MUONIUM IN C₆₀ FULLERITES: STUDIES OF STRUCTURAL AND ELECTRONIC PROPERTIES

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B. S. Virginia Polytechnic Institute and State University, 1990

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

PHYSICS

We accept this thesis as conforming

to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

April 1993

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Abstract

 μ SR studies of crystalline C₆₀ reveal the existence of two distinct paramagnetic states. The experiments described in this thesis confirm that one is an exohedrally bonded muonium radical, while the other is endohedral muonium with a hyperfine parameter A_{μ} close to that of muonium in vacuum. The signal from the muonium-C₆₀ radical—which is characterized by a small A_{μ} (10% of $A_{\mu}^{\rm vac}$) and an anisotropic hyperfine interaction—is sensitive to the molecular dynamics and is used to study the structural phase transition of solid C₆₀ near 260K. Only endohedral muonium is observed in the alkali-metal-doped fullerites K₄C₆₀, K₆C₆₀, and Rb₆C₆₀. From its coherent spin precession, we find all three to be semiconductors with small gaps on the order of 0.5 eV. Our results conflict with the simple band structure model of doped fullerites indicating that electron-electron correlation effects may be important in determining the electronic structure of these solids.

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Acknowledgement

I'd like to thank my advisor Jess Brewer for his support and patience, and for giving me the freedom to choose this interesting and timely topic for my thesis. It has been a pleasure to work with Rob Kiefl. I thank him for the many discussions and experimental collaboration from which I have learned a great deal about μ SR, muonium, and condensed matter physics. I would also like to acknowledge the efforts and contributions of the other E658 collaborators, especially Jürg Schneider, Andrew MacFarlane, and Kim Chow. Special thanks to Curtis Ballard and Keith Hoyle for the technical expertise and advice. The high quality and well characterized samples were provided by Jack Fischer and his colleagues at the University of Pennsylvania.

Chapter 1

Introduction

The recent discovery of the C₆₀ molecule[1] and a simple technique for producing macroscopic quantities of this new form of carbon[2] opened a new chapter in condensed matter physics. Alongside diamond and graphite, crystalline C₆₀ is a third form of solid carbon. Due to the nearly spherical symmetry of the constituent C₆₀ molecule, this solid and other C₆₀ fullerites exhibit very interesting physical properties. Exploring the properties of this unusual class of solids has become an exciting endeavour encompassing the whole range of condensed matter techniques, including μ SR. In fact, the richness of the data obtained by μ SR may be attributed to the occurrence of paramagnetic muonium states in these solids.[3]

The somewhat inadvertent discovery of the C_{60} molecule resulted from an interdisciplinary effort to solve a long-standing mystery in astronomy.[4] Spectroscopy of visible light from stars reveals a series of more that 40 absorption features known collectively as diffuse interstellar bands. None of these are unambiguously associated with any particular origin, although carbon clusters have been a suspect since the 1960's. Hoping to observe similar spectra in the lab, researchers set about trying to produce such carbon clusters using laser ablation and arc-burning of graphite in a helium atmosphere. The group led by Richard Smalley of Rice University along with Harold Kroto of the University of Sussex found that by adjusting the timing of the laser pulses and the pressure of the helium atmosphere, they could produce a preponderance of the C_{60} molecule. Shortly thereafter, they proposed the structure of the molecule to be that of the truncated icosahedron, the symmetry exhibited by the well known soccer ball. Accordingly, the molecule was named buckminsterfullerene, or 'Buckyball' for short, after the architect Buckminster Fuller and his geodesic domes which brought him fame.

The observation by Krätchmer *et al.* that the C₆₀ molecule was readily soluble in bezene provided the means to separate it from the rest of the carbon soot produced in the arc-burning process which they pioneered.[2] Thus the first macroscopic amounts of C₆₀ were synthesized as a brand new form of solid carbon. This led to a rapid growth in research on the properties of the solid. Two interesting phenomena, both of which have been studied using μ SR spectroscopy, motivate the experiments described in this thesis. The first is the existence of a first-order phase transition in the pure solid, and the second is the occurrence of superconductivity at relatively high transition temperatures in alkali-metal-doped C₆₀ fullerites.[6]

The first order phase transition was initially observed via X-ray diffraction, [5] and subsequently by many other techniques. Formation of a paramagnetic muonium radical, bonded exohedrally to the C_{60} molecule, allows us to study this transition and the underlying molecular dynamics. The nature of this transition is now well understood.

The alkali-metal-doped fullerites, $A_x C_{60}$, whre A refers to an alkali metal, are formed by exposure of pure C_{60} powder to the alkai-metal vapour. When doped to the composition $A_3 C_{60}$, metallic and superconducting behaviour results. The superconducting transition temperatures of 18K for K-doped C_{60} and 29K for Rb-doped C_{60} samples are remarkably high and are surpassed only by the cuprates. These fullerites contrast with the related superconducting graphite intercalation compounds such as KC₈, which have transition temperatures below 1 K. The mechanism of superconductivity in these solids is not presently well understood and remains an outstanding issue in the forefront of condensed matter physics.

The A_3C_{60} phase is not the only fullerite produced upon exposure to alkali-metal

vapour. Stable phases with the stoichiometry A_4C_{60} and A_6C_{60} can also be synthesized. We will focus on the electronic properties of these non-superconducting phases. They are studied *via* μ SR of a paramagnetic muonium state which is determined to be endohedral (inside the buckyball). It is hoped that these results will shed light on the underlying band structure model appropriate for the general description of these fullerites and central to any specific model of superconductivity in A_3C_{60} .

Chapter 2

C₆₀ Fullerene and Fullerites

2.1 The C₆₀ Molecule

The unique properties of this third form of solid carbon stem from the underlying structure of the constituent C_{60} molecule (Fig. 2.1a), which is composed of twenty hexagons and twelve pentagons arranged in a truncated icosahedron with a hollow centre. Three of the four valence electrons of each carbon atom are involved in covalent bonds with the neighbouring carbons. By analogy with graphite these are called σ -bonds while the fourth electron is ascribed to a π -like orbital. Due to their non-planarity, however, the hybridization of the σ -orbital is such that it no longer contains all of the *s*-orbital character while the π -orbital is no longer of purely *p*-orbital character.[7] The σ -bond hybridization in C_{60} is somewhat between the hybridizations of graphite (sp^2) and diamond (sp^3).

Within the icosahedral symmetry, the buckyball actually contains two types of C-C bonds (Fig. 2.1b) having different lengths. Comprising the pentagons are the longer (1.45 Å) electron-deficient 'single' bonds. Joining two hexagons one finds the shorter (1.40 Å) electron-rich 'double' bond. As a result the C₆₀ molecule aquires a slightly anisotropic charge distribution having important consequences for the solid, as will be discussed later.

The energies of the sixty π -like molecular orbitals are of central importance since they form the valence and conduction bands in the solid. The one electron levels formed



Figure 2.1: a: Model of the C_{60} molecule (from Ref. 8) b: Model of C_{60} showing the electron-rich 'double' bonds and electron-deficient 'single' bonds (from Ref. 7).

from these radially directed orbitals can be calculated using Hückel molecular orbital theory [7] or a tight-binding approximation. Figure 2.2 shows the energy levels obtained assuming the hopping amplitudes for both types of C-C bond are the same. These eigenstates reflect the icosahedral point group symmetry exhibited by the potential and are labeled by the letters a, t, g, and h referring to degeneracies of 1, 3, 4 and 5, respectively. The subscripts g and u refer to even (gerade) and odd (ungerade) symmetry, respectively. One recognizes the similarity of these states with the angular momentum eigenstates of an electron confined to a spherical surface. In particular, the degeneracies of the L=0,1,2 and L=4 levels are unchanged.

Using distinct hopping amplitudes for each type of bond splits the 9-fold degeneracy of the L=4 level into a 5-fold and a 4-fold degenerate level. The energy levels of the other states shift but their degeneracies remain the same.

Ignoring electron-electron interactions, the electronic configuration of the C₆₀ molecule is obtained by filling each of the thirty lowest-lying states with two electrons of opposite spin. The high symmetry of the buckyball greatly simplifies the complexity otherwise expected for a 60-electron molecule. One finds that the lowest lying 30 states are occupied, completely filling the h_u shell. Approximately 2 eV above this lie the triply degenerate t_{1u} states.

2.2 Crystalline C_{60} and $A_x C_{60}$

2.2.1 Crystal Structure

If we ignore the complications of molecular orientation, crystalline C_{60} can be considered a molecular crystal formed by close packing of spheres. Due to the large diameter of the carbon cage (7.1Å), pristine C_{60} condenses into a face-centered cubic (fcc) lattice with a remarkably large lattice constant of 14.198 Å.[9] As a result, the crystal structure



Figure 2.2: One electron energy levels of the C_{60} molecule calculated using Hückel MO theory (adapted from Ref. 7). The energy is measured in units of t, the hopping amplitude (assumed to be the same for each C-C bond). The l=0,1,2,..5 lablels refer to the analogous angular momentum eigenstates of an electron confined to a spherical surface.

of C_{60} has large interstitial spaces— two with tetrahedral and one with octahedral symmetry per C_{60} molecule—available for deliberate as well as inadvertent doping. (Solvent molecules left over from the extraction process are a particular nuisance which must be dealt with lest they obscure the interesting physics.) This crystal structure gives C_{60} a density of about 1.7 g/cm³, considerably lighter than either graphite (2.3g/cm³) or diamond (3.5 g/cm³).

When pristine C_{60} is exposed to alkali-metal vapour such as potassium or rubidium, alkali atoms are incorporated into the interstitial spaces forming three stable phases as evidenced by X-ray diffraction.[10,11,12] For arbitrary x, A_xC_{60} consists of inhomogeneous mixtures of these three stable phases with x=3, 4, and 6. Attempts to dope in additional alkali atoms beyond the x=6 phase result in formation of regions of pure alkali metal indicating that the x=6 phase is, in some sense, saturated.

The x=3 phase, exhibiting superconductivity and also the largest normal state conductivity, retains the original fcc lattice of pure C₆₀. (The alkali atoms occupy the tetrahedral and octahedral sites.) For stoichiometries greater than x=3, some expansion of the lattice is necessary to hold the additional atoms. The crystal structure therefore transforms to body-centered tetragonal (bct) for A₄C₆₀ and body-centered cubic (bcc) for A₆C₆₀ (see Fig 2.3).

It should be noted that not all the aforementioned phases are obtainable for an arbitrary alkali metal. For example, no stable fcc phase has been achieved with only cesium as the dopant. This has been interpreted as due to the large size of the cesium cation which requires a more open C_{60} lattice such as bcc or bct. At the other end of the mass spectrum, neither Na_xC_{60} nor Li_xC_{60} have been found to have a stable fcc phase although binary mixtures (*e.g.* Na_2AC_{60} A=K,Rb,Cs or Rb₂CsC₆₀) utilizing all three are possible.[13] This thesis will be concerned with the non-fcc phases K₄C₆₀,



Figure 2.3: Crystal Structure for A_3C_{60} , A_6C_{60} , and A_4C_{60} (from Ref. 10).

