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PREFACE

In the spring of 1982, the Solid State Sciences Committee (SSSC), in implementing one of a series of studies important to maintaining the health of this discipline, asked a group of experts to assess the present status and future potential of sources for solid-state research. In August 1982, a Subcommittee of the SSSC undertook the preparation of a report addressing the following concerns:

Definition of method and scientific opportunities
Description of existing sources and facilities both here and abroad
Availability of the various sources
Role of universities in such research
Identification of new directions in the field
Conclusions and recommendations

The Solid State Sciences Committee has reviewed the Subcommittee's report, unanimously approves its conclusions and recommendations, and recommends that it be issued as a report of the SSSC.

Wiliam F. Brinkman, Chairman
Martin Blum, Past Chairman
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1. SUMMARY

Muon spin rotation (μSR) is a relatively new technique, which has experienced considerable growth since about 1975 because of the commissioning of several high-intensity, meson-producing accelerators around the world. Currently there are μSR programs in the United States (LAMPF), Switzerland (SIN and CERN), Canada (TRIUMF), and Japan (KEK). Future facilities are planned in the Netherlands (NIKHEF), Great Britain (Rutherford-Appleton), and the United States (Brookhaven).

I. THE SCIENCE

The interest in the μSR technique lies in the fact that a spin-polarized beam of positive or negative muons can be implanted in almost any sample. The time evolution of the polarization then yields information about the muon's local magnetic environment. The μSR technique is analogous to nuclear magnetic resonance (NMR) in many ways, although there are important differences.

μSR experiments can be conveniently grouped according to the role that the muon plays: (1) a local probe, (2) a light interstitial particle, and (3) a hydrogen-like atom (muonium).

As a local probe the muon samples its magnetic environment, at either an interstitial or a substitutional site (μ^+) or at a lattice site (μ^-) in a crystal. The spin precession and relaxation give information about the static and dynamic local fields. This use of the μSR technique complements other local probes such as NMR, Mössbauer spectroscopy, perturbed angular correlations, and neutron scattering. In some cases μSR can yield information on magnetic-ion correlation times that is inaccessible to these other techniques.

As a light interstitial particle, the muon may be used to study localization and diffusion phenomena for a particle mass intermediate between those of the proton and the electron ($m_p/m_\mu/m_e \sim 938/106/0.5$). Considering the muon as a light isotope of hydrogen allows one to study nonclassical diffusion phenomena unseen in previous experiments using hydrogen.

Under the third category, muonium (μ^+e^- atom) centers can be compared with hydrogen in semiconductors, and muonium and hydrogen reaction rates can be compared in liquids and gases, yielding complementary information. Muonic radicals can also be studied. Unique information is obtained from μSR in materials when hydrogen solubility is low or, as in the case of semiconductors, where no hydrogen paramagnetic states are seen.

II. USER MODES AND FACILITIES

μSR experiments generally require a minimal group size of at least four collaborating scientists. These individuals may come from in-house staff at accelerator facilities or from outside user groups. The accelerator facility generally provides computer and data-acquisition electronics and a general-purpose μSR spectrometer, often including specialized cryogenic or sample-heating capabilities.

One way of estimating the strength of a research program is by counting the number of participating scientists. For this purpose, "full-time" equivalent is used here to mean an individual with a Ph.D. degree whose primary research activity involves using the μSR technique. On this basis, the largest μSR program in the world is currently based at SIN, where about 23 full-time scientists, mostly from Europe, are involved. TRIUMF has the next largest program, with about 15 full-time people. By contrast, the programs at LAMPF, CERN, and KEK each have about 10-13 full-time users. The level of support for both in-house and outside user groups in the United States is considerably below that provided in Europe, Canada, and Japan.

The accelerators at SIN and TRIUMF produce high-intensity dc muon beams, which are best suited for most present types of μSR experiments. The "time-differential" technique appropriate to dc beams requires a determination of the time difference between the muon stop and decay signals. This in turn requires that only one muon be in the sample during the measurement time, in order not to confuse signals from two or more muon stops. The accidental coincidence rate between two or more muon stop signals is lowest for a dc (100 percent macroscopic duty factor) muon beam.

Pulsed beams are optimal only if the pulse duration is quite short (~1-10 ns). Then all muons can be considered to arrive simultaneously, yielding a common stop signal and allowing, in principle, much higher data rates than a dc beam can provide. The KEK accelerator currently produces a relatively low-intensity pulsed beam with a width of 50 ns, making it suitable for a limited but useful class of pulsed-beam experiments. The LAMPF beam width of 750 μs is inadequate for pulsed applications, and the 10 percent macroscopic duty factor (compared to dc) leads to a 90 percent reduction in the overall data rates compared to SIN, for example. However, a productive program of research has been carried out at LAMPF, even under these less-than-optimal conditions.

III. FUTURE DIRECTIONS

In the near future (<3 years) new muon channels will be built at SIN and TRIUMF in order to provide more muon beams with greater luminosity (particles/cm^2/s). Brookhaven National Laboratory (BNL) installed and commissioned a low-intensity channel in early 1983, to be used in part for μSR research. The BNL accelerator is expected to produce a data rate about 4 times that of LAMPF but 2-1/2 times lower than at TRIUMF and SIN. A high-intensity pulsed muon facility is being designed for use at Rutherford-Appleton Laboratory, to complement the materials-science pulsed-neutron-scattering program planned there.

These improvements will likely lead to a growth in the variety of phenomena to be studied, as more researchers trained primarily in solid-state physics and in chemistry enter the field. Such phenomena are certain to include diffusion and localization, dynamic effects in magnetism (e.g., solitons, effects of disorder, itinerancy), surface science, and muonium chemistry. One should also expect new types of experiments using pulsed sample environments at the KEK machine.

In the more distant future (~5 years) the Los Alamos Proton Storage Ring (PSR) could provide an exceptional pulsed muon source. The PSR, now under construction, will operate in two modes: a 1-ns-wide proton burst at 720 Hz and a 270-ns-wide proton burst at 12 Hz. The long-pulse mode could be used to provide a chopped muon beam with a width between 5 and 270 ns. The short-pulse mode would be very useful as designed.

In the long term the more frequent use of higher-luminosity dc and pulsed beams, as well as high time-resolution SR spectroscopy, will allow routine, high-precision measurements of the entire spin-relaxation function or nearly any sample of interest in a variety of sample environments, static or pulsed. The latter could include the pulsed application of pressure, laser irradiation, or strong electric/magnetic fields.

2. CONCLUSIONS AND RECOMMENDATIONS

I. CONCLUSIONS

Muon spin rotation (μSR) is a relatively new technique, in which most work has been carried out since 1975. About 20 American scientists are engaged in μSR at present. The μSR technique has proved fruitful, and a variety of important results have been obtained. Some of these, e.g., diffusion of the positive muon as an example of a light interstitial particle, could not have otherwise been obtained. In areas such as magnetism, electronic structure of metals, and muonium in insulators, μSR yields information complementary to other local-probe techniques and in some cases extends the range of measurable parameters (e.g., electron-spin correlation times) to values unobservable by other methods.

Primarily because μSR relies on facilities already in existence at meson-producing accelerators, it is not a particularly expensive technique. Indeed, the initial phases of this research were supported by the nuclear-physics program and by discretionary funds at these facilities. The current status of U.S. facilities and research is as follows: A productive research program is under way at LAMPF, despite the 10 percent maximum duty factor and the consequent limitation of the data rate. This effort represents about half of the U.S. research in μSR. The limitations of the beam and restricted funding at LAMPF have led other U.S. μSR scientists to pursue their research at accelerators outside the United States, principally at TRIUMF (Canada) and at SIN (Switzerland).

A new muon beam line was dedicated in 1983 at Brookhaven National Laboratory (BNL). It is expected to provide a data rate about 4 times that currently available at LAMPF but 2-1/2 times lower than data rates at other facilities with a dc beam (TRIUMF, SIN). The amount of beam time and the degree of user support available for μSR experiments at BNL have yet to be determined.

As this field starts to grow, its funding will have to be considered relative to other research opportunities in the solid-state sciences.

II. RECOMMENDATIONS--SHORT TERM

The Subcommittee finds that present accomplishments using the μSR technique are of sufficient value to justify continued growth of the field. In view of the fact that the U.S. effort is significantly below that of other nations, we recommend the following:

1. Adequate and stable support, subject to the peer review process, should be provided for U.S. user and in-house groups at domestic and foreign facilities. This should be at a level compatible with the required minimum group size.
2. U.S. μSR facilities should be upgraded to provide greater access to users and to provide higher-quality data.

III. RECOMMENDATIONS--LONG TERM

1. The importance of pulsed muon beams for μSR research should be reviewed within the next year, as results accrue from the KEK facility. The subcommittee tentatively concludes that pulsed beams have the potential greatly to enhance the technique, both qualitatively and quantitatively. Few results have been produced to date, however. The Los Alamos Proton Storage Ring (PSR) has the potential of providing a world-class pulsed μSR facility in about 5 years, and the utility of a future μSR beam line at the PSR should therefore be carefully evaluated.
2. The status of the field as a whole should be reviewed in about 3 years.

3. INTRODUCTION

The first technique used to experimentally verify parity violation in muon decay was implemented by Garwin *et al.*[1] in 1957 and involved the precession of the muon magnetic moment in an applied field. This measurement was thus the precursor of the modern-day muon spin rotation (μSR) technique. In the earliest searches for suitable materials for the study of positive muon decay, it was noticed that the muon polarization remaining after thermalization depended significantly on the type of stopping environment, varying from 10 percent in some liquids like benzene to 100 percent in most metals. Data of this nature contained the beginnings of the application of the μSR technique to the study of basic phenomena in condensed-matter physics and chemistry.

Since 1975 there has been a large growth in the quality and quantity of μSR research owing to the inauguration of several "meson factories" around the world, which produce high-intensity, polarized beams of positive and negative muons. Currently there are μSR programs being carried out in the United States (LAMPF), Switzerland (SIN and CERN), Canada (TRIUMF), and Japan (KEK). Future facilities are planned in the United States (Brookhaven), the Netherlands (NIKHEF), and Great Britian (Rutherford-Appleton). There have been three international conferences[2] on μSR studies, the first held in Rorschach, Switzerland, in 1978, and the second in Vancouver, Canada, in 1980. The third was held in Japan in April 1983, and a fourth is planned for 1986 in Uppsala, Sweden.

The μSR technique relies on the production and implantation of a polarized beam of positive or negative muons into the material of interest and on the subsequent anisotropic decay of the muon into an easily detectable positron (or electron) and two unobserved neutrinos. The fact that the decay is anisotropic allows one to monitor the time dependence of the muon spin polarization in the manner described in Chapter 4. In the simplest experiments, the technique is analogous to free induction decay in nuclear magnetic resonance (NMR), except that (1) the muon spin is polarized, requiring no applied magnetic field, and (2) the relaxation of the spin polarization is detected by particle decay rather than by resonance techniques. Hence, the spin depolarization data provide information on the microscopic magnetic environment encountered by the muon, in analogy to what is obtained in NMR measurements of T_1 and T_2.

It is convenient to group the various types of μSR experiments into categories, according to the role that the muon plays: (1) a local proble, (2) a light interstitial particle, and (3) a hydrogen-like atom. In its role as a local probe, the muon samples its magnetic environment, either at an interstitial or substitutional site (μ^+) or at a lattice site (μ^-) in a pure crystal. The spin precession and relaxation give information about static and dynamic local fields. In this regard the technique is complementary to other spin probes routinely used in condensed-matter physics, such as NMR, electron spin resonance (ESR), Mössbauer effect (ME), and perturbed angular correlation (PAC). This complementarity is illustrated in Table 3.1.

