Muon Level Crossing Resonance Spectroscopy

An application of a novel magnetic resonance technique

Muons provide a valuable probe of the atomic-level properties of materials. Unique information can be obtained using the technique of Level Crossing Resonance (LCR).

LCR can be used to:

- determine free radical structures by measurement of muon hyperfine coupling constants
- investigate the reactions, molecular dynamics and local environment of free radicals
- study spin dynamics in magnetic systems
- determine muon sites, for example in semiconductors

This leaflet provides examples of how the LCR technique can be used.

A quick introduction to the muon technique

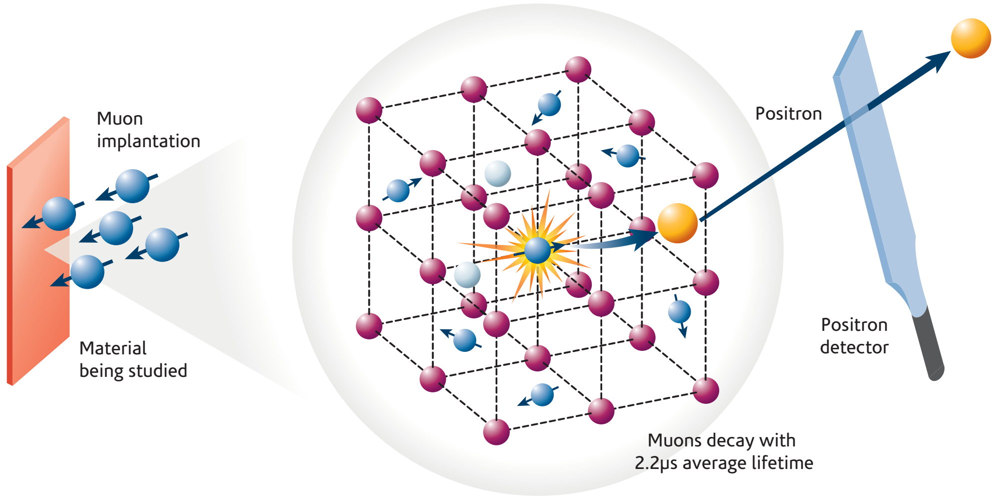
Muon spin resonance spectroscopy is less well known than other spin-spectroscopic techniques such as NMR and EPR, but it provides researchers with an important tool that can be used to study a wide range of problems in physics and chemistry.

The muon technique involves implanting spin-polarised positive muons into a material. Muons are short-lived particles, decaying after an average lifetime of 2.2μs to produce positrons. The decay positrons which emerge from a sample after muon implantation are detected, revealing information about the muons' behaviour inside the material – particularly about how the muon polarisation changed within the sample. This, in turn, this enables us to deduce information about the atomic-level properties of the material.

Muons are very sensitive probes of magnetic systems, often detecting effects that are too weak to be seen by other methods. They also have a wide variety of other applications – for example, in studies of superconductors, molecular systems and chemical reactions, novel battery materials and a variety of organic systems. In some studies, **the positive muon can be thought of as being like a light proton** (muons have a mass of one ninth of the proton mass). Implanted muons will sometimes pick up an electron to form a light isotope of hydrogen called muonium (Mu). By following muon behaviour inside a material we can learn about proton and hydrogen behaviour. This is important in semiconducting materials, proton conductors and hydrogen storage materials.

References on the muon technique include:

- ***Spin polarised muons in condensed matter physics*** *S J Blundell, Contemporary Physics,* ***40*** *(1999) 175*
- ***Implanted muon studies in condensed matter science*** *S F J Cox, J. Phys. C: Sol. Stat. Phys.,* ***20*** *(1987) 3187*
- ***Muon Spectroscopy*** *U A Jayasooriya and R Grinter, Encyclopedia of Applied Physics (2009)*
- ***Muon spin rotation, relaxation and resonance: Applications to condensed matter*** *A Yaouanc, P Dalmas de Réotier, Oxford University Press (2010), ISBN 0199596476*
- ***Using polarized muons as ultrasensitive spin labels in free radical chemistry*** *I McKenzie and E Roduner, Naturwissenschaften,* ***96*** *(2009) 873*



The muon technique – implantation of positive, spin-polarised muons into a sample, followed by detection of positrons emitted when the muons decay.