 K_6C_{60} , and Rb_6C_{60} . Henceforth in the remainder of this paper, the A in A_xC_{60} will be taken to refer solely to K or Rb.

2.2.2 The Phase Transition and Orientational Dynamics of Solid C_{60}

Due to the strong intra- C_{60} covalent bonds, the internal molecular structure is basically unchanged in the solid state. This, taken with the experimental fact that the minimum distance between adjacent C_{60} molecules in the solid is some 3.1Å might lead one to conclude that the inter- C_{60} interaction could be adequately described by a Van der Waals interaction. A spectacular demonstration that this is not quite correct is the existence of a first order phase transition in the solid at approximately 250 K.[5] NMR studies using naturally occurring ¹³C nuclei had initially shown dynamical disorder which decreased with temperature.[14] This was interpreted as a consequence of free rotation of the C_{60} molecules with a gradual slowing down of reorientations as the temperature was lowered. Following this, P. Heiney and co-workers used synchrotron X-ray diffraction in an attempt to determine the low temperature structure of the solid.[5] They found that the low temperature phase is orientationally ordered and stable up to 249 K whereupon the solid undergoes a phase transition to the disordered state characterized by quasi-free rotation of the C_{60} molecules. Differential scanning calorimetry revealed the first-order nature of the transition by indicating a free-energy change of 6.7 J/g at the transition.[5] From the diffraction peaks it was also possible to ascertain that the low temperature lattice can be indexed as simple cubic (sc) with a four-molecule basis.

Neutron diffraction measurements clarified the nature of the fcc \rightarrow sc transition and the low temperature phase, revealing the ordering configuration of the C₆₀ molecules. David *et al.*[15] found that this configuration was the result of an optimized ordering scheme in which the electron-rich, short inter-pentagonal bonds face the electrondeficient pentagon centres of adjacent C_{60} molecules. The icosahedral symmetry of the C_{60} molecules makes this optimization possible for all twelve nearest neighbours and results in the observed four-molecule basis.

Theoretical studies [16,17] including Monte Carlo simulations corroborate these findings upon inclusion of a small anisotropic correction to the previouly assumed Van der Waals interaction. In addition to a Lennard-Jones potential, a small Coloumb potential, parameterized by an effective charge -2q on the short 'double' bonds, is found to reproduce the the transition temperature as well as the orientation of the observed ground state.

However, orientational dynamics persist below T_0 , the ordering temperature, as there are many nearly degenerate orientations for each C_{60} . These orientations are related by $\pi/3$ rotation about a threefold axis and are separated by potential barriers of ~ 300 meV. Resulting from this is a glassy transition characterized by 'frozen in' disorder below a characteristic temperature that depends upon the time scale of the experimental probe.[16] Direct experimental evidence for this transition is found in sound velocity and attenuation measurements[18] and thermal conductivity measurements[19] on single crystal C₆₀.

2.2.3 Electronic Structure

With the molecular energy levels in hand, it is not difficult to arrive at the electronic structure of C_{60} solids, at least within the framework of an independent-electron, tightbinding model. Recall that in the tight-binding approximation, a non-zero amplitude for electrons to hop from one site to the next causes the energy levels of the atom (or molecule as the case may be) to broaden into a band. The validity of such an approach with the fullerites rests upon the fact that the C_{60} molecules in the solid are relatively far apart and consequently have a small hopping amplitude t relative to the on-site energy. Less grounded in certainty is the assumption of non-interacting electrons which is even more of a concern when the energy bands are narrow due to a small t.

Charge transfer, the salient feature of doping with alkali-metal atoms, makes the electronic structure of $A_x C_{60}$ no more complicated. One simply uses the alkali-metal atoms to add electrons to the C_{60} energy bands. The high electron affinity of the C_{60} molecule combined with the low ionization potentials of the alkali metals ensure that the electrons are completely transferred to the formerly neutral C_{60} molecule. Structurally this transfer makes the doped fullerites more ionic and increases the cohesive energy relative to the undoped solid.

Electronically, these considerations give the following results, seen simply by inspection of the C₆₀ molecular energy levels: C₆₀ should be insulating with a relativly large gap of about 2 eV; each added alkali-metal atom per C₆₀ adds one electron into the triply degenerate t_{1u} orbitals so that A₃C₆₀ and A₄C₆₀ should be conducting; and for six added electrons, the t_{1u} orbitals are filled hence A₆C₆₀ should be insulating with a gap of a fraction of an eV.

This approximate behaviour is observed in conductivity measurements on thin films of $A_x C_{60}$.[20] In these experiments thin films of C_{60} are exposed to alkali-metal vapour while the conductivity is monitored *in situ*. The films consist of inhomogeneous mixtures of the stable phases with the quoted x an average value of the alkali composition. The conductivity reaches a maximum for x=3, which presumably contains a large fraction of the stable x=3 phase, and decreases beyond this as the doping proceeds to x=6. The lowest resistivity (approximately 2 m Ω -cm) is quite low for a typical metal and implies an unphysically short scattering length — perhaps an indication that this simple model needs modification. More sophisticated calculations predict the actual k-space dependence of the t_{1u} and other molecular-orbital-derived energy bands, from which one can estimate the density of states.[21,22] These calculations are based on the same ideas, namely complete charge transfer and absence of electron-electron interactions, and therefore provide the same qualitative results. Some authors try to estimate the effect of orientational disorder among the C₆₀ molecules on the electronic properties[23] but here again they use the same underlying molecular energy levels.

2.3 Superconductivity in A_3C_{60}

The observed transition temperatures for fullerite superconductors (18K for K_3C_{60} , 29K for Rb_3C_{60} and 33K for Cs_2RbC_{60}) are higher than any other known molecular superconductors and surpassed only by the cuprates. These superconductors are extreme Type II having a coherence length $\xi(0)$ of 26 Å. The penetration depth of K_3C_{60} as measured by magnetization[24] is 2400 Å, whereas μ SR results[25] find a value of 4800 Å. Measurements using ¹³C NMR[26] find an energy gap consistent with weakcoupling BCS theory while STM measurements[27] favour a larger value supporting strong-coupling models. The mechanism for such high T_c 's in these materials is not agreed upon and both electron-phonon and electron-electron[30] pairing mechanisms have been proposed.

The classic test of BCS theory is the existence of an isotope effect on the transition temperature. This effect has been seen using isotopically pure $K_3^{13}C_{60}[28,29]$ however the interpretation that this confirms the validity of BCS theory is not without difficulty. Chakravarty and Kivelson argue that this would also be seen if the pairing resulted from electron-electron interactions.[31,32]

Relevant to all models of superconductivity is the measured dependence of T_c on the

lattice constant[33] which essentially reflects the dependence of T_c on $N(E_f)$, the density of states at the Fermi energy. One expects $N(E_f)$ to increase with increasing lattice constant since the bands become more narrow as the hopping amplitude decreases. Virtually all of the conventional theories of superconductivity rely on the underlying band structure model for $A_x C_{60}$ described above. The validity of such an approach should be investigated experimentally. This can be accomplished by studying the nonsuperconducting phases of $A_x C_{60}$ in addition to the normal and superconducting states of $A_3 C_{60}$. The electronic structures of $K_4 C_{60}$, $K_6 C_{60}$, and $Rb_6 C_{60}$, which are the subject of part of this thesis, are an important test of any comprehensive theory for the electrical properties of fullerites.

Chapter 3

μ SR and Muonium Spectroscopy

3.1 Introduction

The use of muons for condensed matter studies is possible because of parity violation in the weak interaction and its manifestation in leptonic decays. Spin-polarized beams of low energy muons can be produced; when such muons are stopped in matter, the evolution of their spin polarization may be readily monitored using the experimental techniques of particle physics. Although the method is quite different from that of other spin resonance experiments, the information about the local fields obtained using μ SR is similar and often complementary to that obtained from Nuclear Magnetic Resonance (NMR) or Electron Spin Resonance (ESR).

The muon is a spin- $\frac{1}{2}$ lepton with a mass of $\sim \frac{1}{9}$ that of the proton and a mean lifetime of $\sim 2.2 \ \mu$ s. When negative muons (μ^-) are stopped in solids, they are quickly captured by an atomic nucleus, cascading down to the lowest muonic orbital which has a radius comparable to the nuclear radius. Positive muons (μ^+), however, avoid the positively charged nuclei and take up sites in the interstitial regions. The experiments described in this thesis employed positive muons although some condensed matter studies are done with negative muons.

Aside from the much smaller mass, the positive muon in a solid is completely analogous to an isolated hydrogen-like impurity. This fact has inspired a whole avenue of research concerned with the dynamics of the muon in the solid. Envisioned as a probe of solids, however, spin relaxation of the μ^+ is most simply seen as a microscopic probe of the magnetic properties of materials. Within this picture, the dominant interaction of the muon spin is assumed to be its Zeeman interaction with the local magnetic field. In addition to the applied field, the local field includes the dipolar field arising from the electronic and nuclear moments of the host material.

Like a bare proton, however, the μ^+ is very reactive and does not remain a bare particle in most materials. In good metals it acquires a screening charge which may in turn be polarized by an external field to produce a paramagnetic "Knight shift" of the effective field acting on the μ^+ . In other materials, the muon can pick up and bind a single electron to form a hydrogen-like atom (μ^+e^-) known as muonium or Mu for short. The occurrence of muonium opens up a whole new realm of experimental possibilities as the range of physical properties accessible to μ SR techniques is augmented by the presence of the bound electron.

This unpaired electron couples much more strongly to the local fields of the host material than the muon. In accordance with the Pauli principle, it can have a rather strong exchange interaction with the other electrons of the host material. The symmetry of the electron wavefunction is indicative of the muonium site and its environment. Additionally, the paramagnetic muonium atom is much more sensitive to local magnetic fields than the μ^+ simply because of its much larger magnetic moment. For those solids in which muonium forms, electronic structure as well as structural dynamics may be studied via spin relaxation of muonium. Needless to say, knowledge of the dynamics of muonium in solids is also valuable in its own right because of the scientific and technological interest in the behaviour of hydrogen in materials.

3.2 Basic Principles of Muon Spin Rotation

3.2.1 Parity Violation in Weak Decays

The non-conservation of parity in weak interactions was discovered experimentally by Wu *et al.* using ⁶⁰Co β -decay[34] and Garwin *et al.* using muon decay[35] in 1957 after a theoretical prediction by Lee and Yang.[36] Parity violation in weak decays is not a small effect. In fact, it is maximal, and forms a cornerstone of the V - A theory of weak interactions. In correspondence with this theory is the experimental observation that neutrinos are exclusively left-handed particles only while antineutrinos are right-handed only (i.e. their spins are antiparallel or parallel, respectively, to their momentum). These facts have important consequences in the decay chain $\pi^{\pm} \rightarrow \mu^{\pm} \rightarrow e^{\pm}$, utilized by Garwin *et al.* in 1957 as well as in current μ SR experiments.