The range of local-field correlation times to which μSR is sensitive through its dipole coupling is quite large, from about 10^{-4} s to 10^{-12} s, and again complements the sensitivity of other techniques. Because the response of the muon spin to its local field can be detected within at most a few nanoseconds after implantation, rapid relaxation phenomena inaccessible to NMR (for example, due to a spectrometer dead time of several microseconds) are routinely measured with μSR. Relaxation times greater than 50-100 muon lifetimes (≃100 μs) cannot be detected, however.

When viewed as a light interstitial particle the muon may be used to study localization and diffusion phenomena in a mass regime that is large compared to an electron ($m_\mu/m_e \simeq 200$), but small compared to a proton ($m_\mu/m_p \simeq 1/9$). Nonclassical muon diffusion has been observed in metals such as Cu and Al, where the muon is seen to move more rapidly as the temperature is lowered.

Finally, in certain materials--particularly insulators, semiconductors, liquids, and gases--the μ^+ will bind an

TABLE 3.1 Comparison of Spin-Probe Techniques for Measurements of Dynamic Phenomena

	μSR	NMR, ESR	ME	PAC
Usual probe lattice site	Interstitial	Substitutional	Substitutional	Either
Probe site determination is easy	Sometimes	Usually	Usually	Sometimes
Usual lower limit on applied field	None	1 kOe	None	None
Discriminates between static (inhomogeneous) and dynamic (homogeneous) line broadening	Yes	Yes	No	No
Probe-induced radiation damage	Minimal	No	No	Sometimes
Sensitive to hyperfine field of probe core electrons	No	Sometimes	Yes	Yes
Complication due to probe quadrupole moment	No	Sometimes	Yes	Sometimes
Sensitive to quadrupole interactions	Indirectly	Sometimes	Yes	Sometimes
Interactions between probe spins	No	Yes	Sometimes	Sometimes
Sensitive to diffusion	Yes	Yes	No	No

electron to form muonium (μ^+e^-), an atom analogous to hydrogen. In solids, the formation mechanism and nature of the muonium-like states are of particular interest, because of the relation of muonium to hydrogen in these materials (for example, in semiconductors). Muonium formation may also shed light on the general problem of local moments in solids. In gases and liquids, muonium can react with molecules, allowing the study of isotope effects in chemical reaction rates; compared with hydrogen the muon provides the largest mass ratio encountered in chemical reaction dynamics to date. Spin exchange reactions may also be studied. Finally, muonium may attach itself to a complex molecule, forming a muonic radical with an unpaired electron spin and yielding a characteristic frequency spectrum. Again, isotope effects provide information on differing molecular conformational dynamics. In addition, the muon can be used to "spin-label" a radical, so that radical-radical reaction rates may be studied. This yields information unobtainable by any other technique.

A brief introduction to the μSR technique is given in Chapter 4, and the worldwide status of current μSR facilities with regard to experimental equipment, user modes, and funding are summarized in Chapter 5. Details of scientific contributions of μSR to the fields of condensed-matter physics and chemistry are provided in Chapter 6, and Chapter 7 deals with new directions in the science and facilities.

This document is not intended to be an archival or review article in which all relevant μSR references are cited. Rather, we have attempted to provide a brief overview, relying on other reviews as references where possible. In particular, the interested reader is referred to References 3 and 4 for details regarding the μSR technique, to References 2 and 4 for scientific studies in solid-state physics, and to References 5 and 6 for chemistry studies.

REFERENCES TO CHAPTER 3

1. R. L. Garwin, L. M. Lederman, and M. Weinrich, Phys. Rev. 105, 1415 (1957).
2. Proceedings of the First and Second Int. μSR Conferences; 1978, Rorschach, Switzerland, Hyperfine Interactions 6(1-4) (1979); 1980 Vancouver, Canada, Hyperfine Interactions 8(4-6) (1981). The third conference in this series was held in Japan in April 1983.

3. A. Schenck, Nuclear and Particle Phyics at Intermediate Energies J. B. Warren, ed. (Plenum, New York, 1976), p. 159.
4. E. Karlsson, Phys. Rep. 82(5), 272 (1982).
5. D. G. Fleming, R. J. Mikula, and D. M. Garner, Phys. Rev. 26A, 2527 (1982).
6. P. W. Percival, E. Roduner, and H. Fischer, Chem. Phys. 32, 353 (1978); P. W. Percival, Radiochem. Acta 26, 1 (1979); D. C. Walker, Y. C. Jean, and D. G. Fleming, J. Chem. Phys. 70, 4534 (1978).

4. THE MUON SPIN ROTATION TECHNIQUE[1]

I. PRODUCTION OF SPIN-POLARIZED MUONS

Muons are produced by accelerators from the decay of pions, which themselves are formed when a high-energy proton beam strikes a production target. Pions decay with a lifetime of 26 ns into a muon and a muon neutrino: $\pi^+(\pi^-) \rightarrow \mu^+(\mu^-) + \nu_\mu(\nu_\mu)$. In the rest frame of the pion the muon is 100 percent spin-polarized either along (μ^-) or opposite (μ^+) to its momentum direction. Some of the properties of the muon relevant to μSR are given in Table 4.1.

Muon beams are basically of two types, "decay" beams and "surface" beams.[2] In a decay beam, muons originate from pions that decay in flight. The muons are collected in a beam channel and magnetically separated into "forward" and "backward" beams, depending on whether the muon center-of-mass momentum is parallel or antiparallel to the original pion momentum. The beam channel components for the pion decay section may be made from conventional quadrupole magnets or may consist of a high-efficiency, superconducting solenoidal magnet. Muon polarizations of about 90 percent can be achieved in decay beams. Backward decay beams of ~90 MeV/c momentum (range ~8 g/cm^2 in CH_2) can be stopped in condensed-matter targets of a few millimeters thickness (range spread ~1 g/cm^2 of CH_2).

Surface muon beams originate from the decay of pions that have come to rest near the surface of the production target. The muons so produced are all μ^+ (since π^- are captured by atomic nuclei in the target), of low momentu (~29 MeV/c), and may be completely stopped in very thin targets (range ~140 mg/cm^2 of CH_2, range spread ~40 mg/cm^2 of CH_2). Surface beams have clear advantages for thin or expensive solid-state targets. One of their dis-

TABLE 4.1 Some Properties of the Muon Relevant to μSR

Mass, m_μ	106 MeV 207 m_e 0.113 m_p
Spin, I_μ	1/2
Lifetime, τ_μ	2.197 μs
Magnetic moment, μ_μ	4.49×10^{-26} J/T 3.183 μ_p
Gyromagnetic ratio, $\gamma_\mu/2\pi$	13.5537 MHz/kOe

advantages is the fact that modest magnetic fields bend the beam appreciably: fields greater than ~1.5 kOe perpendicular to the μ^+ momentum can prevent surface beam from reaching the sample. Thus it is advantageous to bring the beam in parallel to the field, so that no bending takes place. The muon spin may be rotated through 90° using a Wein filter (crossed electric and magnetic fields), which also has the advantage of eliminating the large positron contamination of the beam.

The slowing time for muons in matter (from MeV to thermal kinetic energies) depends in part on the density of the target and ranges from ~10^{-11} s in condensed matter to ~10^{-8} s in gases at 1 atm pressure. In gases, most liquids, and insulating solids, muon thermalization is accompanied by muonium (μ^+e^- atom) formation (see Chapter 6, Section IV.A). In metals, even ferromagnets, the muon spin does not precess during such a rapid deceleration, and the implanted muon remains spin polarized.

Positive and negative muons behave differently after thermalization. Negative muons are trapped in tightly bound atomic states near nuclei. Their hyperfine anomaly [i.e., the difference in hyperfine field between (μ^-,Z) and (Z - 1) atoms] reflects the behavior of the electronic wave function in the vicinity of the nucleus and so has some applications in condensed-matter physics. However, the vast majority of μSR experiments have been carried out with positive muons, which are either trapped at interstitial (or substitutional) sites in solids or diffuse between such sites.

As the muon slows down in a solid target, radiation damage is produced by collisions between the muon and the host atoms. There is no experimental evidence to date that muon behavior after thermalization is influenced by the products of its own radiation damage. Indeed, theoretical calculations by Brice[3] have shown that the mean distance between the muon and the nearest vacancy produced by its implantation is typically greater than several thousand angstroms.

II. MEASUREMENT OF MUON POLARIZATION

Positive muons decay via the parity-violating weak interaction $\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu$. The decay positrons exhibit an angular distribution of the form

$$dN_e/d\Omega \propto 1 + a \cos \theta, \qquad (1)$$

where a is the (energy-dependent) decay asymmetry and θ is the angle between muon spin and positron emission directions. This angular dependence gives an indication of the degree and direction of the muon polarization

Since the muon spin precesses around internal or external magnetic fields, its polarization will be time dependent. This dependence is manifest in the positron counting rate

$$dN_e(\Omega,t) = \frac{1}{4\pi\tau_\mu}\, e^{-\underline{t}/\tau\mu}\, [1 + AG_\mu(t)\cos\theta]\,d\Omega dt, \qquad (2)$$

where A is the initial energy-averaged asymmetry and $G_\mu(t)$ represents the time dependence of this asymmetry. Detected positrons have an energy range from 0 to 52.8 MeV, with an average energy of 35 MeV. For 100 percent initial polarization the asymmetry averaged over all energies is 1/3. On occasion positron energy degraders have been placed in the positron telescopes to increase the observed asymmetry,[2] which is larger for high-energy positrons.

III. TIME DIFFERENTIAL μSR

The standard technique used in most μSR experiments to date is time differential μSR. An incident muon triggers a muon "counter telescope" (an array of plastic scintillator counters), stops in the target, and some time later its decay positron triggers a similar counter array. The stopped-muon event starts a high-frequency clock, which is stopped by detraction of the decay positron. The measured time interval is stored in computer memory as a time histogram, and the process is repeated many times until typically between 10^6 and 10^7 events are accumulated.

Any "second-muon" or "second-positron" events can cause severe distortion, particularly at high data rates, and these events must be discarded by a pile-up rejection system. The maximum useful instantaneous stopping rate is determined by Poisson statistics and by the pile-up rejection interval, τ, and is given by $(e\tau)^{-1}$. If one demands that no second muon may come within a 10-μs interval before or after a given muon stop, then $\tau = 20$ μs, and the maximum useful instantaneous stopping rate is about 1.9×10^4 s^{-1}. For a 100 percent macroscopic duty factor, this is also the maximum useful average stopping rate. It is far less than meson factories are capable of producing. The pile-up condition can be overcome if a spatial selection of related μ^+-e^+ events is done by track reconstruction of muons and positrons. Such a device, based on position-sensitive detection of both types of particles,[2] is under development at CERN and is being designed at LAMPF.

The rate at which good events are accumulated depends on the product of the average muon stopping rate and the solid angle-efficiency (ε) of the positron counters. A typical value of ε is about 0.3, yielding a maximum event rate of about 6000 s^{-1}. Therefore, about 3-30 min would be required to accumulate 10^6-10^7 events, using a 100 percent duty-factor beam.

In <u>transverse</u> μSR, a magnetic field is applied perpendicular to the direction of initial muon polarization. The muon spins precess at their Larmor precession frequency ν, and their asymmetric decay patterns sweep past the positron counter telescope. This gives rise to characteristic "wiggles" in the time histogram. In Eq. (2), $\theta = 2\pi\nu t$, and the time distribution function has the form

$$dN(t) \propto e^{-t/\tau_\mu}[1 + AG_x(t)\cos(2\pi\nu t + \phi)], \tag{3}$$

where the function $G_x(t)$ describes the transverse relaxation, and ϕ is the initial phase angle between the muon spin direction and the counter telescope.