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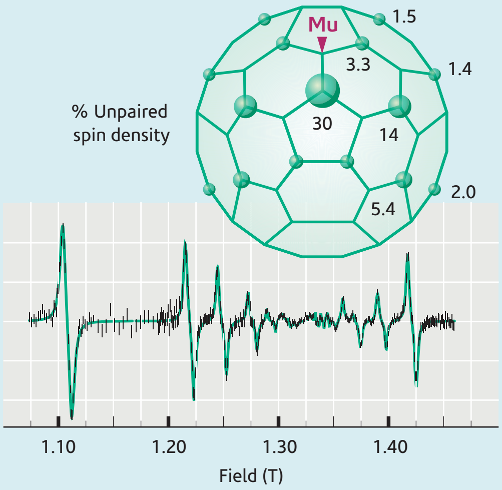
What can LCR tell us about free radicals?

Structure

The structure of a free radical can be inferred from the muon and nuclear hyperfine couplings.

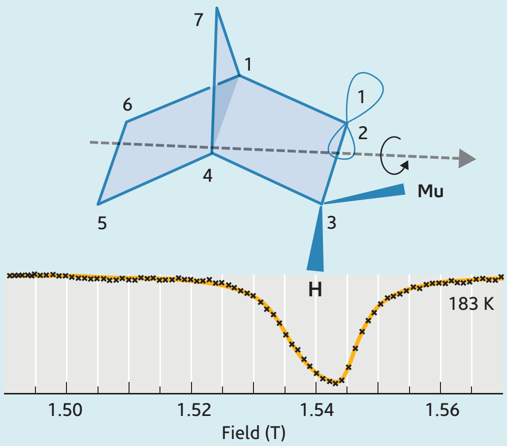


$^{13}C_{60}Mu$ radical. The ^{13}C hyperfine couplings can be determined from the positions of the resonances. They indicate that the unpaired electron is significantly delocalised around the fullerene sphere.

P W Percival et al., Chem. Phys. Lett. ***245*** *(1995) 90*

Molecular dynamics

The resonance lineshape provides information about molecular dynamics in the solid state.

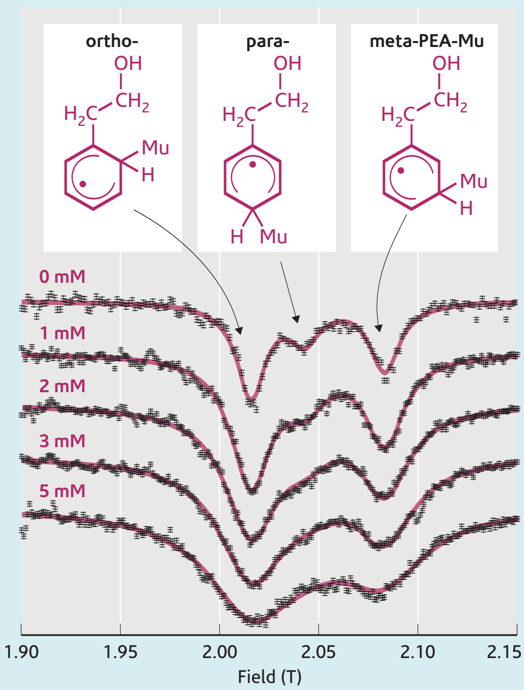


The lineshape indicates that norbornenyl radicals rotate around an axis parallel to C3-C5.

M Ricco et al., Phys. Lett. A ***129*** *(1988) 390; E Roduner et al., Chem. Soc. Rev.* ***22*** *(1993) 337*

Reaction rates

Radical reaction rates can be measured from the broadening of resonances, are a function of reactant concentration.