Spin polarized positive muons are produced from pions from the decay process

$$\pi^+ \to \mu^+ + \nu_\mu,$$

a two-body decay. Conservation of momentum requires that the outgoing muon and neutrino be colinear in the rest frame of the pion. The spin of the pion is zero. Since the neutrino must be left-handed (helicity H = -1), conservation of both linear and angular momentum requires that the muon also be left handed. In the rest frame of the pion therefore, the muon is 100% spin-polarized with a helicity H = -1. If the pions themselves are moving, the muons and neutrinos from the decay—distributed isotropically in the pion rest frame—become Lorentz-boosted into a cone about the initial pion momentum. Hence for a finite acceptance beamline using pion decay in flight, something less than 100% muon polarization is achieved. For positive muons, however, the most common practice is to use a surface muon beam which selects muons from pions decaying at rest near the surface of the production target. In addition to nearly 100% spin-polarization, this type of beam has the advantage of providing low energy muons which are easily stopped in thin samples. It is also amenable to precise beam optics, as it comes from a small, well-defined source.

Measurement of the time evolution of the muon ensemble polarization relies upon the asymmetric distribution of positrons from the decay,

$$\mu^+ \to e^+ + \nu_e + \bar{\nu_\mu}.$$

As this is a 3-body decay, the kinetic energy of the emerging positron can have a continuous range of energies. Using the V - A theory, the angular probability distribution of the positron can be calculated and is found to depend upon the energy of the decay positron (Fig. 3.1). The angular decay probability has the form

$$W(heta,x) \propto 1 + a(x) \cos heta,$$

where $x = \frac{E}{E_{\text{max}}}$ the ratio of the positron energy to the maximum possible energy $(E_{\text{max}} \simeq 52 \text{ MeV})$, θ is the angle with respect to the muon spin and a(x) is the energydependent asymmetry factor, a(x) = (2x - 1)/(3 - 2x) (see Fig. 3.2). Averaging over the energy spectrum one finds that the positron is emitted preferentially along the direction of the μ^+ spin with a net asymmetry of $\frac{1}{3}$. Thus by recording the spatial distribution of a large number of decay positrons from muons with the same initial polarization, one is able to determine the direction of that polarization.

Although the major result of the work by Garwin *et al.* was the experimental verification of parity violation, they also noted an interesting observation concerning the nature of the material used to stop the muons. They found that the muon decay asymmetry in nuclear emulsion was only half that of muons stopped in copper or graphite. Friedmann and Telegdi[37] suggested that this loss of asymmetry was due to rapid depolarization on account of muonium formation. This was soon verified in an experiment



Figure 3.1: Angular Decay Distribution of Positrons from μ^+ Decay.



Figure 3.2: Energy spectrum E(x) and asymmetry factor a(x) of decay positrons.

performed by Orear *et al.* [38] in which a large magnetic field was applied to decouple the muon and electron spins and recover the 'missing' asymmetry.

3.2.2 The Experimental Technique

There are essentially two spectroscopic methods used in the majority of μ SR condensed matter experiments: time-integral and time-differential. In this section, a brief discussion of time-differential μ SR will be given. Several comprehensive reviews of μ SR techniques exist. In particular, the book by Schenck[39] and the review article by Patterson[40] are recommended.

The typical time-differential apparatus includes a number of scintillators surrounding a cryostat containing the sample, all of which are placed in a magnetic field. For the transverse-field setup, shown in Fig. 3.3, the applied field is perpendicular to the initial muon polarization. In a longitudinal-field setup, the applied magnetic field is parallel to the muon polarization. On the way to the sample, an incident muon passes through a thin scintillator (detector M in Fig 3.3) before entering the cryostat *via* a series of Mylar or Kapton windows. A photomultiplier tube amplifies the faint flash of light from the scintillator and generates a pulse which is used to start a digitizing clock.¹ The decay positron from the stopped muon is detected by another scintillator (detector E in Fig 3.3), and that pulse is used to stop the clock.

In this manner, repeated measurements of the time interval between the arrival of a muon in the sample and the detection of its decay positron are made. These time intervals are collected into a histogram which has the form

$$N(t_j) = B + N_0 \exp(-t_j/\tau_\mu) [1 + a_e P(t_j)], \qquad (3.1)$$
$$t_j = j\Delta t \quad (j = 1, N),$$

¹The so-called "clock" is more formally known as a time to digital convertor (TDC).



Figure 3.3: Typical Setup for Tranverse Field μ SR

where B is a time-independent background, N_0 is the normalization, and a_e , the experimental asymmetry. The experimental asymmetry here is not generally equal to the $\frac{1}{3}$ given by the intrinsic angular decay distribution, but instead depends on the experimental setup. This is due to absorption of low energy positrons, which raises the effective average asymmetry, and to the finite solid angle subtended by the scintillator, which lowers it. Fig. 3.4 (top) displays a simple μ SR spectrum of this form, showing clearly the μ^+ precession and the muon lifetime.

The quantity of interest is $P(t_j)$, the component of the muon polarization in the direction of this particular positron counter.² For the transverse-field geometry depicted in Fig. 3.3, $P(t_j)$ is typically the sum of damped sinusoids

$$P(t_j) = \sum_n f_n R_n(t_j) \cos(\omega_n t_j + \phi_n), \qquad (3.2)$$

where the different frequencies may be due to either inequivalent muon sites or formation of paramagnetic muonium states (to be discussed in the next section). The amplitude f_n reflects the relative fraction of muons contributing to the *n*th signal and $R_n(t_j)$ is a relaxation function which depends on the particulars of the solid and is often taken to be a gaussian or an exponential envelope function. As a simple example, assume that no paramagnetic states exist and that the stopped muons are at equivalent sites having a gaussian distribution of B_z the component of the local field along the main applied field $\mathbf{B}_0 = B_0 \hat{z}$, and perpendicular to the muon polarization with width σ centered about B_0 . In this case, the muon spin precesses at the Larmor frequency so that

$$P(t_j) = \exp\left(-\frac{\sigma^2 t_j^2}{2}\right) \cos(\gamma_\mu B_0 t_j + \phi).$$
(3.3)

During the analysis of many experiments, the histograms from two counters placed symmetrically on opposite sides of the sample are combined to form the asymmetry

²The scintillator/phototube combination is usually called a *counter*.



Figure 3.4: Spin precession of the μ^+ in a transverse field. top: raw histogram. bottom: asymmetry.

(not to be confused with a_e , the experimental decay asymmetry)

$$\mathcal{A}_{12}(t_j) = \frac{N_1(t_j) - \alpha N_2(t_j)}{N_1(t_j) + \alpha N_2(t_j)},$$
(3.4)

where $N_1(t_j)$ and $N_2(t_j)$ are the background-subtracted histograms of counters 1 & 2 and $\alpha = \frac{N_1^0}{N_2^0}$ is the relative normalization. This procedure takes out the muon lifetime. Fig 3.4 (bottom) shows an example of the resulting $\mathcal{A}_{12}(t_j)$ which is proportional to $P(t_j)$, provided the experimental asymmetries of the two counters are approximately equal.

3.3 Muonium

The formation of paramagnetic Mu states in solids is a rather complex phenomenon with many open questions. Nevertheless, if these states do form on a timescale of ≤ 10 ns, they may be readily distinguished by their characteristic precession frequencies in transverse field, by their zero-field oscillations, or indirectly from their decoupling curve (recovery of polarization) in longitudinal field. Although the electronic configuration of Mu in a solid may be quite different from that of the isolated muonium atom, study of the hyperfine levels of muonium in vacuum constitutes an instructive starting point for the discussion of the spin dynamics of the composite muon and electron system.

3.3.1 Hyperfine Levels of Muonium in Vacuum

Consider then the isolated muonium atom, which, as mentioned previously, is very similar to an isolated hydrogen atom. The reduced mass m_* of muonium, defined by

$$1/m^* = 1/m_e + 1/m_\mu$$

is only about 0.5% smaller than that of hydrogen. The binding energy,

$$E = -m^* e^4 / 2\hbar^2,$$

is therefore only slightly less than that of hydrogen. Since the first excited state is > 10 ev away, we need only consider the hyperfine structure of the 1S ground state. In this state the electronic configuration is almost perfectly isotropic and the hyperfine Hamiltonian describing the interaction between muon and electrons spins is given by the Fermi contact term

$$\mathcal{H}_{HF} = A_{\mu} \vec{\sigma}^e \cdot \vec{\sigma}^{\mu}, \qquad (3.5)$$

where $\vec{\sigma}^e$ and $\vec{\sigma}^{\mu}$ are the Pauli spin operators of the electron and muon, respectively. The hyperfine coupling constant, A_{μ} , is given by

$$A_{\mu} = \frac{8\pi\hbar^2}{3} \gamma_e \gamma_{\mu} |\Psi(0)|^2 \,, \tag{3.6}$$

with $\gamma_{\mu}(\gamma_{e})$, the gyromagnetic ratio of the muon (electron). One notes that A_{μ} is proportional to the probability density of the electron at the muon; for isolated muonium, the hyperfine frequency (also called hyperfine parameter) is determined to be,

$$\frac{\omega_0}{2\pi} = \frac{A_{\mu}}{h} = 4463$$
 MHz.