In longitudinal geometry, positron counter telescopes are fixed at 0° and 180° with respect to the initial muon spin direction. Hence there are two time histograms, each of which is given by Eq. (2) with $G_\mu(t) = G_z(t)$ and $\cos\theta = \pm 1$. An external magnetic field may be applied in the longitudinal direction, or the experiment can be carried out in zero field. The function $G_z(t)$ describes the longitudinal or spin-lattice relaxation of the muon, in analogy with conventional pulsed nuclear magnetic resonance (NMR).[4]

Analysis of time-differential μSR data consists of extracting relevant properties of the time-dependent muon polarization. These include one or several precession frequencies, initial phase angles, initial asymmetries, and relaxation rates. The frequencies give information on time-averaged internal local fields, and relaxation rates reflect either static field distributions or spin-lattice relaxation processes.[4] The initial phase angle is determined by the sense of precession, which in turn is affected by the direction of the internal field.

IV. STROBOSCOPIC μSR

High-precision, frequency-shift measurements require high statistics, which are prohibitively time-consuming in the conventional time-differential μSR method described above. This limitation can be overcome by the use of a stroboscopic method developed at SIN,[5] if the muon beam itself is modulated at some radio frequency (rf). By variation of the external transverse field, muons in the target are caused to precess at a frequency close to an integral multiple of the beam modulation rf. Thus muons entering the target have nearly the same precession phase as muons that have already spent time there. Decay positrons are detected in a time window synchronous with the beam modulation rf, and in principle all muon stops in the target can be counted. Precisions of a few parts per million in the measurement of a single frequency have been obtained. Since muon frequency shifts (Knight shifts) are typically small in paramagnetic or diamagnetic metals, such precision is often required. More than one frequency cannot be measured simultaneously, however. In addition, the requisite rf structure is often not present or is suppressed owing to time-slewing in the muon beam. The technique is applicable to accelerators where a beam modulation rf is available from the microscopic time structure of the primary proton beam.

V. PULSED-BEAM TECHNIQUES

This class of techniques has been pioneered by the Tokyo University group at KEK[6] and has the potential of producing a new generation of μSR experiments. In the pulsed technique, a large number of muons (limited only by the beam flux and instrumental maximum data rates) is implanted in the target, in a time short compared with τ_μ and with any relaxation times that characterize $G_\mu(t)$ defined above. Apart from the improvement in data rate inherent in such a technique, at least three other features are of interest:

1. The muon beam is off for the time during which positrons are detected, so that beam-associated background is very low.
2. This in turn allows the muon decay to be followed out to long times (>20 μs), so that long muon relaxation times can be measured.
3. Perhaps most importantly, transient experimental conditions, such as pulsed rf fields and laser irradiation, can be applied. In particular, pulsed rf fields can be used to flip the muon spin, e.g., to produce a transverse spin polarization with a field parallel to the muon beam.

These advantages have been stressed in the μSR program at KEK.

REFERENCES TO CHAPTER 4

1. For review of the technique see A. Schenck, Nuclear and Particle Physics at Intermediate Energies, J. B. Warren, ed. (Plenum Press, New York, 1976), p. 159; also E. Karlsson, Phys. Rep. 82, 271 (1982).
2. W. F. Lankford et al., Nucl. Instrum. Methods 185, 469 (1981).
3. D. K. Brice, Phys. Lett. 66A, 53 (1978),
4. A. Abragam, Principles of Nuclear Magnetism (Clarendon Press, Oxford, 1961).
5. M. Camani et al., Phys. Rev. Lett. 42, 679 (1979).
6. K. Nagamine, Hyperfine Interactions 8, 787 (1981); also UT-MSL Newsletter No. 2, May 1982 (Meson Science Laboratory, University of Tokyo).

5. CURRENT μSR FACILITIES AND USER MODES

I. GENERAL OVERVIEW

The major muon physics facilities at which μSR research is now carried out are listed in Table 5.1. There are also muon beam lines at Leningrad, at Dubna, and at NIKHEF in the Netherlands; however, little information about these facilities is available for this report. Future facilities under construction at Brookhaven National Laboratory and possible new beam lines at Rutherford-Appleton Laboratory in the United Kingdom and at Los Alamos are discussed in Chapter 7.

The laboratories listed in Table 5.1 fall into two general categories depending on the macroscopic duty factor of the accelerator. The machines at SIN, TRIUMF, LAMPF, and CERN all have relatively large macroscopic duty factors compared with KEK's. The implication of this is that nearly all of the experiments carried out at these large duty factor machines use the time-differential μSR method, wherein the time difference between the muon's stop and decay signals is measured for each individual muon. (The exception to this is the stroboscopic technique in use at SIN, discussed in Chapter 4.) The machines at SIN, CERN, and TRIUMF all have 100 percent macroscopic duty factors, allowing, in principle, the maximum practical muon stopping rate for time-differential μSR measurements (referred to as the "maximum useful luminosity" in Table 5.1*). In practice,

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*The maximum useful instantaneous stopping rate is discussed in Chapter 4 and is about 1.9×10^{-4} for a 10-μs pile-up rejection interval. For a 100 percent macroscopic duty factor, this is also the maximum useful average rate.

TABLE 5.1 Major Existing μSR Facilities

Facility	Proton Current (μA)	Duty Factor	Number of Muon Channels		Available Muon Beams Decay (D), Surface (S)	Number of "Full-Time" Participants		Maximum Useful Luminosity ($\mu^+/cm^2/s$)
			Total	μSR[a]		Inhouse	Outside	
SIN (Switzerland)	100	1	4	1.6	D, S	0	23	2×10^4
TRIUMF (Canada)	30-130	1	3	0.90	D, S	11	4	2×10^4 [b]
LAMPF (U.S.)	700	0.1	3	0.20	D, S	3	8	2×10^3
CERN (Switzerland)	5-10	1	2	0.20	D,	1	9	5×10^2
KEK (Japan)	1-2	10^{-6}	2	1.0	D, S	9	4	4×10^3

[a] This column gives the approximate number of channel-years being used exclusively for μSR.
[b] At 100 μA or above.

however, the proton current at CERN is too low to reach this saturation rate. Similarly, TRIUMF must run at 100 μA for saturation, a current that is not always available. The reduced duty factor at LAMPF means that the maximum useful stopping rates achievable are about 10 percent of those at SIN.

In contrast to the four large duty-factor machines discussed above, the KEK duty factor of 10^{-6} (a 50-ns-wide pulse every 50 ms) means that the instantaneous stopping rate is so high ($\sim 4 \times 10^{12}\ s^{-1}$) that it is virtually impossible to time each stopping muon. Consequently, all muons arriving within a given burst are assigned to "time-zero," which is therefore known only to within the burst width. This means that the maximum useful event rate is in principle quite high, being given by the total average stopping rate. However, the maximum frequency that can be measured is something less than one half of the reciprocal of the burst width, or about 10 MHz at KEK, compared with a few gigahertz at a large duty-factor machine. Despite this limitation, many experiments that exploit the pulse structure of the KEK machine can be carried out, thus extending the range of μSR experiments in important ways (Chapter 7). All the muon channels listed in Table 5.1, except CERN, have the capability of running surface muon beams (momentum of 29 MeV/c and range about 0.140 g/cm^2 of CH_2). This requires that the muon beam channels be evacuated from the pion production target to an end port very near the experimental sample, so that the low-momentum surface muons are not stopped in the air that would otherwise fill the beam line.

II. DETAILS OF CURRENT FACILITIES

It is appropriate to list the salient features of the major existing μSR facilities. Each of the five μSR centers mentioned above provides a data-acquisition room that contains signal cabling, electronics, and computing facilities for on-line data acquisition. Often software for on-line data analysis is available as well. In addition, the accelerator staff provides logistic and technical support for use of the beam lines and mounting experiments.

The total available muon flux varies by orders of magnitude from one accelerator to the next and depends greatly on the beam momentum and spot size required for a given experiment. Therefore, rather than trying to describe each muon beam line at each accelerator under several possible conditions, we shall limit ourselves to the characteristic features of a given facility. To make this task easier, we shall consider the two general types of beams: "decay beams," with a momentum of about 110 MeV/c and a range spread of about 3 g/cm^2 of CH_2, and "surface beams," of momentum 29 MeV/c and a range spread of about 0.040 g/cm^2 of CH_2.* Given these parameters, a useful quantity for comparison is the luminosity, or the number of muons per square centimeter per second. Except where mentioned, the μ^+ decay flux is about five times the μ^- decay flux. In the estimates of the number of individuals working at each institution, a "full-time" equivalent is defined as an individual with a Ph.D. degree, whose primary research activity involves the μSR technique.

SIN.† Located in Villigen, Switzerland, SIN currently has the largest μSR physics program in the world with about 23 "full-time" participants (all from outside SIN). These are mostly from Europe, though there are some visitors from the United States and Canada. The accelerator has a 100 percent macroscopic duty factor, with a microscopic pulse structure of 50 MHz. There are at present three muon beam lines for decay beams (μE1, μE2, μE4), two of which employ a superconducting solenoidal pion-decay section. The μE4 channel can also be tuned for a surface muon beam. A fourth muon channel is also used for a surface μ^+ beam. All of these channels are now used for other kinds of muon experiments besides μSR, which is allocated about 40 percent of the total muon beam time. The decay μ^+ luminosity is about 10^6/cm^2/s. A spot size as small as 3 x 5 mm^2 has been achieved.

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*A surface muon beam generally contains an enormous flux of positrons, which must be removed to make a useful μSR beam, as mentioned in Chapter 4. The techniques for removing the positrons also reduce the raw μ^+ flux as well. Since the exact methods employed at each laboratory are not known, the surface μ^+ fluxes quoted here must be considered to be uncertain by at least 50 percent.

†The information regarding SIN has been obtained from A. Schenck and C. Pettitjean, SIN, through private communication.

The μSR facilities at SIN come from a wide range of well-funded user groups. There exists one stroboscopic apparatus for high-precision frequency determinations; four general-purpose transverses and zero-field spectrometers (two for surface and two for decay beams); a high-frequency resolution, transverse-field spectrometer (~4.6 GHz); and a superconducting, longitudinal-field spectrometer for surface beams. Several conventional (2-300 K) cryostats are also in use.

TRIUMF.* TRIUMF, located in Vancouver, B.C., is a variable-energy cyclotron that operates between 200 and 500 MeV and has a proton current of between 30-130 μA and a 100 percent macroscopic duty factor. The accelerator operates about 6 months/year in a mode suitable for muon physics. The μSR program is carried out by about 15 "full-time" people, most of whom are associated with TRIUMF itself.

There are three conventional-magnet muon beam lines (M9, M13, M20), but most of the μSR research is carried out at channel M20, where about 90 percent of the available beam time is allocated to μSR. M20 can run both decay and surface muons, whereas M13 runs only surface beams. Currently, at 100-μA primary proton current, the luminosity for M20 decay muons is about 7 x $10^3/cm^2/s$ and for surface muons about 4 x $10^4/cm^2/s$. There are four μSR spectrometers at TRIUMF capable of applied fields up to 10 kOe. Several of these are specialized for liquid and gas chemistry experiments requiring large targets. Standard cryogenics exists for temperatures between 2-300 K, as well as a ^{3}He evaporation refrigerator with a lower temperature of about 0.5 K.