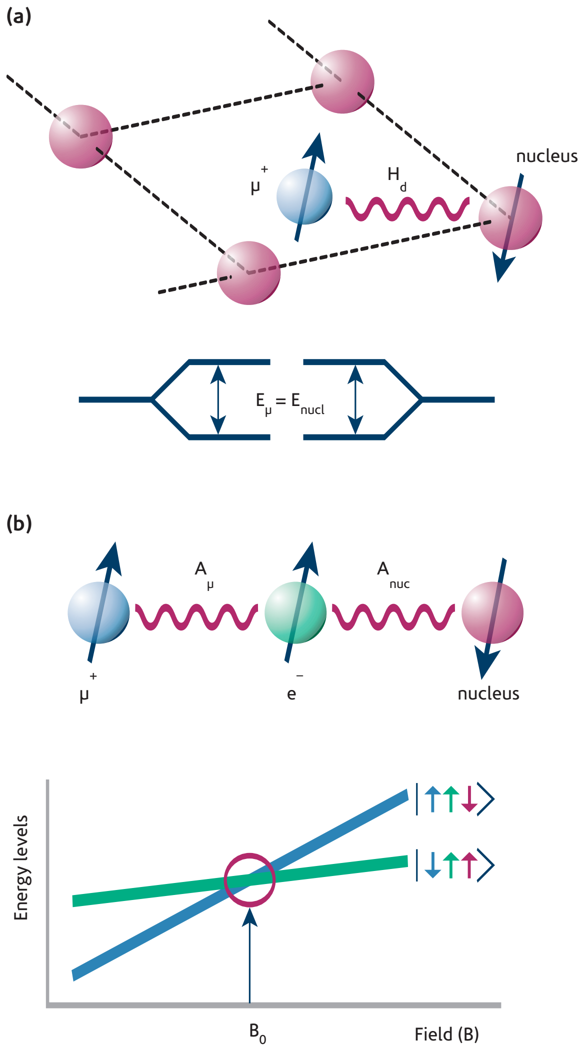
Reaction of cyclohexadienyl radicals with paramagnetic Ni^{2+}.

H Dilger et al, Physica B ***374-375*** *(2006) 317*

Muon LCR: the basic idea

Once implanted inside a material, muons interact with their local atomic environment. This interaction can be particularly strong when an energy level in the muon system matches one within the environment. The muons and their surroundings are then put on ‘speaking terms’, and this can strongly affect the muons’ behaviour.

Such resonances – called level crossing resonances, LCR, (or, sometimes, ‘avoided level crossing resonances’) – between the muons and their environment can be produced by changing the applied magnetic field in a muon experiment. The resonances can be detected by observing the muon polarisation – they are seen as a dip in the polarisation as the applied field is changed. Observation of such resonances gives us additional information about the muons’ atomic environment.



*Level crossing resonances occur when muons are put 'on speaking terms' with their surroundings. This might be directly with neighbouring nuclei via dipole-dipole coupling as in **(a)**, or via hyperfine coupling with an unpaired electron – as found in radical systems – as in **(b)**.*

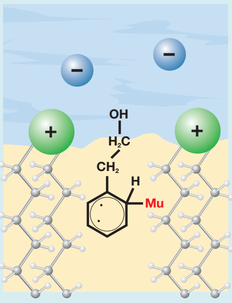
Example applications of LCR

LCR as a probe of soft matter

LCR can be used to determine the local environment and dynamics of co-surfactants present in low concentrations in soft matter structures such as lamellar phases. In the example here, phenylethanol co-surfactants are spin labeled by the addition of muonium.

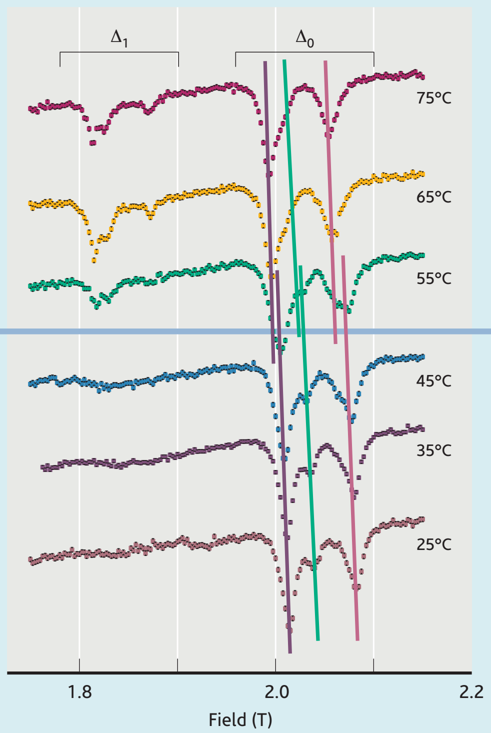
*R Scheuermann et al., Langmuir **29** (2004) 2652; A Martyniak et al., Phys. Chem. Chem. Phys. **8** (2006) 4723*