In a magnetic field the Hamiltonian includes the Zeeman terms for the muon and electron. The spin Hamiltonian for muonium becomes

$$\mathcal{H} = -\gamma_e \hbar \vec{\sigma}^e \cdot \mathbf{B} - \gamma_\mu \hbar \vec{\sigma}^\mu \cdot \mathbf{B} + A_\mu \vec{\sigma}^e \cdot \vec{\sigma}^\mu.$$
(3.7)

For a uniform B-field, this Hamiltonian is easily diagonalized. [41,42] Taking the field to be along the z-axis and using a basis

$$\chi_1 = |++\rangle \qquad \chi_2 = |-+\rangle \qquad (3.8)$$

$$\chi_3 = |--\rangle \qquad \chi_4 = |+-\rangle,$$

where the first +(-) refers to the muon spin up (down) along the z-axis, the second similarly to the electron spin, we find the eigenstates

$$|1\rangle = |++\rangle \qquad |2\rangle = \sin\xi |+-\rangle + \cos\xi |-+\rangle \qquad (3.9)$$
$$|3\rangle = |--\rangle \qquad |4\rangle = \cos\xi |+-\rangle - \sin\xi |-+\rangle.$$

The mixing angle ξ is given by

$$\cos \xi = \frac{1}{\sqrt{2}} \left(1 + \frac{x}{\sqrt{1+x^2}} \right)^{\frac{1}{2}},$$

where x is the dimensionless reduced magnetic field, $x = B/B_0$, with $B_0 = A_{\mu}/(\gamma_e + \gamma_{\mu})$. We note that in the high-field limit (Paschen-Back regime), the eigenstates are simply the χ_i 's (3.8) we started with as a basis. The corresponding energy eigenvalues are found to be

$$E_{1} = \frac{A_{\mu}}{4} + \frac{B_{z}}{2}(\gamma_{e} - \gamma_{\mu}) \qquad E_{2} = -\frac{A_{\mu}}{4} + \frac{\sqrt{A_{\mu}^{2} + (\gamma_{e} + \gamma_{\mu})^{2}B_{z}^{2}}}{2}$$
$$E_{3} = \frac{A_{\mu}}{4} - \frac{B_{z}}{2}(\gamma_{e} - \gamma_{\mu}) \qquad E_{4} = -\frac{A_{\mu}}{4} - \frac{\sqrt{A_{\mu}^{2} + (\gamma_{e} + \gamma_{\mu})^{2}B_{z}^{2}}}{2}. \quad (3.10)$$

and are plotted as a function of the reduced magnetic field (a so-called Breit-Rabi diagram) in Fig. 3.5. An unphysical value of $(\gamma_e - \gamma_\mu)/(\gamma_e + \gamma_\mu)$ is used in the diagram in order to show more clearly the relative behaviour of E_1 and E_2 .³

3.3.2 Zero-Field and Transverse-Field µSR of Isotropic Muonium

In the preceding section, the spin eigenvalues and eigenvectors of vacuum muonium in a external magnetic field were given. Greatly simplifying the problem was the assumption that the muonium was in the 1S state, thereby reducing the hyperfine Hamiltonian to an isotropic term $\vec{\sigma}^e \cdot \vec{\sigma}^\mu$ multiplied by a constant, A_μ . We now consider zero or

 $^{^{3}}$ *I.e.*, their crossing at 19 and respective slopes for large. For the true value of (e)(e+), the crossing occurs at 100 and the slopes of 1 and 2 in the high-field limit are nearly identical, making these features difficult to portray graphically.



Figure 3.5: Breit-Rabi diagram of vacuum muonium. The eigenstates are labeled by their energies $E_1 - E_4$; $x = \frac{B}{B_0}$ with $B_0 \simeq 1585G$ for vacuum muonium.
tranverse-field μ SR of muonium characterized by the Hamiltonian of (3.7), leaving A_{μ} unspecified, and referring to the system simply as *isotropic muonium*.⁴

In μ SR one observes the time-dependent muon spin polarization,

$$\mathbf{P}(t) = \langle \vec{\sigma}^{\mu}(t) \rangle. \tag{3.11}$$

As an example, the behaviour of $\mathbf{P}(t)$ in zero-field will be calculated explicitly.

The zero-field case is particularly simple, for in the absence of an external field we can choose the axis of quantization to be parallel to the initial muon polarization, $\mathbf{P}(0)$. The electron is assumed to be unpolarized, therefore the initial state is a mixture of $|++\rangle$ and $|+-\rangle$, each with a population of 50%. The eigenstates in zero field are

$$|1\rangle = |++\rangle \qquad |2\rangle = \frac{1}{\sqrt{2}} (|+-\rangle + |-+\rangle) \qquad (3.12)$$
$$|3\rangle = |--\rangle \qquad |4\rangle = \frac{1}{\sqrt{2}} (|+-\rangle - |-+\rangle).$$

We see that $|++\rangle$ is an eigenstate, hence 1/2 of the polarization does not change with time. The state $|+-\rangle$, however, is a superposition of eigenstates,

$$|+-\rangle = \frac{1}{\sqrt{2}} \left(|2\rangle + |4\rangle\right),$$

and will therefore change with time. We denote the time-dependent spin state for this half of the ensemble by $|\Psi(t)\rangle_{\uparrow\downarrow}$. The time dependence is found by applying the time-evolution operator,

$$|\Psi(t)\rangle_{\uparrow\downarrow} = \mathcal{U}(t)|+-\rangle = \exp\left(-\frac{i}{\hbar}\mathcal{H}t\right)|+-\rangle.$$

Using a basis of eigenstates of the Hamiltonian,

$$\mathcal{U}(t) = \sum_{n} |n\rangle e^{-\mathcal{E}_{n}t} \langle n|,$$

⁴Isotropic muonium states with hyperfine parameters different from that of vacuum are known to exist in semiconductors and insulators e.g. Si, GaAs, diamond, and molecular crystals.[40,39]

thus

$$|\Psi(t)\rangle_{\uparrow\downarrow} = \frac{1}{\sqrt{2}} \left(e^{-E_2 t} |2\rangle + e^{-E_4 t} |4\rangle \right).$$

The time-dependent z-component of the polarization⁵ is given by

$$\begin{split} P_z^{\uparrow\downarrow}(t) &= \langle \sigma_z^{\mu} \rangle &= \langle \Psi(t) | S_z^{\mu} | \Psi(t) \rangle \\ &= \frac{1}{2} \left(\langle 2 | \sigma_z^{\mu} | 2 \rangle + \langle 4 | \sigma_z^{\mu} | 4 \rangle + e^{i\omega_0 t} \langle 4 | \sigma_z^{\mu} | 2 \rangle + e^{-i\omega t} \langle 4 | \sigma_z^{\mu} | 4 \rangle \right), \end{split}$$

using

$$\omega_0 = (E_2 - E_4)/\hbar = \frac{A_\mu}{\hbar}.$$

The action of the operator σ_z^{μ} on the χ_i 's is given by

$$\begin{array}{lll} \sigma_{z}^{\mu} \mid ++ \rangle & = & + \mid ++ \rangle \\ \sigma_{z}^{\mu} \mid +- \rangle & = & + \mid +- \rangle \\ \sigma_{z}^{\mu} \mid ++ \rangle & = & - \mid -+ \rangle \\ \sigma_{z}^{\mu} \mid ++ \rangle & = & - \mid -- \rangle, \end{array}$$

from which we have,

$$\begin{split} &\langle 2|\sigma_z^{\mu} \ |2\rangle = \langle 4|\sigma_z^{\mu} \ |4\rangle = 0, \\ &\langle 2|\sigma_z^{\mu} \ |4\rangle = \langle 4|\sigma_z^{\mu} \ |2\rangle = 1, \end{split}$$

therefore,

$$P_z^{\uparrow\downarrow}(t) = \frac{e^{i\omega_0 t} + e^{-i\omega_0 t}}{2} = \cos(\omega_0 t).$$

The simple result is that this half of the polarization oscillates between +1 and -1 at the hyperfine frequency, $\nu_0 = \omega_0/2\pi$. We note that this back and forth oscillation of P_z is quite different from a 'precession' in the classical sense of a rotating spin, since

⁵It can be shown by a similar calculation that the other components, x and y, remain zero at all times.

no transverse components develope, and consequently is sometimes referred to as the *muonium heartbeat* oscillation.

The time dependence of the muon polarization of isotropic muonium in a tranverse field is calculated following a similar procedure, facilitated by use of the density matrix formalism.[42,39,40] With the initial polarization along the x-axis and the field along the z-axis, the polarization is found to oscillate at four frequencies [39], according to

$$P_{x}(t) = \frac{1}{4} [(1+\delta)\cos\omega_{12}t + (1-\delta)\cos\omega_{14}t + (1+\delta)\cos\omega_{34}t + (1-\delta)\cos\omega_{23}t]$$

$$P_{y}(t) = \frac{1}{4} [-(1+\delta)\sin\omega_{12}t + (\delta-1)\sin\omega_{14}t + (1+\delta)\sin\omega_{34}t + (\delta-1)\sin\omega_{23}t]$$

$$P_{z}(t) = 0,$$
(3.13)

where $\omega_{ij} = (E_i - E_j)/\hbar$, corresponding to transitions between energy levels of the Breit-Rabi diagram (Fig. 3.5), and $\delta = \cos^2 \xi - \sin^2 \xi = x/\sqrt{1+x^2}$.

3.3.3 Anisotropic Muonium

The isotropic hyperfine Hamiltonian of (3.5) is inadequate to deal with the phenomenology of muonium centres found in many crystalline solids. It is necessary to consider an anisotropic Hamiltonian

$$\mathcal{H}_{HF} = \vec{\sigma}^e \cdot \mathbf{A} \cdot \vec{\sigma}^\mu, \qquad (3.14)$$

where \mathbf{A} is now a tensor. This generalization of \mathbf{A} from a scalar to a second rank tensor reflects the fact that the electron spin density distribution around the muon is in general anisotropic, having non-S-wave components. In an external field, the total Hamiltonian now reads

$$\mathcal{H} = -\gamma_e \hbar \vec{\sigma}^e \cdot \mathbf{B} - \gamma_\mu \hbar \vec{\sigma}^\mu \cdot \mathbf{B} + \vec{\sigma}^e \cdot \mathbf{A} \cdot \vec{\sigma}^\mu.$$
(3.15)

In general, the energy eigenvalues of this Hamiltonian have analytic solutions only if the field is applied along one of the pricipal axes (x', y', z') of **A**. For the case of **B** $\parallel \hat{z'}$, the energy eigenvalues as a function of the field are

$$E_{1} = \frac{1}{4} \left[A_{zz} + \sqrt{(A_{xx} - A_{yy})^{2} + 4B_{z}^{2}(\gamma_{e} - \gamma_{\mu})^{2}} \right]$$

$$E_{2} = \frac{1}{4} \left[-A_{zz} + \sqrt{(A_{xx} + A_{yy})^{2} + 4B_{z}^{2}(\gamma_{e} - \gamma_{\mu})^{2}} \right]$$

$$E_{3} = \frac{1}{4} \left[A_{zz} - \sqrt{(A_{xx} - A_{yy})^{2} + 4B_{z}^{2}(\gamma_{e} - \gamma_{\mu})^{2}} \right]$$

$$E_{4} = \frac{1}{4} \left[-A_{zz} - \sqrt{(A_{xx} + A_{yy})^{2} + 4B_{z}^{2}(\gamma_{e} - \gamma_{\mu})^{2}} \right]$$
(3.16)

These energy levels are show as Breit-Rabi diagrams (Fig 3.6) for 3 types of representative hyperfine tensors: isotropic ($A_{xx} = A_{yy} = A_{zz} = \hbar\omega_0$), axially symmetric ($A_{xx} = A_{yy} \neq A_{zz}, A_{zz} = \hbar\omega_0$), and completely anisotropic ($A_{xx} \neq A_{yy} \neq$ $A_{zz}, A_{zz} = \hbar\omega_0$). In all cases, the field is directed along the z'-axis. For these diagrams, the relative values of the unequal elements of **A** are taken to be quite different in order to conveniently show all four energy levels.