LAMPF.† LAMPF, located in Los Alamos, New Mexico, is an 800 MeV proton linear accelerator with a 10 percent macroscopic duty factor and a nominal operating current close to 700 μA. There are at present about 11 "full-time" μSR scientists working at Los Alamos; three of these are stationed at LAMPF, and the remainder come from universities and other laboratories in the United States and abroad. There are two conventional-magnet beam lines available for decay beams (SMC and Biomed) and

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*The information regarding TRIUMF has been obtained from D. Fleming, University of British Columbia, through private communication.

†The information regarding LAMPF has been obtained from R. H. Heffner, Los Alamos National Laboratory.

two available for surface muon beams (SMC and P^3). Currently, μSR experiments are carried out only at SMC, using about 20-25 percent of the available running time, the remainder being used for nuclear- and particle-physics experiments. For a proton current of 700 μA, the decay μ^+ beam luminosity at SMC is about 2 x $10^6/\text{cm}^2/\text{s}$, and the corresponding surface beam luminosity is about $10^6/\text{cm}^2/\text{s}$. LAMPF has a general-purpose μSR spectrometer for use in transverse, zero, and longitudinal applied fields (5 kOe maximum, 10^{-2} Oe minimum). Cryogenic and heating systems are available for sample temperatures from about 0.03 K (dilution refrigerator) to about 900 K.

CERN.* The μSR program at CERN uses the 600-MeV SC cyclotron, which produces a macroscopically dc proton beam with a 50 MHz microstructure and 5-10 μA current. There are about 10 "full-time" scientists engaged in μSR research at CERN. Most of the μSR studies are carried out at a single beam line, where about 20 percent of the total beam time is used. The decay μ^+ luminosity is about 5 x $10^2/\text{cm}^2/\text{s}$. A second beam line is available, with a luminosity of about 2 x $10^3/\text{cm}^2/\text{s}$; however, positron contamination at this port is large, and hence few μSR experiments are carried out there.

The CERN μSR apparatus includes transverse and longitudinal field spectrometers. In addition, CERN has built a wire-chamber spectrometer used to project the trajectories of individual muon and positron events back to the target region to reduce background. Finally, the CERN group has been the first to use a dilution refrigerator to achieve very low (~0.03 K) sample temperatures.

KEK.† 500-MeV proton synchrotron booster at the National Laboratory for High Energy Physics (KEK) in Tsukuba, Japan, is used to produce pulsed stopping muon beams with a 50-ns burst width every 50 ms. The proton current is 1-2 μA. There about 13 "full-time" μSR scientists working at KEK, 9 of whom are from the Tokyo group. The facility has a superconducting-solenoidal muon channel and a conventional-magnet surface beam

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*The information regarding CERN has been obtained from R. Heugart and A. Yaouanc, CERN, private communication.

†The information regarding KEK has been obtained from T. Yamazaki and K. Nagamine, University of Tokyo, private communication.

channel, each of which is used about 50 percent for μSR. The decay μ^+ luminosity is about $4 \times 10^3/\text{cm}^2/\text{s}$.

The μSR spectrometers available at KEK include the following: transverse field (0-300 Oe), longitudinal field (0-1000 Oe), and longitudinal (0-3000 Oe) and superconducting-longitudinal field (0-40,000 Oe) for use with a 40-MHz pulsed rf field. Each of these is used with a conventional cryostat (2-300 K). There is also a dilution refrigerator available.

III. USER REQUIREMENTS

We now briefly describe the user modes, beam time, and availability of equipment at the accelerators mentioned above. Brookhaven (BNL) is also included in anticipation of future use.

Approval for use of a beam port at LAMPF is obtained by writing a proposal and defending it before a solid-state program advisory committee (PAC), which acts in an advisory capacity to the accelerator director. The PAC meets twice a year, and beam time is allocated quarterly. A typical delay from proposal to experiment does not exceed six months. BNL, SIN, and TRIUMF have similar formal review procedures. Approximate μSR beam port hours currently used per year at the major μSR facilities are summarized below. Figures for BNL are not yet available.

	Approximate μSR Use in 1982				
	LAMPF	SIN	TRIUMF	KEK	CERN
Beam port hours	1000	6000	2600	600	1000

Use of a specific piece of μSR apparatus (such as a spectrometer) is usually possible for outside users through cooperation or collaboration with individuals at the facility responsible for the equipment.

The computer and data-acquisition electronics are usually supplied by the accelerator facility and its equipment pool. The electronics arrangement has become relatively standardized and remains nearly set up from one run to the next. Computer programs for collection, display, writing to magnetic tape, and analysis of on-line data are also generally available.

Personnel requirements to carry out a μSR experiment depend on one's proximity to the accelerator facility and

TABLE 5.2 Rough Qualitative Comparison of the Situation Confronting U.S. Scientists Who Wish to Do Experiments at Various Facilities[a]

Limitations for Use	LAMPF	BNL	TRIUMF	SIN	KEK	CERN
Funds for U.S. group	2	2	2	2	2	2
Beam ports	0.5	1	0	0	0.5	1
Beam structure	2	1	0	0	1	0
Beam intensity	0	1	0	0	1	2
Travel to facility						
From Eastern U.S.	1	0.5	1	2	2	2
From Western U.S.	0.5	1	1	2	2	2
Availability of in-house support[b]	1	?	1	0.5	1	1
Administrative availability of facility to U.S. Users	0[c]	0[c]	1[d]	2[e]	2[e]	2[e]

[a] The numbers represent the degree of difficulty: 0, no problem at all; 1, some problem; 2, considerable problem.

[b] The in-house support determines the amount of help available to outside users. The size of the local μSR community at SIN makes this less of a problem there. The availability of in-house support at Brookhaven is yet to be determined.

[c] Funded U.S. facilities are completely available to funded U.S. users with approved experiments.

[d] At present, TRIUMF can accommodate a modest number of small user groups from the United States. Large user groups or programs from the United States could be welcome but would be expected to bring considerable support and equipment.

[e] The United States does not directly support these foreign institutions, and so noncollaborative experiments or large U.S. programs could face some problems.

also on the extent of one's collaboration with other scientists. A self-sufficient μSR team needs at least four scientists for a typical 24-hour-a-day experiment, using 2 two-man shifts per day. Less than this is probably unsafe and would not allow necessary adjustments in the apparatus. At least one person per shift must be capable of leading the experiment. This minimal size group would find it difficult to handle experiments longer than several days and to maintain and upgrade equipment. In spite of this "minimal size," an outside user group can be as small as one person, if that individual collaborates closely with an in-house or a larger outside user group. Funding, including overhead, for a minimal university user group, operating independently of in-house scientists, might then be as follows:

Sr. Scientist Summer Salary	$ 15,000
Post-Doc	30,000
Two Graduate Students	25,000
Travel - U.S.	15,000
Travel - Foreign (SIN)	20,000
Equipment and Supplies	10,000
Computer Time	5,000
	$120,000

This funding scenario assumes that the group need not bear the costs of a μSR spectrometer and associated cryogenics. For comparison, the local group at LAMPF, currently supported from medium-energy physics funds,* receives about $280,000, which includes resources for the construction and maintenance of necessary equipment. The three NSF-funded μSR groups (Rice University, William and Mary, and University of California, Riverside) receive about $175,000 total, and the Department of Energy (medium-energy physics) provides about $20,000 for the Lawrence Berkeley Laboratory group. Independent user groups at LAMPF, upon having an approved experiment, are given a "dowry" of up to about $5,000 for assorted expenses.

In Table 5.2 we show a rough qualitative comparison of the situation confronting U.S. scientists who wish to do experiments at various facilities.

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*This funding will terminate at the and of fiscal year 1983.

6. μSR AND BASIC MATERIALS SCIENCE

I. GENERAL OVERVIEW

The muon can generally play one or more of the following roles in solid-state research:

1. A local probe,
2. A light interstitial particle,
3. A hydrogen-like atom (muonium) or particle.

In the first case, the primary interest is a property of a given host material, which may be studied through its effect on the static and dynamic local field seen by the muon. The μSR technique complements other techniques such as NMR, Mössbauer spectroscopy, perturbed angular correlations (PAC), and neutron scattering.

In the second and third cases, the concern is more with the muon itself. Quite often it is useful to compare the behavior of the muon with that of hydrogen, which may be considered a heavier isotope. The behavior of these particles in a solid or in a chemical reaction is important both for technological reasons and for its relevance to other basic sciences such as biology. A major interest under the second category is diffusion and self-trapping in metals, where the intermediate mass of the muon makes it a desirable particle for studying questions of localization and quantum diffusion. Under the third category, muonium centers can be compared with hydrogen in semiconductors, and muonium and hydrogen reaction rates can be compared in liquids and gases, yielding complementary information. Unique information is obtained from μSR in materials where hydrogen solubility is low.

There is obviously a good deal of overlap among these three categories. For example, the muon cannot be used as a reliable probe of its local field unless the mutual effects of the field and the muon on one another are understood. Specific examples and details are given in the following sections.

II. THE MUON AS A LOCAL PROBE

Qualitative comparisons of μSR with other techniques for investigating properties of solids are contained in Table 3.1. These may be referred to and kept in mind when reading the following examples.

A. Electronic Structure of Metals

The muon can be used as a probe of electronic structure via the Knight shift of its resonance, which is proportional to the spin susceptibility times the probability amplitude $|\psi|^2$ of the conduction electrons at the muon position. Whereas the NMR of a host nucleus such as Cu measures a "true" $|\psi|^2$, the muon does perturb the electronic wave function. However, the alteration of $|\psi|^2$ is itself of fundamental interest because this represents a particularly simple perturbation--that of a single positive charge. Hydrogen in metals provides the same simplicity in principle but is not sufficiently soluble in simple alkali and other nontransition metals for NMR studies, whereas the muon can be implanted in essentially any system.

This simple impurity problem has generated considerable theoretical interest, and much effort has gone into calculating quantities that can be compared with observed Knight shifts.[1] Most comparisons between theory and experiment have been based on nonlinear-response jellium theory, and these have not been overly successful.[1] More nearly, *ab initio* cluster band-structure calculations do tend to be in agreement with data, however; but since only a few such calculations have been performed, their ability to reproduce systematic trends has not yet been tested. A striking experimental trend found in cubic nontransition metals[1] concerns an exponential dependence of $|\psi|^2$ on $\rho(E_F)$, the unperturbed density of states. The former is extracted from the combined Knight shift and spin susceptibility data, while the latter is obtained from the electronic specific heat. This finding presents an interesting challenge to theoretical understanding.

In metals where proton NMR is possible, the muon and proton Knight shift data correspond closely to each other, indicating that both particles are indeed associated with the same local electronic structure. The small isotope effects that are found are nonetheless interesting in their own light, however. In particular the s-electron- and d-electron-induced Knight shifts change in opposite directions when the muon and proton data are compared. The Knight shift can also be used to investigate phase transitions in which the electronic structure changes. Studies of the valence transition in cerium and a cerium-thorium alloy have shown that the 4f electron charge distribution is the same in both phases.[1] Finally, an interesting set of measurements in single-crystal antimony[2] has revealed a strongly temperature-dependent, anisotropic Knight shift, increasing to very large values (10^{-2}) at temperatures below 20 K. This was interpreted as being due to the formation of a local moment or virtual bound state. Antimony-based alloys such as <u>Sb</u>Sn and <u>Sb</u>Bi thus provide the opportunity[3] to study muonium formation in systems intermediate between metals and semiconductors.