High temperature L_α phase



- Δ_1 resonances
- Resonance field indicative of non-polar environment.

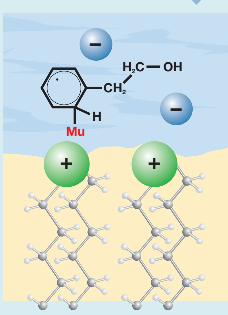
Co-surfactants reside in the bilayer with the hydroxy group near the interface. The cosurfactants are rapidly rotating around an axis.



Low temperature L_β phase

- No Δ_1 resonances
- Resonance field indicative of aqueous environment.

Co-surfactants are expelled from the bilayer and reside in the aqueous layer.

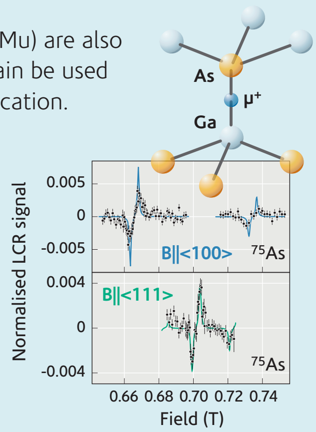


Muon sites in semiconductors

In semiconducting materials muons are frequently used as light proton isotopes to model hydrogen behaviour, as hydrogen itself can be very difficult to study directly.

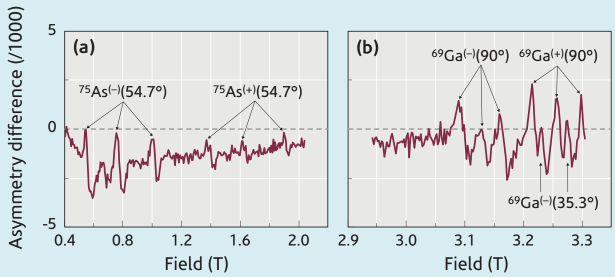
LCR has been used to determine the lattice site of diamagnetic muons (μ^+) in p-type GaAs. Ga and As are quadrupolar nuclei (I>1/2), and so level crossing resonances occur at fields for which the muon Zeeman energy matches the combined Zeeman and quadrupolar energy of a nucleus. The positions of the resonances allow both the distances and angles of the muon with respect to neighbouring nuclei and crystal directions to be found.

Paramagnetic muonium species (Mu) are also present in GaAs, and LCR can again be used to determine its precise lattice location.



***Right:** Quadrupolar resonances of μ^+ with As nuclei for two different field directions in GaAs, together with the muon site. B E Schultz et al., Phys. Rev. Lett. **95** (2005) 086404*

***Below:** Bond-centred muonium resonances in GaAs. R F Kiefl et al., Phys. Rev. B **58** (1987) 1780*

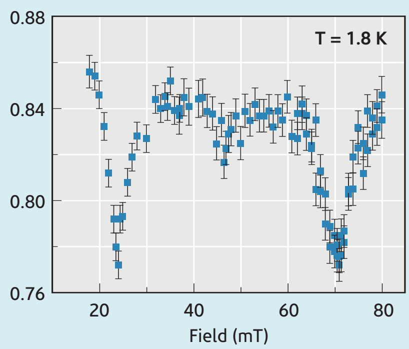


Magnetic systems

Muon level crossings in magnetic systems have been used to study spin dynamics in the single-ion magnet $LiY_{1-x}Ho_xF_4$. The enhancement of the spin lattice relaxation at the crossing in a magnetic system is due to a direct exchange of energy between the electronic and probe reservoirs, which results in a cross relaxation. The position, shape and relative intensity of the peaks in the measured spin lattice relaxation provide important information about the spin Hamiltonian of the system and the details of its interaction with the spin probe and its environment.