As with isotropic muonium, the muon polarization of anisotropic Mu in a transverse field consists of components oscillating at frequencies ν_{12} , ν_{23} , ν_{14} , and ν_{34} , given by the $\Delta m = \pm 1$ transitions between the corresponding energy levels of equations (3.15). However, the amplitudes for the 4 frequency components for anisotropic Mu depend upon the field in a much more complicated way than for isotropic Mu.

Of particular interest is the zero-field behaviour evident in the Breit-Rabi diagrams. For isotropic Mu, one observes only one oscillating component of the muon polarization, at the hyperfine frequency. In contrast, axially symmetric Mu exibits three frequencies (1 relatively low and 2 relatively high), while completely anisotropic Mu results in six frequencies (3 low and 3 high). The zero-field Hamiltonian [equation (3.13)] is invariant with respect to a rotation of the coordinate axes; the frequencies, therefore, will not



Figure 3.6: Breit-Rabi diagrams for (a) isotropic, (b) axially symmetric, and (c) completely anisotropic muonium.

depend upon the direction of the initial muon polarization. For the anisotropic cases, the amplitudes, however, will depend quite strongly on the initial direction of $\mathbf{P}(t)$, in principle allowing a determination of the orientation of the hyperfine tensor with respect to the crystalline axes.

3.4 Spin Relaxation of Muonium: Spin Exchange with Free Carriers

The preceding considerations of the spin dynamics of muonium have neglected relaxation of the muon polarization. In addition to analogous μ^+ relaxation mechanisms⁶ such as (reversible) dephasing due to a distibution of fields or (irreversible) spin transitions due to a fluctuating field, spin relaxation of muonium can occur *via* several other processes. For example, muonium could form with a distribution of hyperfine parameters, giving rise to dephasing similar to that resulting from a distribution of fields. Another possibility would be transitions between muonium states with different hyperfine parameters, which can be viewed as producing a fluctuating effective field at the muon. Still another mechanism, most relevant to the present studies, is due to the interaction of the muonium electron with the electrons of the medium.

3.4.1 Spin Exchange Relaxation

A spin-independent interaction V, such as the Coloumb repulsion between two electrons, combined with the exclusion principle, leads to a so called exchange interaction in the Hamiltonian for the two electrons of the form [43]

$$\mathcal{H}' = 2J\vec{\sigma}^1 \cdot \vec{\sigma}^2,\tag{3.17}$$

⁶Here we are referring to a + experiencing only the Zeeman interaction with the local magnetic field.

describing a spin-spin interaction between electrons 1 and 2. This term is proportional to J, the overlap integral, which is

$$J = -\int \Psi_{ab}^* V \Psi_{ba} d^3 \mathbf{x}_1 d^3 \mathbf{x}_2 = -\int \Psi_{ba}^* V \Psi_{ab} d^3 \mathbf{x}_1 d^3 \mathbf{x}_2, \qquad (3.18)$$

where

$$\Psi_{ab}(\mathbf{x}_1, \mathbf{x}_2) = \Psi_a(\mathbf{x}_1)\Psi_b(\mathbf{x}_2). \tag{3.19}$$

Here Ψ_a and Ψ_b are energy eigenfunctions for a single electron with energies E_a and E_b , respectively.

With one of the electrons the Mu-electron, and the other a Bloch electron of the solid, we can treat \mathcal{H}' as a brief, time-dependent perturbation to the muonium spin Hamiltonian of equation (3.7), and find that \mathcal{H}' induces spin-exchange transitions between the two electrons:

$$|++\rangle_{Mu}|-\rangle_{e} \iff |+-\rangle_{Mu}|+\rangle_{e}$$
$$|--\rangle_{Mu}|+\rangle_{e} \iff |-+\rangle_{Mu}|-\rangle_{e}.$$
(3.20)

These spin-exchange transitions only involve spin flips of the muonium electron, yet the also affect the muon spin to which it is coupled. A number of authors have evaluated the resulting time evolution of the muon polarization upon the phenomenological inclusion of electron spin relaxation, spin-exchange being one possible mechanism. [44,45,46,47,48] We summarize the results for longitudinal and transverse fields in the limiting cases of fast and slow ν , the spin exchange rate.

Longitudinal Field: For fast spin-exchange, $\nu \gg \omega_0 (1 + x^2)^{\frac{1}{2}}$, the time dependence of the μ^+ polarization[45,46] is

$$P_z^{\mu}(t) \simeq \exp(-t/\tau_1), \qquad (3.21)$$

where

$$\tau_1 = 4\nu/\omega_0^2. \tag{3.22}$$

That is, the muon polarization is exponentially damped at a rate which is independent of the strength of the applied field, but that *decreases* with *increasing* ν . Qualitatively, this reflects the weakening of the hyperfine coupling of the electron and muon spin by the large spin-flip rate; the muon behaves more as if it were 'free'.

For slow spin-exchange, $\nu \ll \omega_0(1+x^2)^{\frac{1}{2}}$, one finds from equation (7.80) from Schenck[39], that

$$P_z^{\mu}(t) = \frac{1+2x^2}{2(a+x^2)} \exp\left(-\frac{\nu}{1+x^2}t\right) + \frac{1}{4(1+x^2)} \exp\left(-\frac{(3+4x^2)\nu}{2(1+x^2)}t\right) \\ \times \left(2\cos\omega_0(1+x^2)^{1/2}t + \frac{(5+8x^2)\nu}{\omega_0(1+x^2)^{3/2}}\sin\omega_0(1+x^2)^{1/2}t\right)$$

Averaging over the high frequency oscillating terms, which are unresolved in conventional experiments, we have

$$P_z^{\mu} = P_0 \exp(-t/\tau_2) \tag{3.23}$$

with $\tau_2 = (1 + x^2)/\nu$ and

$$P_0 = \frac{1+2x^2}{2(1+x^2)}.$$
(3.24)

We see that for $x \to 0$, the muon spin relaxes at the electron spin-exchange rate. For increasing x, however, the decoupling of the electron and muon spin reduces the muon spin relaxation rate. This effect provides an enormous practical advantage for longintudinal field measurements of ν . One can select the strength of the applied field in order to place the relaxation rate in the range convenient for μ SR measurements (*i.e.* 0.1 to 10 μ s⁻¹). For example, if ν is strongly dependent on the temperature, one can choose the appropriate field for the temperature range of interest. **Transverse Field:** Again we consider the two limits of fast and slow spin exchange. For fast spin-flipping, [42] $\nu \gg \omega_0 (1 + x^2)^{\frac{1}{2}}$,

$$\tilde{P}^{\mu} \equiv P_x^{\mu} + i P_y^{\mu} \simeq \exp\left[\left(-i\omega_{\mu} - \frac{1}{\tau_1}\right)t\right], \qquad (3.25)$$

where τ_1 is the same as in equation (3.21). As in longitudinal field, the muon polarization relaxes at a rate inversely proportional to ν , and the muon behaves as if it were a 'free' muon precessing at the Larmor frequency, ω_{μ} . For a slow spin-flip rate, $\nu^2 \ll (\omega_0/2)^2 x^4$, Gurevich *et al.*[49] have calculated the *x*-component of the μ^+ polarization. Neglecting the usually unobserved terms with frequencies ω_{14} and ω_{24} , their result is

$$P_x^{\mu} = \frac{1}{2} \exp(-t/\tau_3) \left[\left(\cos \Omega_{\gamma} t + \frac{\Omega \sin \Omega_{\gamma} t}{3\tau_3 \Omega_{\gamma}^2} \right) \cos \omega_- t + \left(\frac{2\omega_+ \Omega^2}{\omega_0 \Omega_{\gamma}^2} \right) \sin \Omega_{\gamma} t \sin \omega_- t \right]$$
(3.26)

where

$$\begin{split} \omega_{-} &= \frac{1}{2}(\omega_{12} + \omega_{23}) = \frac{1}{2}(|\omega_{e}| - |\omega_{\mu}|) \\ \omega_{+} &= \frac{1}{2}(|\omega_{e}| + |\omega_{\mu}|) \\ \Omega &= \frac{1}{2}(\omega_{23} - \omega_{12}) = \frac{1}{2}\omega_{0}[(1 + x^{2})^{\frac{1}{2}} - 1], \end{split}$$

and the ν -dependent beat frequency is

$$\Omega_{\gamma} = \Omega (1 - \nu^2 / 4\Omega^2)^{\frac{1}{2}}.$$

The exponential damping of the precession signal is given by

$$\tau_3 = 2/3\nu. \tag{3.27}$$

For small fields (≤ 10 G), where $\omega_{12} \simeq \omega_{23} \equiv \omega_{Mu}$, P_x^{μ} is given simply by

$$P_x^{\mu} = \frac{1}{2} \exp(-t/\tau_3) \cos \omega_{\rm Mu} t.$$
 (3.28)

3.4.2 Temperature Dependence of the Spin-Exchange Rate

We have seen in the last section that spin-exchange interactions give rise to an exponential relaxation of the muonium signal. For a given ν , the time evolution of the muon polarization in a longitudinal or transverse field is known. We now consider what factors determine ν and in particular we calculate the temperature dependence of ν for two simple band structures: (1) a partially-filled band at T=0, *i.e.* a *metal*, and (2) a filled band at T=0, above which is a conduction band separated by a gap E_g , *i.e.* a *semiconductor*.

The spin-exchange rate can be written as

$$\nu = \mathcal{W}_{k\uparrow,\downarrow} f(E_{k\uparrow}) \left[1 - f(E_{k\downarrow}) \right], \qquad (3.29)$$

where $W_{k\uparrow,\downarrow}$, the transition probability per unit time for an electron of wavevector **k** and spin \uparrow to be scattered to a state with wavevector **k'** and spin \downarrow , is multiplied by the probability $f(E_{k\uparrow})$ of finding the state $|\mathbf{k},\uparrow\rangle$ occupied and by the probability $\left[1-f(E_{k\downarrow})\right]$ of finding the state $|\mathbf{k}',\downarrow\rangle$ empty. From perturbation theory, we have that

$$W_{k\uparrow,\downarrow} = \frac{2\pi}{\hbar} |\langle \mathbf{k}, + |\mathcal{H}'|\mathbf{k}', - \rangle|^2 \delta(E_{k\uparrow} - E_{k\downarrow} - \frac{A_{\mu}}{2}) = \frac{8\pi}{\hbar} J^2 \delta(\mathbf{k} - \mathbf{k}') \delta(E_{k\uparrow} - E_{k\downarrow} - \frac{A_{\mu}}{2}).$$
(3.30)

With this, we can convert the sum over \mathbf{k}, \mathbf{k}' in equation (3.28) to an integral over initial and final state energies of the electron,

$$\nu \propto \frac{8\pi}{\hbar} J^2 \int \int \rho(E_{k\uparrow}) \rho(E_{k\downarrow}) f(E_{k\uparrow}) \left[1 - f(E_{k\downarrow}) \right] \delta(E_{k\uparrow} - E_{k\downarrow} - \frac{A_{\mu}}{2}) dE_{k\uparrow} dE_{k\downarrow},$$

where ρ is the density of states (DOS). Ignoring the Zeeman hyperfine energy $A_{\mu}/2$, we have

$$\nu \propto \frac{8\pi}{\hbar} J^2 \int \rho^2(E) f(E) \left[1 - f(E)\right] dE.$$
(3.31)

Thus the entire temperature dependence comes from the Fermi distribution function f(E) in the above integral which we evaluate for the two cases mentioned above.