B. Static Local Fields in Magnetic Materials

Since the first observation of muon spin precession in Ni and Fe, much work has been devoted to the study of muons in magnetically ordered materials. This work has perhaps been most successful in clarifying the nature and origin of the μ^+ hyperfine field at interstitial sites in elemental ferromagnets.[4,5] The principal features that distinguish μSR from other hyperfine techniques are the following:

1. The muon samples a local field at an interstitial site and therefore yields information difficult to obtain by other techniques.
2. The muon inevitably perturbs the host more or less strongly. This complicates the problem but provides a sensitive test of theories of impurities in magnetic materials.
3. Signals often remain visible through magnetic phase transitions, owing to the very good initial time resolution (short dead time) inherent in the technique.

A somewhat artificial but useful distinction between two contributions to the local field $B_\mu(R_\mu)$ at the μ^+ site R_μ can be made:

$$B_\mu(R_\mu) = B_{hf}(R_\mu) + B_{dip}(R_\mu), \tag{1}$$

where $B_{hf}(R_\mu)$ arises from the interaction with the polarized conduction-electron cloud around the muon, and $B_{dip}(R_\mu)$ comes from the interaction with all magnetic moments localized at host lattice sites. (The contribution from any applied field is neglected here.) The symmetry of the dipolar interaction sometimes allows a determination of the muon stopping site. This determination is necessary for detailed comparison with the theory and is often nontrivial.

Values of $B_\mu(R_\mu)$ are obtained from the zero-field μ^+ precession frequency in metals, and the sign of B_μ can often be obtained from the variation of the frequency with applied field.[4] Measurements of Fe, Co, Ni, Gd, and Dy are summarized in Table 6.1. The data have stimulated a considerable amount of recent theoretical activity,[5] which indicates the degree of interest in both the interstitial electronic polarization and the extent to which the presence of the muon perturbs this polarization. Both properties are sensitive tests of the validity of the wave functions used in the calculation and emphasize the utility of hyperfine techniques in the study of magnetic materials.

Zero-field μ^+ precession frequencies have also been observed in a number of insulating magnetic compounds, such as α-Fe_2O_3, $FeTiO_3$, and orthoferrites. In some of

TABLE 6.1 Summary of μSR Results in Ferromagnetic Metals[4,a]

Structure	Saturation Moment (kG)	B_μ(kG)	B_{hf}(kG)	Muon Site
Fe bcc	1.750	−3.67 ± 0.10	−11.1 ± 0.2	?
Co hcp	1.415	−0.317 ± 0.010	−6.1 ± 0.2	octah.
Ni fcc	0.528	+1.48 ± 0.10	−0.71 ± 0.01	?
Gd hcp	2.010	+1.10 ± 0.05	−6.98 ± 0.10	octah.
Dy hcp	2.995	±12.30 ± 0.20	−25.2 or −0.7 ± 1.0	?

[a] All data are extrapolated to 0 K.

these materials the existence of a muon bond, analogous to the hydrogen bond, has been inferred from the data.[5]

Critical behavior of the paramagnetic-state frequency shift and the zero-field precession frequency can be studied near a magnetic phase transition. Data have been reported for Ni and the weak itinerant magnet MnSi.[6] Such measurements should also be informative for antiferromagnets and systems that exhibit more complicated kinds of order, because a local spin probe such as the μ^+ couples more directly to the order parameter than to the uniform magnetization. It must be shown, however, that the presence of a muon does not seriously perturb the critical properties under investigation.

Finally, μSR studies of spin glasses near the temperature at which a frozen-in, random-spin configuration sets in have revealed details of the freezing process in both zero and nonzero applied fields.[7,8] It is hoped that further experimental results and analysis of theoretical models will help to determine whether this "glass transition" is a true cooperative phase transition.

C. Dynamic Effects in Magnetism

Electronic moments produce a local field at the site of the muon, and time-dependent fluctuations of the electronic moments are mirrored in the time dependence of the local field. Fluctuations in the local field in turn produce a decay of the muon polarization, which can be observed via the angular distribution of the decay positrons as described in Chapter 4. The technique is similar to nuclear spin-lattice relaxation measurements in nuclear magnetic resonance (NMR), and much of the relevant theory can be taken from the NMR literature.[9] The problem of muon motion itself must be addressed, and this can often be determined from auxiliary measurements, discussed below. Also, one generally assumes that the muon populates a random distribution of interstitial sites.

Like NMR, the Mössbauer effect, and perturbed angular correlation (PAC), μSR is a local probe from which information is obtained about the correlations of an electronic moment with itself (at a different time) and with nearby spins. These techniques are complementary to inelastic neutron scattering, which yields data on the spatial Fourier transform of spin-correlation functions. Spin probes also respond strongly to slow fluctuations, to which neutron scattering is insensitive owing to the small energy transfer involved.[1] μSR is compared with the other spin-probe techniques in Table 3.1. Spin-probe techniques are useful tests of various models of the spin dynamics, because comparisons can be made with predicted values for the temperature and field dependences of electronic correlation times, local field distributions, and other parameters.

μSR measurements can be made on paramagnets, systems with long-range magnetic order (e.g., ferromagnets and antiferromagnets), and random spin systems, including spin glasses. The latter have perhaps been of greatest current interest, with groups at TRIUMF,[8] LAMPF,[7] and SIN[11] involved in active programs investigating the systems CuMn, AuFe, and AgMn. The muon is known to be essentially immobile in these systems at the low temperatures of interest (see Section III.C below). μSR measurements in spin glasses have concentrated on elucidating the nature of impurity-spin fluctuations in the neighborhood of the glass temperature T_g (defined by the cusp in the low-frequency ac susceptibility[12]) and at low temperatures $T \ll T_g$. Just below T_g the most recent studies have found a frozen-in static field distribution, reminiscent of an "order parameter" behavior.[7] The data do not seem to suggest superparamagnetic blocking of clusters.[12] At low temperatures the measured μ^+ relaxation rates in spin-glass AgMn are orders of magnitude more rapid than expected from a spectrum of harmonic excitations[7]; this may indicate the importance of slow fluctuations between nearly degenerate equilibrium configurations. The latter are a specific consequence of the random nature of the spin system and must be understood more thoroughly before the random problem can be considered solved. It is important to note that there is good overlap between the correlation time "window" available to μSR and the region (10^{-5}-10^{-10} s) important for spin-glass phenomena near T_g. NMR, in particular, is limited by the "dead time" of pulsed NMR spectrometers (~1-10 μs); many of the important relaxation phenomena in spin glasses are inaccessible to NMR.

In crystalline magnets, μSR has been used to study dynamic critical phenomena in the vicinity of phase transitions in the itinerant-electron magnet MnSi

(Reference 6) and recently in Ni.* The effects of superconductivity on magnetic fluctuations in the magnetic superconductors (Ho,Lu)Rh_4B_4 (Reference 13) and $ErRh_4B_4$ (Reference 14) have also been investigated. These studies have revealed a strong influence of the rare-earth crystalline electric field on the spin fluctuation spectrum, as well as an anomalous enhancement of muon relaxation in the re-entrant superconducting state of $Ho_{0.7}Lu_{0.3}Rh_4B_4$.[13] Crystal-field effects are also involved in studies of paramagnetic rare-earth (RE) compounds $REAl_2$.†

The experimental situation is not so mature in the study of dynamic effects as, for example, in measurements of static local fields. As a consequence, perhaps, not so much theoretical interest has been drawn to interpretation of the results to date. The availability of accurate data is increasing, however, as the programs mentioned above continue to characterize relaxation behavior in a variety of systems. Intrinsic interest in dynamic phenomena is high, and theoretical treatment of spin-probe measurements should increase.

D. μSR with Negative Muons

Although the majority of μSR experiments use positive muons, there have been several experiments on μ^-SR. These experiments are more difficult, in part because μ^- beams of comparable quality to μ^+ beams have been less common and in part because μ^-SR is much more difficult. This difficulty arises from the fact that in cascading down to the atomic 1s state where the decay is observed, the μ^- loses much of its polarization (typically 80 percent). In addition, a certain fraction of the muons is captured by the nucleus and thus produces no decay events at all. (The decays from different elements in a compound target can be separated by the different capture lifetimes if the nuclear charges are sufficiently different. Otherwise, this can be an inherent difficulty in μ^-SR.)

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Only limited use has been made of negative muons (μ^-SR) to date. Since the 1s bound state of the μ^- is highly localized in the vicinity of the nucleus (see Section I), μ^-SR probes hyperfine fields in a manner similar to NMR. Two classes of experiments have been reported. In the first, a μ^- bound state around an even-even nucleus ($I = 0$) permits hyperfine studies in cases where NMR is not possible. Experiments have been carried out ($\mu^- + {}^{16}O$) in MnO and ($\mu^- + {}^{28}Si$) in MnSi, which are both ordered magnets. In the second kind of experiment the hyperfine field at a nucleus of atomic number ($Z - 1$) is compared with that at a ($\mu^- + Z$) bound state. These hyperfine fields should be the same to a first approximation, since the "nuclear" charges are equal. Such a comparison has been carried out between Rh and (μ^- + Pd) in palladium metal, where the surprisingly large hyperfine anomaly $[H_{hf}(\mu^-Pd) - H_{hf}(Rh)]/H_{hf}(Rh) = -36$ percent was observed.[15] This gives detailed information on charge and polarization densities in the vicinity of the nucleus. It appears that the use of μ^-SR will become more widespread if associated technical difficulties can be overcome.

III. THE MUON AS A LIGHT INTERSTITIAL PARTICLE

A fundamental question at the forefront of current solid-state physics research concerns the formation and properties of localized versus extended states of a light particle. Mass is a crucial parameter in determining whether a particle is localized. Because the muon mass often falls in the intermediate range between definite localization (for protons) and definite band states (for electrons and positrons), it is perhaps uniquely suited to investigate these problems. The details of both site location and diffusion are relevant to the issue of localization.

A. Localization and Site Identification in Pure Materials

The depolarization rate of a muon depends on its dipolar coupling with host nuclei, which in turn depends on the type of site the muon occupies and whether it is in a localized or extended state. Copper is the only nonmagnetic metal for which a static, interstitial site location has been determined in the nominally pure material. Here data show the muon to be localized in an octahedral site between about 10 and 100 K.[16] The strong electronic dipole fields can be used to distinguish muon sites in magnetic materials, as discussed above in Section II.B.

B. Localization and Site Identification in Impure Materials

In the absence of defects, the muon is highly delocalized in Al and the bcc metals, as evidenced by the lack of depolarization in samples of the highest purity.[17] (The depolarization rate averages to zero for rapid motion or a highly delocalized wave function, owing to motional narrowing.) Impurities or vacancies can provide trapping centers at which a muon is localized for a sufficiently long time to be depolarized by the local fields of the host and impurity nuclei.

Two types of information have been obtained in studies of defect-induced depolarization in Al and the bcc metals[17]: (a) trapping properties, such as the trap location and the spatial extent and binding energy of the trap, and (b) the manner in which a muon diffuses to the trap. Muon trapping at vacancies has been observed in electron-irradiated, neutron-irradiated, and quenched Al; in deformed metallic samples; and in nonstoichiometric compounds.[18] No trapping by vacancies in thermal equilibrium was found in Cu or Al at high temperatures.[18] Further examples under (a) include measurements of the energetics and trap radii associated with muon trapping near extrinsic defects such as Mn in Al or N in Nb. Specific information about traps is germane to the broad subject of defects in metals and metallurgical studies, and μSR can be regarded as complementary to the positron annihilation technique. Information about diffusion in the presence of traps (b) is discussed below.

C. Diffusion

The problem of muon diffusion is part of the larger one concerning the motion of light interstitials in solids. This motion may involve coherent (bandlike) or incoherent hopping and may or may not include induced lattice distortion accompanied by self-trapping (small polaron formation). Considering the muon as an isotope of hydrogen provides for an extremely wide range over which isotope effects can be studied (a factor of 27 between ^{3}H and μ^+), and such effects generally involve fundamental quantum considerations.

