enabled great improvements in signal detection sensitivity using mechanical resonators. The force sensitivity is determined by the thermal force noise of the detector; this, in turn, depends on temperature T (k_B is Boltzmann's constant) and detection bandwidth Δv, as well as characteristics of the resonant mechanical detector, i.e., its spring constant k and characteristic frequency f_c [38,42,43]:

$$F_n = (2kk_BT\Delta v/(\pi Qf_c))^{1/2}.$$

The magnetic field gradient performs a second key function in addition to providing the coupling to the sensitive force detector: as in MRI it selects the volume of material hundreds of angstroms or even microns beneath the surface that will be studied. The resonant frequency of a nuclear spin is proportional to the magnetic field it experiences. If the applied field varies spatially, then the correspondence between applied field and resonant frequency translates into a correspondence between position and frequency. The strength of the field gradient and the magnetic resonance line width $\Delta\omega_{lw}$ determine the size (say Δz) of the selected resonant volume:

$$\Delta z \approx (\Delta\omega_{lw}/\gamma|\nabla_x\mathbf{B}|).$$

Field gradients sufficiently large to obtain Å scale resolution can be obtained using lithographically defined permanent magnets; the key to obtaining high spatial resolution is to optimize the sensitivity of the microscope. The theoretical limit for mechanical detection is a single nuclear spin. This enhanced sensitivity allows one to reduce the volume of the sample isolated for study (i.e., allows one to improve the spatial resolution of the microscopic study) while maintaining adequate signal to noise ratios.

The ability to perform high sensitivity magnetic resonance in sub-surface microscopic volumes in general samples would open exciting new approaches to understanding the complex behavior of correlated electron systems. While much work remains to be done, the rate of improvement in MRFM capabilities is cause for optimism that such experiments will be within our grasp within a modest period of time.

Magnetic resonance is one of the most powerful and effective tools at our disposal for understanding condensed matter systems. Great progress has been made in overcoming the poor sensitivity of the technique, its primary limitation, leading to an ever-expanding range of conditions and materials where it has been profitably employed.

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