Temperature Dependence of ν in a Metal: In this case, f(E)[1 - f(E)] is large only within about kT of E_f . Since $kT \ll E_f$, we can pull $\rho(E)$ out of the integral, evaluating it at E_f . We also notice that

$$f(E)[1-f(E)] = -kT\frac{df}{dE},$$

so that

$$u \propto \frac{8\pi}{\hbar} J^2 \rho^2(E_f) kT \int_0^\infty \left(-\frac{df}{dE}\right) dE$$

and thus

$$\nu \propto \frac{8\pi}{\hbar} J^2 \rho^2(E_f) kT.$$
(3.32)

Not surprisingly, this result is very similar to Korringa relaxation in NMR where the relaxation rate is found to be proportional to the temperature and the square of $\rho(E_f)$. [50,51]

Temperature Dependence of ν in a Semiconductor: In a semiconductor the Fermi level lies somewhere between the valence and conduction bands. The actual value of E_f is determined by the 'law of mass action' which simply states that the number of electrons excited into the conduction band is equal to the number of holes in the valence band.[52] To find the spin-exchange rate, the integral of equation (3.30) is split into two parts representing the contribution of electrons in the conduction band and that of the holes in the valence band. Omitting the details of the calculation, the two parts are found to be equal; for $kT \ll E_g$, we find that

$$\nu \propto \frac{16\pi}{\hbar} J^2 \rho(E_c) \rho(E_v) kT \exp\left(-\frac{E_g}{2kT}\right), \qquad (3.33)$$

where $\rho(E_c)$ is the density of states (DOS) evaluated at the bottom of the conduction band E_c , and $\rho(E_v)$ is the DOS evaluated at the top of the valence band E_v . In this derivation we assume that the exchange integrals for the conduction electrons and the holes are the same, *i.e.* $J_{el} = J_{hole} = J$, which might be expected if the wavefunctions of the conduction and valence bands are the same. In general, this will not be so, hence the overall constant of proportionality will be different. We have also assumed that the energy level of the bound muonium electron does not lie in the gap. If this were the case, additional relaxation from the process Mu + hole $\rightarrow \mu^+ \rightarrow Mu$ + hole would be observed. This type of charge-exchange relaxation—quite similar to spin-exchange relaxation—is negligible if the bound state energy of the electron is far below the Fermi level.

Throughout this discussion of spin-exchange relaxation, we have tacitly assumed the existence of muonium states in metals and semiconductors. While muonium is observed in many semiconductors, its formation in metals is usually inhibited by screening of the positive charge by electrons at the fermi surface. The metallic phase A_3C_{60} presents an interesting exception in that screening may not be possible inside the large cavity of the C_{60} molecule. In fact, muonium in Rb₃C₆₀ has recently been observed[53] confirming this notion. In the next chapter we present results showing spin-exchange relaxation of muonium in other doped fullerites which are found to be semiconducting.

Chapter 4

Results and Discussion

4.1 Muonium States in Solid C₆₀

Previous μ SR experiments show that positive muons stopped in solid C₆₀ form two distinct paramagnetic centres.[3] In addition to a small diamagnetic fraction (~ 2%), these two centres are easily distinguished in a field of ~ 100G. The Fourier transform of data taken at 5 K (Fig 4.1) shows a doublet with a comparitively narrow linewidth centered around 150 MHz and two much broader lines near 90 MHz and 240 MHz. The field dependence of the frequencies of these lines allows us to attribute the doublet to the ν_{12} and ν_{23} transitions of a muonium state with a hyperfine (hf) parameter of 4341 ± 24 MHz—remarkably close to that of vacuum muonium (4463 MHz). Similarly, the much broader lines are ascribed to the ν_{12} and ν_{34} transitions of a paramagnetic state, in which the isotropic part of the hyperfine interaction Tr[A]/3 is equal to 325 MHz at room temperature (at 5K it is 332 MHz). This is typical of a muonium-substituted radical.[54] From the respective asymmetries of these two signals, we can estimate the relative fractions of implanted muons which form these states: $12\pm2\%$ for the 4341 MHz signal and $60\pm10\%$ for the 325 MHz signal. The explanation then, based soley upon these considerations, is that the signal with the vacuum-like hf parameter of 4341 MHz is due to endohedral muonium (*i.e.* Mu inside the buckyball cage, denoted $Mu@C_{60}$), while the the 325 MHz signal is due to muonium bonded exohedrally to the carbon cage ($C_{60}Mu^{-}$).



Figure 4.1: The Fourier power spectrum of μ SR in C₆₀ at 100G and 5K. The doublet centred at 150 MHz is from the ν_{12} and ν_{23} transitions of Mu@C₆₀, the two broad lines at 90 and 240 MHz are the ν_{12} and ν_{34} transitions of C₆₀Mu[·].

As discussed in chapter 3, the hyperfine parameter is proportional to $|\psi_e(0)|^2$. With a hf parameter close to that of vacuum, the spin density of the electron of the 4341 MHz centre is not greatly altered with respect to vacuum. This indicates a very small interaction with the buckyball carbons. The 325 MHz centre, on the other hand, indicates a much stronger interaction with the carbon cage. It is typical of a positive muon in a covalent bond, forming what is known as a muonated radical. Since carbon prefers a tetrahedral bonding scheme, we expect that the curvature of the C₆₀ molecule makes the radical more likely to form on the outside of the C₆₀ cage. This notion is supported by theoretical calculations of the potential energy surfaces of C₆₀H [55,56], which show that the most stable configuration has the H attached to one C atom on the outside of the buckyball.

We can see that this picture agrees with the observed fractions by the following argument. Suppose all of the implanted muons stopping inside of a buckyball form $Mu@C_{60}$ while those stopping outside form $C_{60}Mu$. The ratio of the formation fractions then would follow from volume considerations and be simply the packing fraction of the C_{60} lattice. Due to the large distance between C_{60} molecules, the packing fraction is much smaller than that of the close-packed fcc lattice ($f_{fcc}=0.74$). Using a diameter of 7.1 Å for the C_{60} molecule and a lattice constant of 14.04 Å, one finds the packing fraction to be 0.27. This implies that $C_{60}Mu$ should form 3.7 times as often as $Mu@C_{60}$ whereas the observed ratio is 5. The difference is easily explained by supposing that the muon must overcome some potential barrier to get inside the C_{60} cage.

Experimental results discussed in this thesis show that the $C_{60}Mu^{-}$ signal is much more sensitive the to the C_{60} molecular dynamics than $Mu@C_{60}$. Along with the observation of $Mu@C_{60}$ in the doped fullerites, this supports the basic picture of the two centres presented above. Recently Prassides *et al.* [57] has reported the observation of $Mu@C_{70}$ and use its zero-field μ SR oscillations to study the molecular dynamics of the C_{70} molecule.

4.2 The First-Order Phase Transition in C₆₀

We examined a 500-mg sample of high-purity C_{60} powder using the M15 beam line at TRIUMF. Conventional transverse-field μ SR data were taken in an applied magnetic field of 1.5 T at 22 temperatures ranging from 5 K up to room temperature. The precession frequencies of Mu@C₆₀ are too high to observe at this field, leaving only the signal from the diamagnetic μ^+ and the C₆₀Mu[·] radical. In a large field only two frequencies of C₆₀Mu[·], the ν_{12} and ν_{34} transitions, have an appreciable amplitude. If the spin Hamiltonian of C₆₀Mu[·] were isotropic, they would depend appoximately upon the field as

$$\nu_{12} \simeq \frac{\gamma_{\mu}B}{2\pi} - \frac{A_{\mu}}{2h}$$

$$\nu_{34} \simeq \frac{\gamma_{\mu}B}{2\pi} + \frac{A_{\mu}}{2h},$$
(4.1)

where A_{μ} is the isotropic hyperfine parameter. If the spin Hamiltonian is anisotropic, however, we can use equation (4.1) (substituting A_{zz} for A_{μ}) only if the applied field is along a principal axis of **A**, the hyperfine tensor. For an arbitrary direction \hat{z} of the applied field, these frequencies are [39]

$$\nu_{12} = \left[\left(\frac{\gamma_{\mu} B_z}{2\pi} - \frac{A_{zz}}{2h} \right)^2 + \frac{A_{zx}^2 - A_{zy}^2}{4h^2} \right]^{\frac{1}{2}}$$

$$\nu_{34} = \left[\left(\frac{\gamma_{\mu} B_z}{2\pi} + \frac{A_{zz}}{2h} \right)^2 + \frac{A_{zx}^2 - A_{zy}^2}{4h^2} \right]^{\frac{1}{2}}$$
(4.2)

where the components of **A** are now given in the x, y, z system. If the anisotropy is small (*i.e.* $A_{xx} \simeq A_{yy} \simeq A_{zz}$), the off-diagonal terms will be small. Ignoring them and using the Euler matrices to find A_{zz} in terms of the principal axis components, we have

$$\nu_{12} = \frac{\gamma_{\mu}B_{z}}{2\pi} - \frac{A_{zz}}{2h}$$

$$\nu_{34} = \frac{\gamma_{\mu}B_{z}}{2\pi} + \frac{A_{zz}}{2h},$$
(4.3)

 with

$$A_{zz} = A_{xx} \sin^2 \psi \sin^2 \theta + A_{yy} \cos^2 \psi \sin^2 \theta + A_{zz} \cos^2 \theta.$$
(4.4)

The ψ and θ are two of the standard Euler angles. We see that unless the hyperfine Hamiltonian is isotropic, these frequencies depend on the orientation of the C₆₀Mu[·] with respect to the applied field. From the difference

$$\nu_{34} - \nu_{12} = A_{zz}/h, \tag{4.5}$$

one could determine A_{zz} if every C₆₀Mu[·] had the same orientation. More realistically, this difference would give us \bar{A} , the average of A_{zz} over all possible orientations.

Fig. 4.2 shows the Fourier transform in the frequency range surrounding ν_{12} for data at selected temperatures. At room temperature, the linewidth is quite narrow and comparable to that measured for muonium substituted radicals in liquids.[54] Below $T_0=260$ K, another signal appears at a slightly lower frequency, having a significantly broader linewidth. Between 242 K and 260 K, both signals are present although the amplitude of the higher frequency signal decreases with the temperature and is matched by a corresponding increase of the lower frequency amplitude. Below 242 K, the linewidth of the remaining signal grows steadily with decreasing temperature. At 5 K the lineshape resembles a broad gaussian.