Muon diffusion rates are inferred from the observed depolarization rate Λ. True single-particle motion can be observed without the complication of interactions present in NMR, where fairly large concentrations of the heavier hydrogen isotopes are required. The situation is straightforward in a system like Cu, which has abundant host nuclei with strong magnetic moments. In such a case a muon at rest experiences a large static local field and therefore a large depolarization rate. A rapidly moving muon sees a field that averages to zero as the particle jumps from site to site, and thus has a small Λ. Such behavior has been verified in Cu, where Λ is observed to decrease with temperature above about 100 K.[17] This is interpreted in terms of incoherent hopping, which increases with temperature. However, Λ decreases somewhat with decreasing temperature below 10 K, which implies some delocalization as the temperature is lowered.[17] The muon motion in this regime is very slow, however, and is not understood theoretically.

Similar behavior has also been suggested in Al.[17] As discussed in the previous section, no muon depolarization is seen in pure Al, presumably because the muon diffuses too rapidly or is too delocalized over the entire temperature range. Impurities and vacancies, however, do produce trapping centers at which depolarization occurs. Because the overall time for depolarization includes the time required to reach a trap, the observed Λ can yield information about diffusion.[17] Systematic studies have revealed that muon diffusion to these traps is incoherent above 1 K but suggest coherent bandlike motion below 1 K.[19]

Diffusion rates have also been inferred in the bcc metals V, Nb, and Ta from the trap-induced depolarization.[17] As noted earlier, no depolarization is observed in the highest-purity samples because of the rapid diffusion. Diffusion can also be measured in pure Fe because of the large hyperfine field and magnetically inequivalent sites. The anomalous temperature dependence of Λ in the region of 50 K may be due to coherent diffusion, but it is not yet clear whether this behavior could also be caused by a small concentration of impurities.

Metals such as Ag and Au do not have sufficiently strong nuclear moments to produce depolarization. Here a successful technique has been to introduce paramagnetic impurities that relax the muon spin via the strong interaction with the impurity's electron spin.[20] The situation is analogous to NMR of rapidly moving nuclei in superionic conductors and hydrides, where paramagnetic impurities are known to be a dominant source of relaxation. Muon diffusion in Ag and Au is absent at low temperatures ($T < 50$ K), and at high temperatures has been found to be well described by a classical, barrier-hopping picture, much like that found for hydrogen in these metals. This behavior is in sharp contrast to muon motion in Cu, where barrier tunneling is involved.

The quantum motion of light interstitials has generally been analyzed in the context of small polaron theory, whereby the particle self-traps. However, the muon bandwidth is sufficiently large that the usual approximations for polaron formation are questionable. The dependence of hopping rates on temperature and the temperature at which crossover from incoherent to coherent motion occurs do not conform to standard polaron theory, and significant theoretical revisions are likely to be necessary.[19]

IV. THE MUON AS THE HYDROGEN-LIKE ATOM MUONIUM

Much of the interest in the muon stems from the importance of hydrogen as a simple and abundant element. The comparison and contrast of muonium and hydrogen atoms appear to have important physical and chemical consequences.

A. Muonium-like States in Solids

When a positive muon enters a solid it undergoes a large number of inelastic collisions, slowing it down to kinetic energies of a few keV. From this energy to a few hundred eV its velocity is comparable with that of the valence electrons, and the electron capture cross sections are large. The μ^+ therefore captures and loses electrons until its energy decreases to about 200 eV, after which muonium can form. A bare muon may also capture electrons resulting from the ionization it produces as it thermalizes further. In either case muonium, or muonium-like centers, results for some fraction of the muons. The time to thermalize is short, $<10^{-10}$ s, and little polarization is lost.

Muonium or muonium-like centers have been observed in only a relatively few nonmetals. Although this may mean that the muonium formation probability is too low or that muonium is not stable, in many cases it may also result from muonium depolarization resulting from nuclear hyperfine interactions. Experiments to determine why muonium is not seen in many materials are not yet abundant enough to generalize.

The earliest observation of muonium in a solid by μSR was in quartz, which is currently the only well-studied insulator. At high temperatures (>200 K) muonium diffuses rapidly in α-SiO_2. Consequently the hyperfine interaction is nearly isotropic and has an average splitting about 1 percent greater than free muonium.[21,22] The hyperfine transition at 4496.2 MHz has been observed directly, and the temperature dependence has been measured.[22] At low temperatures (<100 K) the muonium site has lower symmetry, and several differently oriented but otherwise equivalent centers have been observed.[21,22] The results are somewhat similar to the results of EPR on hydrogen in α-SiO_2, with several significant differences resulting from the much smaller mass of muonium.

A double-resonance technique, which is a variant of μSR, has been demonstrated using muonium in quartz.[23] It is called DEMUR, for double electron muon resonance, and involves driving allowed magnetic dipole transitions of the electron spin with an intense near-resonant rf magnetic field and observing structure in the μSR frequency spectrum. DEMUR can permit the observation of EPR transitions of muonium-like centers even if they are not visible in the μSR spectrum.

The study of μSR in semiconductors has produced several unexpected results, particularly the observation of two unusual muonium-like defect centers in each of the group IV crystals, diamond, silicon, and germanium, in addition to μ^+. Although the EPR of hydrogen in many insulators has been observed and studied, no observations of EPR from hydrogen-like centers have been reported for any semiconductor. Consequently μSR is the only way at present to study hydrogen-like centers, even if only by inference and analogy.

The two muonium-like centers found in the group IV crystals have been called normal muonium (Mu) and anomalous muonium (Mu*). Normal muonium has an isotropic hyperfine interaction (like free muonium), but the hyperfine splitting is about 1/2 the free value. Anomalous muonium has a very small, highly anisotropic hyperfine interaction, whose principal axis is <111>. The hyperfine parameters (A) measured for Mu and Mu* in diamond,[26] silicon,[24] and germanium[25,27] are given in Table 6.2. Although no atomic-hydrogen-like center has been observed in these materials (or in any semiconductor), those atomic hydrogen centers that have been studied in other solids have hyperfine interactions that are within a few percent of the free hydrogen value. Thus both Mu and Mu* represent centers that as yet have no observed hydrogen analogs.

The hyperfine parameters for the Mu and Mu* states have been determined to a precision of $1{:}10^4$, and the temperature dependence has been measured over the entire temperature range in which the μSR can be observed. The electronic g-factor is close to 2 in all cases and has been shown to be anisotropic for Mu*. Evidence for nuclear hyperfine interactions has been obtained at low magnetic fields. This interaction is the principal reason that Mu* in Ge and Si has not been observed at very low fields.

Depolarization measurements have been made on both Mu and Mu* at various temperatures. The most interesting of these studies shows that Mu becomes Mu* at high temperatures (~600 K) in diamond.[26] In Si and Ge doped with shallow donors or acceptors, there is a depolarization of Mu at low temperatures that increases as the dopant concentration increases.[27] This has been ascribed to exchange coupling between normal muonium and the shallow impurity. The relaxation due to carriers in the conduction or valence band has been observed for Mu* in Ge.

Although many properties of normal and anomalous muonium are known, the nature of their structure and other properties is still unclear. Because a point positive charge is a simple impurity, and because the

TABLE 6.2 Hyperfine Parameters of Muonium-like Centers at T = 0 K (in Megahertz)

System	A for Mu	For Mu*	
		$A_{\parallel}$	$A_{\perp}$
Diamond	3711 ± 21	-167.98 ± 0.06	392.59 ± 0.06
Silicon	2006 ± 2	16.819 ± 0.011	92.59 ± 0.05
Germanium	2359.5 ± 0.2	27.269 ± 0.013	131.04 ± 0.03
Free muonium	4463.3020 ± 0.0015		

group IV crystals have been of interest to theorists describing point defects, the theoretical activity in these problems is considerable. Virtually all of this theoretical effort has been directed toward normal muonium and has assumed a tetrahedral interstitial position. Although all theories are successful in obtaining a low hyperfine interval for normal muonium, the actual nature of the state is still uncertain. Anomalous muonium remains a mystery.

B. Chemistry of Muonium

Although the formation of muonium is itself of fundamental interest, the primary motive in muonium chemistry studies lies in exploiting the chemical reactivity of the muonium atom compared with hydrogen. There are basically two reasons for this. The first is the isotopic ratio of 1/9: there is simply no comparable isotope effect in any other system, and the study of mass effects in chemical reaction dynamics has long been central to an understanding of the theory of reaction rates. The second reason has to do with the fact that many of the reported hydrogen rate constants for the same reaction typically differ by factors of 2 or more, often because of the difficulty encountered in determining the hydrogen concentrations accurately. Because there is only one muonium atom in the reaction system at a time (in the usual time-differential mode), there can be no "second-order" effects involving muonium, so that the reaction kinetics are in principle much more straightforward than in hydrogen chemistry. Indeed, if the isotope effects between muonium and hydrogen are ever predictable a priori, one could measure a variety of "hydrogen" reactions in different media, particularly those of biological interest.

The main drawback with the muonium chemistry technique is that it measures a bulk thermal rate constant, which represents a weighted average of the reaction cross section $\sigma(E)$, whereas most of the theoretical interest lies in a determination of the energy dependence of $\sigma(E)$. It is unlikely that one will ever be able to approach the sophistication now available in atomic- and molecular-beam studies, which in some cases are now measuring "state-to-state" reaction cross sections (routine in nuclear physics studies for over 30 years). Nevertheless, muonium now plays a unique role in reaction kinetic studies.[28]

The large mass difference affects σ(E) and therefore the rate constant k via the zero-point energy and tunneling. The ratio k_{Mu}/k_H has been measured for the X + G reaction (X = Mu or H, G = F_2, Cl_2, Br_2, HBr, C_2H_4, H_2, O_2, NO), and a significant isotope effect has been found.[28] Detailed theoretical calculations have been carried out for F_2, Cl_2, and H_2.[28] Success, particularly with H_2, points to the possibility that measurements of muonium reaction rates can predict the topology of potential energy surfaces.

There have also been wide-ranging studies of muonium reaction kinetics in the liquid phase,[28] but relatively little theoretical input to date. Indeed, from the point of view of testing reaction-rate theories, the gas phase will most likely remain the preferred medium; many-body effects often tend to obscure the interpretation of reaction rates in liquids. There is, nevertheless, much interest in the now rather impressive array of muonium reaction rates in liquid (primarily aqueous) media. Over 50 rate constants have been measured, and the variation seen in k_{Mu}/k_H is generally much wider than observed in the gas phase; from 150 in the reaction Mu + NO_3^- to <0.01 in the reaction Mu + ethanol.

C. Muonic Radicals

In its chemical reaction with conjugated bond systems, muonium will inevitably form a muonic radical where the (still polarized) muon will interact with an unpaired electron via a much reduced hyperfine interaction (compared to muonium itself). The classic example is the reaction of muonium with benzene, which forms the muonic analog of the cyclohexyldienyl radical. This is probably the best known and most widely studied radical by ESR.

To date, something like 30 muonic radicals have been identified, including a recent observation of a radical in solid.[28] Their resonance frequencies show large isotope effects when compared with ESR results for corresponding proton radicals, even after account is taken of the differing magnetic moments of the proton and muon. These are indicative of differing conformations between muonic and protonic radicals; the increased zero-point vibrations of the muonium-substituted radicals provide larger internal barriers to rotation, with the result that muonium-substituted radicals tend to favor equilibrium conformation where muonium is eclipsed by the half-filled P_z orbital.