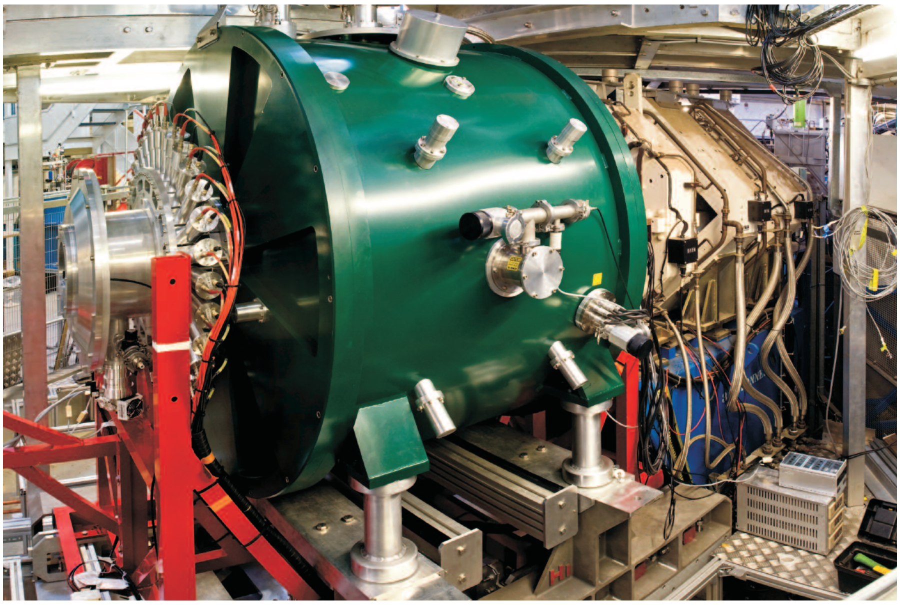
Magnetic field dependence of the muon spin relaxation rate in $LiY_{0.998}Ho_{0.002}F_4$

*M J Graf, et al., Phys. Rev. Lett. **99** (2007) 267203*



Facilities for Muon Spectroscopy

Europe is fortunate in having two muon sources that are complementary. The beam structure of the SμS, located at the PSI in Switzerland, makes it ideally suited for applications where high timing resolution is essential, such as following fast muon precession or rapid spin depolarisation. In contrast, the pulsed muon beam operated by the STFC in the UK, allows low background time differential data to be captured at high data rates. It also enables the effect of beam synchronous stimuli (such as Radio Frequency or laser radiation) to be investigated. Together, these facilities provide beams of muons for a wide variety of atomic-level studies in condensed matter, molecular, chemical, biological, geological and engineering materials. Further details of the various instruments and sample environment equipment can be found on the facility web sites.



***Above**: High field muon spectrometer at PSI, Switzerland.*

***Left**: High field muon spectrometer at ISIS, UK*

At both facilities a number of spectrometers are available with specialist sample environment equipment to enable a broad range of condensed matter and molecular studies on solid, liquid and gaseous samples. Temperature studies can extend from millikelvin temperatures to 1500 K and solid-sample pressures up to 2.5 GPa can be applied. Both facilities have recently completed major instrument upgrades to provide high magnetic fields; at ISIS fields of 5 T parallel to the muon spin are possible, while PSI provides a 9.5 T spectrometer optimised for spin rotation measurements.

Using the Facilities

Both facilities welcome experiment proposals from scientists of all disciplines. Calls for proposals occur twice a year: deadlines at ISIS are 16 April and 16 October, while at PSI deadlines are 10 December and 11 June. Proposals can be made using the online systems available through the respective web pages – typically a two-page science case is required.

Members of both groups are available to give advice on all aspects of muon science and running muon experiments. They can be contacted to discuss ideas for experiments, for technical and practical information on the muon instruments and to offer advice on draft proposals.

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