These observations suggest an anisotropic hyperfine interaction for $C_{60}Mu^{-}$ — the broad static linewidth at 5 K is due to the orientational dependence of the transverse field precession frequency. Consider the direction of the applied **B**-field in the principal



Figure 4.2: Frequency spectra near ν_{12} of C₆₀Mu[·] at selected temperatures. The applied field is 1.5T.

axis system of A. The unoriented nature of the crystallites results in a random distribution of this direction.¹ One would expect a powder pattern; however, some additional broadening— probably from a distibution of hyperfine parameters due to the inequivalence of sites with respect to the crystalline axes—effectively produces the gaussian lineshape seen in the Fourier transform at 5 K. At higher temperatures, motional narrowing due to thermally excited rotation of the C₆₀Mu⁻ accounts for the decrease in the linewidth.

Using a rotating-reference-frame (RRF) transformation[58], the data were initially fit to an exponential relaxation function. With the RRF, the two frequencies (ν_{12} and ν_{34}) are estimated independently, while the exponential decay constant, T_2^{-1} , is assumed to be the same for both components of the time signal. We used the estimated frequencies, as prescribed in equation (4.2), to find \bar{A} . Fig. 4.3 shows the temperature dependence of (a) the linewidth, T_2^{-1} , and (b) the average hyperfine parameter, \bar{A} . The first-order phase transition is clearly seen as a discontinuity at T_0 , the ordering temperature, in both the linewidth and \bar{A} .

Below T_0 , the correlation times for reorientation of C₆₀Mu[•] (Fig. 4.3c) were estimated by fitting the data at each temperature using the Abragam relaxation function [59]

$$R(t) = \exp[-\sigma^2 \tau_c^2 (e^{-t/\tau_c} - 1 + t/\tau_c)].$$
(4.6)

The static linewidth parameter $\sigma = 21.2(1.1) \ \mu s^{-1}$ was obtained from the lowest temperature run and held constant for fits of the other runs. The temperature dependence of the correlation time between 200 and 250 K was fit to an Arrhenius law, $\tau_c^{-1} = \Lambda \exp(-E_a/k_B T)$, with $\Lambda = 6.4(2.4) \times 10^{12} \text{ s}^{-1}$ and $E_a = 219(7) \text{ meV}$. At 200 K, $\tau_c = 52(17)$ ns, and agrees quite well with the NMR result [64] of 64 ns for C₆₀.

¹Even for an oriented crystal, the icosahedral symmetry of C_{60} alone would nearly accomplish this.



Figure 4.3: (a) The linewidth T_2^{-1} , (b) the average hyperfine parameter \bar{A} , and (c) the inverse correlation time τ_c^{-1} extracted from simultaneous fits to the ν_{12} and ν_{34} frequencies of the C₆₀Mu⁻ radical in μ SR time spectra taken at 1.5T.

Above T_0 , the lineshape increases with temperature, contrary to what is expected from motional narrowing. Very rapid rotation of the C₆₀Mu⁻ causes electron-spin relaxation, induced by the coupling of the electron spin to the molecular-rotational-angular momentum.[60] For this mechanism, the linewidth can be approximated as

$$T_2^{-1} = \frac{\sigma_{\rm SR}^2 \tau_c}{1 + \omega_e^2 \tau_c^2},\tag{4.7}$$

where $\sigma_{\rm SR}$ is the electron-spin-molecular-rotation coupling constant and $\omega_e = \gamma_e B$. The data above T_0 were fitted to an Arrhenius law using equation (4.3) with $\sigma_{\rm SR} = 4.9(1.0) \times 10^8 \text{ s}^{-1}$, $\Lambda = 5.1(7) \times 10^{12} \text{ s}^{-1}$, and $E_a = 98(16)$ meV. The correlation times above T_0 shown in Fig. 4.3(c) were obtained from the measured linewidth using this fitted value of $\sigma_{\rm SR}$. At 300 K, $\tau_c = 8.5(2.0)$ ps, also in good agreement with NMR results.[14,65]

The discontinuity in \bar{A} at T_0 shows that the electronic structure of $C_{60}Mu^{\circ}$ also changes abruptly at the phase transition. Most likely, this reflects a shift in the C-Mu bond length. Since the lattice constant decreases only by a small amount (0.044 Å)[5]at T_0 , we suggest that the electronic structure depends upon the molecular dynamics of $C_{60}Mu^{\circ}$. The shift of \bar{A} could reflect a change in the motion of $C_{60}Mu^{\circ}$ -from one characterized by jumping between orientations with nearly equivalent potential minima to one involving quasi-free rotation.

Along with the sharp behaviour of T_2^{-1} at T_0 , the discontinuity of \bar{A} is suggestive of a first-order transition. The observation of coexistence of both phases just below T_0 supports this hypothesis. Because of defects, impurities or finite size effects, the individual crystallites may have slightly different transition temperatures, or part of the high-T phase may be pinned upon cooling. If the transition were of a higher order, one would expect an additional broadening of the lineshape just below T_0 , the result of a distribution of \bar{A} 's, rather than two distinct signals. Additional details concerning this work were reported by Kiefl et. al. [61]

4.3 C₆₀ in Zero Field

Analysis of the transverse-field data, described in the last section, led us to postulate an anisotropic hyperfine interaction for $C_{60}Mu^{\cdot}$. The details of the anisotropy, however, are not evident from the transverse-field results. Is the hyperfine tensor of $C_{60}Mu^{\cdot}$ axially symmetric or completely anisotropic? How large is the anisotropy? (*I.e.* how large are the relative differences between the principal axis components of A?) Zero-field (ZF) μ SR provides the answers to these questions as well as giving us another handle on the molecular dynamics of $C_{60}Mu^{\cdot}$.

As noted in chapter 3, an axially symmetric spin Hamiltonian will exhibit three transition frequencies in the ZF spectrum—two high (singlet-triplet transitions) and one low (inter-triplet transition) —for a small anisotropy. A completely anisotropic spin Hamiltonian, on the other hand, will show six—three high and three low—for a small anisotropy. Furthermore, these frequencies will not depend upon the orientation of the paramagnetic centre. A distribution of orientations thus will not lead to relaxation due to dephasing, it will affect only the overall *amplitude* of the signal at each frequency.

Fig. 4.4 shows the zero-field μ SR spectrum in C₆₀ at 9 K. At this temperature, the orientational motion of the C₆₀ molecules is frozen. Three low frequency oscillations characteristic of a completely anisotropic hyperfine interaction are clearly seen in the time and Fourier spectra. They lie on top of a very low frequency (~ 0.07 MHz) background. The unresolved (from one another) high frequency oscillations appear as a single broad component in the first 50 ns of the time spectrum (see inset). The magnitudes of the three low frequencies, 1.2(.1) MHz, 7.4(.1) MHz and 8.6(.1) MHz, are a direct measure of the hyperfine anisotropy. Comparing these to the high frequency

of 332.5(.8) MHz tells us that the anisotropy is small.

Using equations (3.16) one finds

$$\nu_{12} = (A_{zz} - A_{yy})/2h$$

$$\nu_{13} = (A_{yy} - A_{xx})/2h$$

$$\nu_{23} = (A_{zz} - A_{xx})/2h.$$
(4.8)

We denote the measured low frequencies, in increasing magnitude, ν_1 , ν_2 , and ν_3 . Taking $A_{xx} < A_{yy} < A_{zz}$, we can unambiguously assign ν_3 to ν_{23} ; however, we can't say whether $\nu_1 = \nu_{12}$ or ν_{13} (similarly for ν_2). This prevents us from finding the actual components of the hyperfine tensor. The high frequency, $\bar{\nu}$, should be the average of ν_{14} , ν_{24} , and ν_{34} , *i.e.*

$$\bar{\nu} = \frac{\nu_{14} + \nu_{24} + \nu_{34}}{3} = \frac{A_{xx} + A_{yy} + A_{zz}}{3h} \equiv \frac{\langle A \rangle}{h}.$$
(4.9)

The result is $\langle A \rangle / h = 332.5$ (.8) MHz, in good agreement with the high-TF data. In order to unambiguously determine the principal components of **A**, one would have to measure the field-dependence of the low frequencies for small applied magnetic fields in aligned single crystals of C₆₀. We can, however, give the fractional anisotropies $\langle \delta A / \langle A \rangle$) along the principal axes: 0.036(3), 0.223(3), and 0.259(3). Interestingly, the low frequencies are close to those observed in single crystal α -quartz,[62,63] but since $\langle A \rangle / h \simeq 4500$ MHz for quartz, these anisotropies are more than 100 times larger than for quartz.

At 9 K the low-frequency signals have an exponential relaxation rate, $\lambda \simeq 1.0 \ \mu s^{-1}$, presumably due to slightly inequivalent sites. At higher temperatures, thermallyactivated 'ratcheting' of C₆₀Mu' contributes to an addition relaxation. The fitted relaxation rate is plotted as a function of temperature in Fig. 4.5. Assuming that the increase in the relaxation rate is proportional to the 'hop' rate of C₆₀Mu', we extract



Figure 4.4: $C_{60}Mu^{\cdot}$ in zero field: (a) time spectrum with the inset showing the first 50 ns; (b) frequency spectrum.

from a fit to an Arrhenius dependence an activation energy $E_a = 200(20)$ meV. This value agrees very well with $E_a = 219(7)$ meV determined from the transverse-field data.

As mentioned above, there is a background in the data which appears to be an oscillation at a very low frequency. The frequency is temperature dependent, decreasing from 0.07(.01) MHz at 9 K to 0.02(.01) MHz at 200 K; at room temperature it disappears altogether or is too small to measure. An interesting possibility is that this may come from Mu@C₆₀ as the result of its own weakly anisotropic hyperfine interaction. However, it would be premature to conclude this from the present data. Prassides *et al.* [57] report zero-field μ SR in C₇₀ and argue that the low-frequency oscillations seen below 270 K are from Mu@C₇₀ with an anisotropic hyperfine interaction.

4.4 Endohedral Muonium in the Fullerites

The temperature dependence of the signal characterized by a 4341 MHz hyperfine frequency in pure C_{60} is less dramatic than that of the C_{60} Mu[·] radical (see Fig. 4.6). Above 230 K and across the phase transition, its frequency and relaxation rate remain essentially constant. If this signal is from Mu@C₆₀ with an isotropic hyperfine interaction, the dominant source of line broadening expected at the lowest temperatures would be the weak dipolar interaction with naturally abundant $(1.1\%)^{13}$ C nuclei. The measured relaxation rate as $T \rightarrow 0$ is about twice that expected from a simple calculation of the rms width of nuclear dipolar fields at the center of the C₆₀ molecule. This may indicate an additional effect due to the zero-point motion of the muonium or the extended nature of the muonium electron. Alternatively, the hyperfine interaction may have a slight anisotropy, as hypothesized in the previous section. Above 100 K, the decreasing linewidth is consistent with with motional averaging of either the anisotropic nuclear dipole interaction or any hyperfine anisotropy, resulting from rapid



Figure 4.5: Temperature dependence of λ , the relaxation rate of C₆₀Mu⁻ hyperfine oscillations in zero applied field. The solid line is a fit to an Arrhenius dependence giving a activation energy of 200(20) meV.



reorientation of the C_{60} cage.