In addition to being able to determine conformational dynamics, μSR provides an important handle on the measurement of chemical reaction rates of the radical itself. These rates are generally difficult to determine in ESR studies because the chemical reaction of radical R with reactive solute S competes with the reaction of R with itself, i.e., R-R recombination processes. Having a radical "spin labeled" by a muon is then a very nice feature, because there can be no interaction of the muon radical with itself: thus the desired reaction R + S → products can be studied free of competing R + R processes, a tremendous advantage of μSR studies.

REFERENCES TO CHAPTER 6

1. A. Schenck, Helv. Phys. Acta 54, 471 (1981).
2. O. Hartmann, E. Karlsson, L.-O, Norlin, K. Pernestal, M, Borghini, and T. Niinikowski, Hyperf. Int. 4, 7 (1979).
3. D. L. Williams, TRIUMF Research Proposal 232 (November 1982).
4. A. B. Denison, H. Graf, W. Kündig, and P. F. Meier, Helv. Phys. Acta 52, 460 (1979).
5. Numerous references on these subjects can be found in Proc. 2nd Int. Topical Meeting on Muon Spin Rotation, published in Hyperf. Int. 8 (1981).
6. M. Takigawa *et al.*, J. Phys. Soc. Jpn. 49, 1760 (1980); R. S. Hayano *et al.*, J. Phys. Soc. Jpn. 49, 1773 (1980).
7. R. H. Heffner, M. Leon, M. E. Schillaci, D. E. MacLaughlin, and S. A. Dodds, J. Appl. Phys. 53, 2174 (1982).
8. Y. J. Uemura and T. Yamazaki, Physics (Utrecht) B + C 109-110, 1915 (1982).
9. See A. Abragam, *Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961).
10. The neutron spin-echo technique [F. Mezei and A. P. Murani, J. Magn. Magn. Mat. 14, 211 (1979)] overcomes somewhat this insensitivity to slow fluctuations.
11. K. Emmerich and C. Schwink, Hyperf. Int. 8, 767 (1981).
12. J. A. Mydosh, J. Magn. Magn. Mat. 7, 237 (1978),
13. C. Boekema, R. H. Heffner, R. L. Hutson, M. Leon, M. E. Schillaci, J. L. Smith, S. A. Dodds, and D. E. MacLaughlin, J. Appl. Phys. 53, 2625 (1982).

14. C. Y. Huang et al., Bull. Am. Phys. Soc. 27, 245 (1982).
15. T. Yamazaki, R. S. Hayano, J. Imazato, K. Nagamine, S. E. Kohn, and C. Y. Huang, Phys. Rev. Lett. 42, 1241 (1979).
16. M. Camani, F. N. Gygax, W. Rüegg, A. Schenck, and H. Schilling, Phys. Rev. Lett. 39, 836 (1977).
17. See references in review by E. Karlsson, Phys. Rep. 82, 271 (1982).
18. M. Doyama, Hyperf. Int. 8, 701 (1981); K. G. Lynn, Hyperf. Int. 8, 687 (1981).
19. K. W. Kehr, D. Richter, J.-M. Welter, O. Hartmann, E. Karlsson, L.-O. Norlin, T. O. Niinikowski, and A. Yaouanc, Phys. Rev. B26, 567 (1982).
20. J. A. Brown, R. H. Heffner, R. L. Hutson, S. Kohn, M. Leon, C. E. Olsen, M. E. Schillaci, S. A. Dodds, T. L. Estle, D. A. Vanderwater, P. M. Richards, and O. D. McMasters, Phys. Rev. Lett. 47, 261 (1981).
21. J. H. Brewer, D. G. Fleming, and D. P. Spencer, in Nuclear and Electron Resonance Spectroscopies Applied to Materials Science, E. N. Kaufmann and G. K. Shenoy, eds. (Elsevier North-Holland, Amsterdam, 1981).
22. E. Holzschuh, W. Kündig, and B. D. Patterson, Helv. Phys. Acta 54, 552 (1981).
23. J. A. Brown, R. H. Heffner, M. Leon, S. A. Dodds, D. A. Vanderwater, and T. L. Estle, Phys. Rev. Lett. 43, 1751 (1979).
24. B. D. Patterson, A. Hintermann, W. Kündig, P. F. Meier, F. Waldner, H. Graf, E. Rechnagel, A. Weidinger, and T. Wichert, Phys. Rev. Lett. 40, 1347 (1978).
25. E. Holzschuh, H. Graf, E. Rechnagel, A. Weidinger, T. Wichert, and P. F. Meier, Phys. Rev. B 20, 4391 (1979).
26. E, Holzschuh, W. Kündig, P. F. Meier, B. D. Patterson, J. P. F. Sellschop, M. C. Stemmet, and H. Appel, Phys. Rev. A 25, 1272 (1982).
27. A. Weidinger, G. Balzer, H. Graf, E. Rechnagel, and T. Wichert, Phys. Rev. B 24, 6185 (1981).
28. See references in review by D. G. Fleming, Workshop on Muon Science and Facilities, Los Alamos National Laboratory, Los Alamos, New Mexico, March 1982, LA-9582-C.

7. NEW DIRECTIONS

I. FUTURE FACILITIES: PROPOSED AND UNDER CONSTRUCTION

We now briefly discuss the known plans for expansion of μSR facilities around the world, focusing on the period of the next 5 years.

At SIN, current plans call for converting another beam line, ΠM3, into a surface μ^+ facility sometime in 1984. This will provide surface muons to a dedicated μSR area, with a spin rotator and low-temperature (dilution refrigerator) facility. Finally, the upgrade to produce 1-2 mA of beam for the SIN accelerator will have been completed within the next 2 years.

TRIUMF is undertaking an upgrade of its M20 channel to increase the flux and to provide two legs to be used either for surface or decay beams. The channel will have a dc separator and spin rotator and should be installed during the period January through May 1983. In addition, within the next 2 years TRIUMF is planning to build a new surface muon channel (M15), which will use two dc separators and new beam optics to provide an exceptionally clean, high-luminosity-surface muon beam. The expected luminosity will be about $5 \times 10^5/\text{cm}^2/\text{s}$ at 100 μA. They are also planning a μSR facility that will include a dilution refrigerator and its associated spectrometer to be used at this beam line. If TRIUMF builds a "kaon factory," very-high-luminosity dc or pulsed beams would be available in a decade.

The design of a new μSR spectrometer to increase the useful data rates at LAMPF is under way. The scheme would utilize the capability of spatially correlating the muon and positron trajectories, in effect subdividing the targets so that the maximum stopping rate would be associated with each subsection, instead of the target as a whole. This technique has been under development at CERN. It seems likely that such a scheme could increase data rates by at least a factor of 5, making the LAMPF data rates competitive with those now at SIN. Another way to increase data rates at LAMPF would be to utilize the dc beams potentially available at a new LAMPF II accelerator in about a decade.

Design studies are also under way to assess the future of pulsed muon beams at LAMPF. One scheme under investigation is the feasibility of providing a chopped surface muon beam at one of the existing muon beam lines. Pulses of short duration could provide higher data rates (Chapter 4) and provide pulsed-beam capabilities as well. Surface beams are important for this application, because their low momentum makes rapid chopping feasible.

The Los Alamos Proton Storage Ring (PSR) would provide an ideal pulsed μSR source. The μSR, now under construction, will operate in two modes, a 1-ns-wide proton burst at 720 Hz with an average current of 12 μA and a 270-ns-wide burst at 12 Hz with an average current of 100 μA. The PSR could provide a unique capability because of its high intensity and short pulse mode (1-ns width). The long pulse mode could also be used to provide a chopped surface beam with a pulse width between 5 and 270 ns. A proposal to build a muon beam facility at the PSR is currently being written.

The KEK facility has come on-line within the last 2 years at a beam intensity of about 1 μA. An upgrade to provide 10 μA of beam is planned in about 2 years. The construction of a high-frequency rf system and the provision for laser irradiation of samples will be used to further exploit the currently unique KEK pulsed-beam structure. Thoughts are also being given to upgrading the beam intensity to about 100 μA.

A new stopping muon channel has been assembled at BNL using many of the components from the old Space Radiation Effects Laboratory (SREL). A 1-μA proton beam of 28-GeV energy impinging on a thick production target will be used to produce an estimated μ^+ decay luminosity of about $1.2 \times 10^4/\text{cm}^2/\text{s}$, with a momentum spread of 2 MeV/c and macroscopic duty factor of 40 percent. The machine can also produce 20- to 30-ns-wide bunches about every 2 sec, with an average intensity of about $10^3/\text{cm}^2/\text{s}$. The feasibility of making a surface muon beam is also being studied.

The new SNS machine at Rutherford-Appleton Laboratory will be an 800-MeV proton synchrotron with 200-μA design intensity, producing two 100-ns-long pulses 230 ns apart every 20 ms. The primary purpose for this machine has been to produce an intense source of pulsed neutrons. An additional plan is under way to place an in-line target upstream of the neutron production target, to produce a surface muon beam for μSR research. Two kicker magnets will be used to provide two simultaneous chopped beams of 10- to 100-ns width, each using 100 μA of beam.

II. NEW DIRECTIONS: THE TECHNIQUE

Very-high-luminosity low-momentum muon beams will be needed to extend μSR to a wider range of samples. Assuming dc beams, intensities of the order of 5 x 10^6 $\mu^+/cm^2/s$ would allow maximum useful rates with samples whose cross-sectional area is as small as 1 mm^2. Performances comparable with this are currently available at beam line πE3 at SIN and will be exceeded when SIN increase the proton beam current to the 1-2 mA value. Comparable performance exists for surface beams at LAMPF, except for the duty factor loss of about a factor of 10. In the more distant future (~10 years) higher-intensity stopping muon beams will possibly be available from proton synchrotrons (100 μA at 16-30 GeV energy) in the planning stages at LAMPF and TRIUMF.

A second important new direction of μSR research, which will extend the technique to new phenomena, involves the use of pulsed sources. The advantages of a pulsed source are twofold: (a) increased event rates and (b) exploitation of pulsed environments. The increased event rate arises from the fact that the muon pileup problems are virtually eliminated, since all the muons arrive "simultaneously." In order to obtain excellent time resolution, however, the pulse width must be of the order of a few nanoseconds or less. This can be accomplished by chopping a wider pulse, with loss of intensity (as proposed at both the SNS and PSR) or by using the intrinsically narrow pulse structure that would be available at machines like the PSR at Los Alamos.

The limitation on the event rate with a pulsed beam is therefore determined by the available luminosity and by the speed of the pulse-processing electronics. It is estimated that for 20-ns time resolution, machines at Rutherford or Los Alamos could produce useful muon stopping rates of the order of $10^6/cm^2/s$, compared with 5 x $10^4/cm^2/s$ at a dc accelerator. A small,

Table 7.1 Present and Possible Future Pulsed Muon Facilities

Facility	Pulse Width (ns)	Repetition Rate (Hz)	Proton Current (μA)
KEK	50	20	1-2
SNS	5-100 (chopped)	50	100
PSR (long)	5-270 (chopped)	12	100
PSR (short)	5	720	12

bright beam spot is required in order that essentially all of the muons stop in the target (and not in the surrounding material), because the high instantaneous rate precludes the use of a beam-defining counter.

The facility at KEK has already demonstrated the power of pulsed muon techniques. One obtains a signal/noise ratio about 100 times that achieved at a dc source, since the beam is shut off when the decay positrons are counted. Because of this the signal can be easily followed for up to 20 μs, compared with a typical time range of 10 μs at a dc source, which represents another two decades change in the relaxation function. Finally, muon spin resonance measurements have been carried out, using a high-power pulsed-rf source, for muons stopped in several materials. This is the first example of experiments requiring very intense magnetic or electric fields, which are only possible with pulsed fields and, correspondingly, pulsed muons. As an extreme example, if intensities $>>10^6$ $\mu^+/cm^2/s$ were available in the future, it might even be possible to do experiments in which the samples were actually destroyed, but sufficient data were obtained, in a single beam pulse. Table 7.1 shows some characteristics of the KEK and other possible future pulsed facilities.