Figure 4.6: Temperature dependence of the linewidth T_2^{-1} of the TF- μ SR signal from Mu@C₆₀ in pure C₆₀ in an applied field of 100 G.

We also observe muonium centres with vacuum-like hyperfine parameters in K_4C_{60} , K_6C_{60} and Rb_6C_{60} . Fig 5.7 shows the Fourier transforms of the μ SR spectra for K_4C_{60} and K_6C_{60} at 5 K in transverse fields of ~ 100 G. In these doped fullerites, most of the implanted muons form a diamagnetic centre and the $C_{60}Mu^{\cdot}$ radical is conspicuously absent (compare Fig. 4.7 with Fig. 4.1). As in pure C_{60} , the two observed frequencies correspond to transitions between the spin-triplet states of Mu. The sum of the two frequencies $\nu_{12} + \nu_{34} = \gamma_e B/2\pi$ is approximately the Larmor frequency of a free electron. Their difference provides a measure of $A_{\mu}[40]$:

$$A_{\mu} = \frac{h}{2} \left[\frac{(\nu_{12} + \nu_{23} + 2\nu_{\mu})^2}{\nu_{23} - \nu_{12}} + \nu_{12} - \nu_{23} \right], \qquad (4.10)$$

where the Larmor frequency of the muon $\nu_{\mu} = \frac{\gamma_{\mu}}{2\pi} B$ (where $\frac{\gamma_{\mu}}{2\pi} = .01355342 \text{ MHz/G}$), is used to determine the field. The estimates of A_{μ} obtained with this equation are given in Table I.

The observation of Mu in the alkali-metal-doped fullerites leaves no doubt to the hypothesis that this muonium is endohedral. The magnitudes of A_{μ} for Mu in the doped fullerites are similar to that of Mu in pure C_{60} — and only a few percent less than that of Mu in vacuum—indicating a weak interaction with the C_{60} lattice. Given that the $A_x C_{60}$ solids are essentially ionic compounds of A^+ and C_{60}^{-x} , an endohedral site for Mu is likely to be the most stable. The absence of the C_{60} Mu radical is presumably due to the weakening of the covalent C-Mu bond resulting from the addition of electrons upon forming the C_{60}^{-x} ion. Estreicher *et al.* argue that the stability of $C_{60}H^{x-}$ (here H refers to hydrogen or muonium) is maximum for x=0 and decreases with increasing x [55]. The formation fractions for Mu in $A_x C_{60}$ are somewhat less than that in pure C_{60} (see Table I). This might be due to the electrostatic repulsion between the implanted μ^+ and the charged C_{60}^{-x} ion.

While we might have expected to find Mu@C₆₀ in K₆C₆₀ and Rb₆C₆₀, which are predicted to be semiconductors with gaps of ~0.5 eV,the observation of Mu@C₆₀ in K₄C₆₀ is somewhat surprising. According to the simple band model described in chapter 2, K₄C₆₀ should be metallic. Consequently, we would expect that spin exchange with free carriers would preclude the observation of Mu spin precession—either by extreme line broadening or (for larger carrier concentrations) by effectively decoupling the muon and electron spins, allowing simple μ^+ precession in the fast spin-exchange limit. Using equations (3.32) and (3.33), we can get an idea of the spin-exchange enhancement upon



Figure 4.7: μ SR frequency spectra for (a) K₄C₆₀ and (b) K₆C₆₀. The line at 150 MHz in the top spectrum is from the TDC.

going from a semiconductor to a metal. Assuming the same density of states, the metal would have a spin-exchange rate which is larger by a factor of roughly $\exp(E_g/2kT)$. At T=5 K and for $E_g = 0.5$ eV, this factor is e^{600} (> 10^{260})! Apparently K₄C₆₀, like K₆C₆₀ and Rb₆C₆₀, is insulating at low temperatures.

The temperature dependence of the Mu@C₆₀ linewidths reveals that all have a similar band structure: they are all semiconductors with relatively small bandgaps. Fig. 4.8 shows the T_2^{-1} linewidth parameter obtained by fitting the μ SR time spectra to an exponential decay of the muonium precession amplitude $R(t) = \exp(-t/T_2)$. The data were taken using an applied field of ~5 G. Recall that in a low applied field $\nu_{12} = \nu_{23}$, so the full muonium amplitude precesses at the same frequency. The fact that we see muonium spin precession at all tells us that the spin-exchange rate ν is slow and hence $T_2^{-1} \propto \nu$ [see equation (3.28)]. Indeed, with the addition of a constant background term λ_0 , the linewidth T_2^{-1} for all three fullerites exhibits the exponential temperature dependence expected for a semiconductor (equation 3.33). We estimate the bandgaps from a fit to the function

$$T_2^{-1} = \alpha kT \exp(-E_g/2kT) + \lambda_0.$$
(4.11)

The estimated bandgap E_g , prefactor α and background relaxation λ_0 for the three solids are given in Table I.

Our results for K_4C_{60} conflict with the simple band-structure model of doped fullerites. In this model, the four added electrons partially fill the bands formed from the triply degenerate t_{1u} molecular orbitals. Consequently, K_4C_{60} is predicted to be metallic. We must conclude that some mechanism splits the degeneracy of the t_{1u} orbitals resulting in a filled band for x=4. Alternatively, electron-electron interactions may be responsible for the insulating behaviour. Although there is a large statistical uncertainty in the measured gaps, our data suggest that the gap in K_4C_{60} is larger



Figure 4.8: T_2^{-1} linewidths for Mu@C₆₀ in (a) K₄C₆₀, (b) K₆C₆₀, and (c) Rb₆C₆₀.

than that of K_6C_{60} . The gap in K_6C_{60} is presumably the difference between the t_{1u} and the next higher t_{1g} orbitals. NMR results on Rb_4C_{60} show a non-Korringa-like and strongly temperature dependent T_1T , also indicative of a non-metal.[26]

The parameters for Rb_6C_{60} are noticeably different than those of $K_4\text{C}_{60}$ and $K_6\text{C}_{60}$. The energy gap is about $\frac{1}{3}$ that of either $K_4\text{C}_{60}$ or $K_6\text{C}_{60}$. Also the prefactor α , which is related to the DOS (equation 3.33), is much smaller and λ_0 is much larger for Rb_6C_{60} . The enhanced background relaxation λ_0 of Rb_6C_{60} may come from a contribution to λ_0 from the dipolar fields of the alkali ions—in $A_6\text{C}_{60}$ each C_{60} is surrounded by 24 A ions. In this case, λ_0 would scale with the magnetic moment, which for rubidium is ~ 3.4 times that of potassium.

The estimates of α and E_g for Rb₆C₆₀ also disagree with the simple band picture. With a larger lattice constant and hence smaller hopping amplitude, Rb₆C₆₀ should have a smaller bandwidth. Consequently, we would expect it to have both a higher density of states and a slightly larger bandgap in comparison to K₆C₆₀. Our results show both a much smaller bandgap and a reduction in the density of states. The statistical uncertainties for the Rb₆C₆₀ may be underestimated, however, as one can fit the data with an α and E_g similar to that of K₄C₆₀ and K₆C₆₀ without a significant increase in the χ^2 /degrees of freedom (0.6 versus 1.2).

The results for K_4C_{60} and K_6C_{60} along with additional details concerning these experiments were previously reported by Kiefl *et al.*[66]

Table 4.1: Fraction of injected muons which form a diamagnetic center (f_D), muonium (f_{Mu}) or radical (f_R) at 5K. A_{μ} is the the muon-electron hyperfine parameter of muonium and α , E_g , and λ_0 are fitted parameters defined in Eqn. 4.11.

(-g)							
	f_D	f_{Mu}	$\mathbf{f}_{\mathbf{R}}$	A_{μ}	α	E_g	λ_0
	(%)	(%)	(%)	(MHz)	$(eV^{-1}s^{-1})$	(eV)	(μs^{-1})
C ₆₀	2(5)	12(2)	60(10)	4341(24)			-
K_4C_{60}	68(5)	7(2)	_	4342(66)	$3.8(5) imes 10^{7}$	0.40(20)	1.20(6)
K_6C_{60}	69(5)	6(2)		4230(63)	$1.5(2) \times 10^{8}$	0.35(12)	1.40(10)
$\mathrm{Rb}_6\mathrm{C}_{60}$	81(5)	7(2)	_	_	$4(20) imes 10^3$	0.10(3)	4.30(20)

Chapter 5

Conclusion

The work described in this thesis further characterizes the two muonium centres observed in crystalline C_{60} . Zero-field measurements show that the hyperfine tensor of C_{60} Mu⁻ is completely anisotropic and give a measure of the anisotropy. Low-field measurements on single crystals are needed, however, to unambiguously determine the pricipal components of the hyperfine tensor. Apart from its being vacuum-like, less is known about the hyperfine interaction of Mu@C₆₀; there is some hint that it may also be slightly anisotropic as in the case of Mu@C₇₀.[57]

Transverse-field μ SR of C₆₀Mu[·] provides evidence for the first order nature of the orientational phase transition in solid C₆₀ and shows a change in the rotational dynamics at T_0 , the ordering temperature. Below T_0 , the activation energy for reorientation of C₆₀Mu[·] is independently estimated using the zero-field and the transverse-field data. Both results agree within the given uncertainties.

The observation of coherent spin precession of muonium in pure C_{60} and the several doped fullerites we examined establishes that all are nonmagnetic at low temperatures. Although this aspect of the experimental results was not discussed in this thesis, we can be sure that any electronic moments in these materials would have to be smaller than a fraction of a nuclear magneton since the positive muon alone is capable of detecting moments on this order. In the presence of electronic moments, one would expect an exchange interaction with the Mu electron which would either substantially broaden the Mu lines or greatly alter them. A detailed analysis with some estimate of the exchange interaction could in principle set limits on both static and fluctuating moments at low temperatures.

Finally, we find μ SR of Mu@C₆₀ in the doped fullerites to be sensitive to the electronic band structure. This is a promising avenue for future experiments, although it may prove advantageous to use longitudinal field μ SR at higher temperatures—one could select a convenient value of the applied field for a given temperature range making a detailed study of the gap structures possible. Our results are at odds with the simple band structure model, which predicts metallic behaviour for K₄C₆₀ and similar energy gaps for K₆C₆₀ and Rb₆C₆₀. Perhaps the threefold degeneracy of the t_1u molecular orbitals is lifted in crystalline C₆₀ in such a way as to have a filled shell for 4 added electrons. Another possiblility is that electron-electron interactions are important in this class of materials.

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