III. NEW DIRECTIONS: THE SCIENCE

The principal value that μSR enjoys as a resonance probe of materials is its complementary relation to other techniques such as neutron scattering, Mössbauer spectroscopy, and NMR. Given this complementary role, one can expect that μSR will continue to be applied to new materials and phenomena in much the same way that other techniques have been. In what follows we briefly outline some of the scientific areas to which the μSR technique is likely to contribute. In the immediate future the most dramatic contributions are likely to come from a growth in the variety of phenomena to be studied with μSR as more researchers trained primarily in solid-state physics and chemistry enter the field. In the more distant future (>3 years) the impact of new techniques and facilities (such as pulsed and high-luminosity dc beams) will be felt.

A. Immediate Future (<3 Years)

Electronic Structure of Metals

Knight shifts in the simple metals show trends that have yet to be explained by theory, so there is a more immediate need for theory than experiments in this area. However, it would be illuminating to see what experimental trends exist in alloys and intermetallic compounds. Relatively little μSR has been done in metal hydrides, whereas considerable work has been done on proton NMR and the theory of electronic properties. Given the interesting similarities and differences between muon and proton probes, it seems natural that μSR be used to explore the electronic structure of the hydrides. Muons could also be used to monitor changes in electronic structures at phase transitions in metal systems. The most obvious candidate is the metal-insulator transition, but other more subtle structural transitions are likely to show effects similar to those already observed for the valence transitions in cerium.

Static Local Fields

μSR measurements of paramagnetic-state shifts and zero-field resonance frequencies near magnetic phase transitions will be particularly useful in materials for which no NMR exists or where rapid spin-lattice relaxation broadens the NMR signal excessively.

Of particular interest for the future should be studies of metals where strong hybridization between unfilled (3d, 4f, 5f) electronic shells and the conduction band renders an otherwise localized magnetic moment either itinerant or unstable (Kondo instability or intermediate valence).

Dynamic Effects in Magnetism

For the future, μSR appears to be a useful and even unique probe of spin fluctuation phenomena in numerous systems of current interest. A partial list of topics might be the following:

1. Studies of nonlinear excitations (e.g., solitons) in appropriate systems.
2. Fluctuations in systems without phase transitions, i.e., below lower critical dimensionality.
3. The effect of disorder on critical dynamics, e.g., near percolation thresholds.
4. The development of new kinds of fluctuations in disordered systems at low temperatures (e.g., barrier modes in spin glasses).
5. Fluctuations in unstable-moment rare-earth compounds, where mixing with conduction electrons produces a many-body singlet ground state. Examples are $CeAl_3$, $CeCu_2Si_2$, and CeB_6.
6. Spin fluctuation phenomena in itinerant magnetic systems.

Diffusion, Trapping, and Localization

The role of disorder in producing localization is of fundamental current interest, and this could be studied effectively by, for example, a systematic measurement of Cu or Al alloys (as opposed to the small impurity concentrations investigated so far in Al). Amorphous metals and semiconductors are also good candidates. Low-dimensional motion is known both in electronic and ionic conductors. If low-dimensional muon motion could be observed in favorable structures, it would provide a unique means of studying true single-particle hopping and localization phenomena in one or two dimensions.

Diffusion in a "pure" nonmagnetic metal has been observed only in Cu. It clearly would be desirable to extend this list, possibly by careful searching with improved sensitivity among elements with nuclear moments, such as the alkali metals.

The wide range of mass differences between the muon and the normal hydrogen isotopes has only rarely been exploited to determine isotope effects in the same material at the same temperature. Efforts, both in H and muon diffusion, should be made to obtain more overlap. Another case where overlap is needed concerns muon diffusion in Cu compared with muon diffusion in Au and Ag. The former has a much lower activation energy and prefactor than the latter two, suggesting fundamental differences. However, different measurement techniques and temperatures (relative to the Debye temperature) are involved.

Muon diffusion in metal hydrides is another high-interest area where little has been done. Here one has the possibility of studying the motion of a tagged particle (muon) in the presence of a large number of diffusing particles (protons), and striking correlation effects are expected. Since the muon hopping is likely to be influenced by the mobility of hydrogen vacancies, the experiments can also lead to information about hydrogen diffusion.

Trapping studies where the defect type (charge or size, for example) and concentration have been varied systematically are largely lacking. Such investigations are needed to shed insight on the nature of the trapping phenomena and perturbed potentials.

Muonium Chemistry

A strong case can be made for pursuing the present kinds of Mu reaction studies for some years to come, since many more data need to be accumulated in order to provide a wide-ranging comparison between H and Mu reaction constants. This is particularly true in the gas phase. Concomitantly, it will be important to have more accurate H atom data.

In a like manner, further studies of μ^+ radicals, particularly measurements of their chemical reactivity, will continue to be of importance to the vast field of ESR studies in chemistry. Additional and more detailed information about the location of the muon in the molecule and its conformational dynamics can be obtained from detailed analysis of fine-structure splittings at lower magnetic fields.

Unlike the study of muonic radicals, very little is known about the diamagnetic environment of the μ^+. This missing information is, in some instances, one of the big drawbacks in the study of muonium chemistry. Knowing the environment of the μ^+ is clearly important to the correct interpretation of diamagnetic yields observed in the slowing-down process of the μ^+, which could be helpful in deciding between spur and hot-atom models[1] in condensed media, for example. Similarly, in the gas phase it seems likely that molecular ions form in the slowing-down process (e.g., $Ne\mu^+$), but there is no direct evidence for this. Also, being able to identify reaction products in chemical reactions would be useful in understanding the detailed nature of the reaction process (e.g., Mu + HBr → MuH or MuBr?), which to date relies totally on comparison with the analogous (and often not well understood) H atom reactions. Information could be obtained from precise chemical shift measurements and possibly by observing light emitted from vibrational excited states.

Insulators and Semiconductors

The study of the possible existence and characterization of muonium or muonium-like defects should be extended to a much wider class of insulators and semiconductors. Such studies could have important implications for the understanding of local moment formation. In this context the study of materials whose behavior is between a metal and a semiconductor could be important.

More theoretical work is required to understand the Mu and Mu* states seen in diamond, silicon, and germanium. The lack of visible hydrogen analogs is interesting here.

Surface Science

Another new regime in which muons may be useful probes is the study of surface science, which may include studies of catalytic reactions. Preliminary measurements on quartz powders have indicated that muonium might be diffusing to and migrating about the surface, becoming trapped and detrapped as the temperature is changed. The use of muonic x rays emanating from the capture of ultralow-energy negative muons (<1 eV) may also become a powerful probe of surface molecules. The x-ray energies and intensities are excellent determinants of the elemental charge and the chemical environment of the capturing species. Low-energy muons could be stopped in a thin layer of hydrogen and subsequently transferred to a monolayer of material. The production of such muon beams requires high intensities, such as those currently available at LAMPF and SIN or in a decade at the possible high-intensity upgrades of LAMPF and TRIUMF.

B. Long Range (>3 Years)

Statics and Dynamics in Magnetism

The study of the topics mentioned above in Section A are likely to be greatly enhanced by the higher counting statistics available with a good time-resolution (<10 ns) pulsed beam. Such studies would allow high-precision measurement of the entire relaxation function in essentially all magnetic materials. Furthermore, the beam time structure would permit monitoring the return to equilibrium of a system <u>after</u> an initial perturbation. It is possible, for example, that the relaxation spectrum of a spin glass depends on changes in applied magnetic field.

Static and Dynamic High Pressure

Pressure is a powerful tool in studying solid-state phenomena, so it is natural that it be combined with μSR. Knight shifts versus pressure could be particularly valuable in elucidating how the various band and core terms depend on interatomic spacing. A new area of physics and chemistry concerns behavior under shock. Shock waves have been shown to induce polarization, free radicals, and numerous point defects. By combining shock waves with pulsed μSR, one would have the possibility of doing real-time, local-probe studies of shock-induced processes.

Diffusion, Trapping, and Localization

Most experiments have so far measured only the characteristic time Λ^{-1} (inverse depolarization rate) for the relaxation function G(t) to decay to 1/e of its initial value. Considerable additional information and detailed comparison with theory is possible if the complete time dependence of G(t) were measured. For example, the long-time behavior in zero field can distinguish between diffusion to a trap and release from a trap. It would be possible as well to measure much smaller Λ's, with the hope of detecting the rapid diffusion or high delocalization that apparently exists in many metals.

Questions of localization are closely tied to lattice relaxation. If subnanosecond μSR or combined time-resolved phonon spectroscopy with μSR could be done, then the exciting possibility exists of studying the dynamics of polaron formation.

In addition to studies of point defects in metals, it is worthwhile to examine the effects of dislocations, grain boundaries, and microscopic cracks on muon diffusion and trapping. Part of this interest stems from problems of hydrogen embrittlement. It is believed that such defects play a significant role in the embrittlement problem, but the small amounts of hydrogen involved preclude proton NMR as a local probe, whereas the situation is well suited for μSR.

Muonium Chemistry

There are a number of exciting possibilities in the future using pulsed muons in conjunction with pulsed lasers. In the study of reaction dynamics, very often the reaction from the vibrational ground state of the target molecule ($v = 0$) is thermoneutral or even endothermic, in which case the reaction rate is very slow and difficult to measure (Mu + H_2, Mu + HCl are cases in point). If one were able to excite the $v = 1$ state, the reaction rate would increase by several orders of magnitude, which would provide additional, and in some cases crucial, information pertinent to testing different reaction theories.

The production of a muonium beam would truly revolutionize the subject of kinetic studies, by permitting measurements of cross sections rather than bulk rate constants.

General Pulsed Techniques

As an example of an untried class of measurements in which high intensities and short pulses would be important, we discuss optical-μSR experiments. Lasers are currently available that can cover the wavelength range from the extreme UV into the far IR, and continuous tunability is available over much of this range. For example, YAG-pumped dye lasers, tunable from 195 to 5000 nm with 10-ns pulse lengths, 30-Hz repetition rates, and 10^7-W peak powers are available.[2] These pulse lengths and repetition rates are comparable with those that could be obtained at present and future pulsed-muon facilities. Thus it should be possible to do experiments in a wide variety of optical environments.

Consider the search for the optical transitions from the ground state of muonium or a muonium-like defect center in a nonmetallic crystal. A tunable laser could be stepped in wavelength, with separate μSR spectra obtained for each wavelength. While on or near an optical transition the μSR spectrum would be weakened or destroyed, thus allowing the location of the transitions. If the excited state is long-lived (lifetime $\gtrsim$0.1 μs), optical transition can be pumped with a short pulse (~1 ns) and the subsequent μSR spectrum will be a superposition of the ground and excited state μSR spectra. If long laser pulses are used, then the system may be coherently driven between ground and excited state, with characteristic effects on the μSR spectrum, such as the production of sidebands. Similarly, production of optically induced spin polarization, using circularly polarized light, might be observable.

REFERENCES TO CHAPTER 7

1. D. G. Fleming, D. M. Garner, L. C. Vay, D. C. Walker, J. H. Brewer, and K. M. Crowe, Positronium and Muonium Chemistry, Advances in Chemistry Series No. 175, H. J. Ache, ed. (American Chemical Society, Washington, D.C., 1979).
2. H. P. Kortz, Laser Focus, July 1982, p. 57.