

Detection of Quadrupole Interactions by Muon Level Crossing Resonance*

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The positive muon proves to be a very versatile and sensitive magnetic resonance probe: implanted in virtually any material its polarisation may be monitored via the asymmetry in its radioactive decay, giving information on the sites occupied by the muon in lattices or molecules, and the local fields experienced at these sites. The scope of these experiments has been greatly extended by the development of a technique of cross relaxation or level crossing resonance which allows quadrupole splittings on nuclei adjacent to the muon to be measured. The principles of the technique and the conditions necessary for detection of the spectra are described, together with a number of applications. Of especial interest is the manner in which muons mimic the behaviour of protons in matter. In metal lattices, for instance, muons invariably adopt the same interstitial sites as do protons in the dilute hydride phases, so that they can be used to study problems of localisation and diffusion common to those of hydrogen in metals. Studies of the muon level crossing resonance in copper have given valuable information on the crystallographic site, electronic structure and low temperature mobility of the interstitial defect. In semiconductors, muons are expected to trap at other impurities – notably acceptors – in processes analogous to the passivation of dopants by hydrogen. Muon resonance offers the exciting prospect of spectroscopic study of these passivation complexes. In molecular materials, substitution of protons by muons can be thought of rather like deuteration. Muons implanted in ice produce a significant change in the quadrupole coupling constant of adjacent ^{17}O nuclei which may be traced to the effects of the large muon zero point energy; the resonance spectrum also exhibits temperature dependent features which may be informative on the nature and lifetime of defects in the ice structure. Muon level crossing resonance has already been studied in an oxide superconductor and this relatively young field is now wide open for quadrupole interaction studies in other materials, using a variety of nuclei.

1. Introduction: The Muon-Proton Analogy and μSR Techniques

This article concerns the use of positive muons to mimic the behaviour of protons, especially in materials where protons themselves are difficult to observe. This is one of the principal motivations for studies by the techniques known collectively as μSR , namely *muon spin rotation, relaxation and resonance* [1], which are practised at those accelerator laboratories where low energy muon beams are available. Like protons, positive muons carry unit charge; implanted in the material of interest, they quickly thermalise and usually reach the same thermodynamic or chemical equilibrium state as would implanted protons, despite

their relatively short lifetime, $\tau_\mu = 2.2 \mu\text{s}$ ¹. Muons also have spin $\frac{1}{2}$, and a magnetic moment about 3 times that of protons, so that there is a useful analogy between the μSR techniques and proton NMR.

The remarkable sensitivity of the μSR techniques derives from the high intrinsic polarisation of the muon beams, together with the particular properties of the muon decay, which provide a means of monitoring how the muon polarisation evolves after implantation. The decay positrons are emitted preferentially in the instantaneous direction of the muon polarisation (this is the classic example of parity violation in radioactive decay). These positrons may be counted individually using scintillation detectors and the asymmetry in their emission probability is such that, at full polarisation, the count rate in the forward or parallel direction is about double that in the backward or antiparallel direction.

¹ The microsecond timescale occasionally offers the possibility of studying metastable or precursor states, however, as is notably the case in semiconductors.

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Even in materials where protons (or, more generally, hydrogen in any of its charge states) are easily detected by conventional spectroscopies, μ SR studies may be beneficial, especially in cases where the dynamical behaviour is not fully understood. The muon-proton analogy is exemplified by the formation in many circumstances of *muonium*, $\text{Mu} = \mu^+ e^-$, which diffuses, traps or reacts chemically like atomic hydrogen. Quantitative comparisons of the behaviour of muonium and protium exploit the fact the muon mass is only about $1/9$ that of the proton, so that muonium behaves as a *light isotope* of hydrogen [2]. Substitution of hydrogen by muonium therefore leads to a variety of dynamic isotope effects (e.g. in one-electron molecular properties, or in motional phenomena) which are considerably enhanced relative to those observed by deuteration, and provide a severe test of theoretical models. Use of the light isotope also favours observation of specifically quantum effects, i.e. those involving zero point motion or tunnelling.

Applications of the basic μ SR methods are now widespread in Physics and in Chemistry, and have been reviewed by several authors [1–3]; the present article is devoted to a description of experiments which resemble Nuclear Quadrupole Resonance. This development is sufficiently recent for all investigations undertaken to date to be mentioned: these already include studies in a metal (Section 2 and 3), a semiconductor (Section 5), a molecular material (for which new data is presented in Section 6) and, of course, a high- T_c superconductor (Section 7). The article is for the most part descriptive, concentrating on applications, but some more formal aspects are examined briefly (Section 4 and the Appendix). Prospects for further studies are explored in the concluding section (Section 8).

2. Muon Level Crossing Resonance

The proposal for an extension of μ SR techniques to double resonance is due to Abragam [4], who realised that certain energy level separations within the host system – such as nuclear quadrupole splittings – could be measured by tuning the muon Zeeman energy to match. The first demonstration experiment was performed on muons implanted in copper metal [5], for which the matching or resonance condition is illustrated in Figure 1 a. The muons and their neighbouring quadrupole nuclei (^{63}Cu and ^{65}Cu , both having

spin $J = 3/2$) are put “on speaking terms” at a certain value of the external magnetic field, so that cross relaxation can occur between them *via* flip-flop transitions. Abragam dubbed the method *muon level crossing resonance*, and the acronym μ LCR is now common in the literature. The most recent data on copper [6, 7] are shown in Fig. 1 b, with the resonant depolarisation appearing as a dip in the muon decay asymmetry at an applied field of about 80 Gauss.

3. Significance of the Cu Data: Localisation and Diffusion of Light Interstitials

Copper provides a good example of a metal in which interstitial protons – the archetypal light interstitial defects – are difficult to study, hydrogen being too insoluble for detection by the conventional spectroscopies. Ordinarily, the quadrupole splittings on the Cu nuclei are zero, the electric field gradient vanishing by symmetry at undisturbed lattice sites in the cubic (fcc) structure. The direct field gradient from an interstitial muon at a neighbouring Cu nucleus is also quite small, the muon’s positive charge being effectively screened in a small radius by a local accumulation of conduction electron density, as it is for hydrogen (i.e. screened protons) in metals.

The quadrupole interaction measured in the μ LCR experiment therefore arises from the local distortion of the lattice about the interstitial defects. μ SR linewidth measurements had previously given an estimate of its magnitude [8], but μ LCR provides a precise value with which to confront models of the local structure, and especially the predictions of screening theory. μ SR linewidths had also shown a significant narrowing at temperatures below 50 K which could be ascribed either to a site change of the interstitial muon, or to motional narrowing, in which case the muon mobility must increase with *decreasing* temperature. Persistence of the muon level crossing resonance, undisplaced, in this regime confirms that no site change is involved, so that the effect is indeed motional. It is now understood to signal the onset of a form of quantum diffusion of this particularly light interstitial defect, its mobility in the cold lattice, and in the absence of other defects, being limited only by a surprising sluggishness on the part of the screening charge [9]. The muon also becomes mobile in the lattice at *higher* temperatures, as expected, this motion being phonon-assisted. Effects on both the resonant and low field cross relaxation are evident in Figure 1 b.

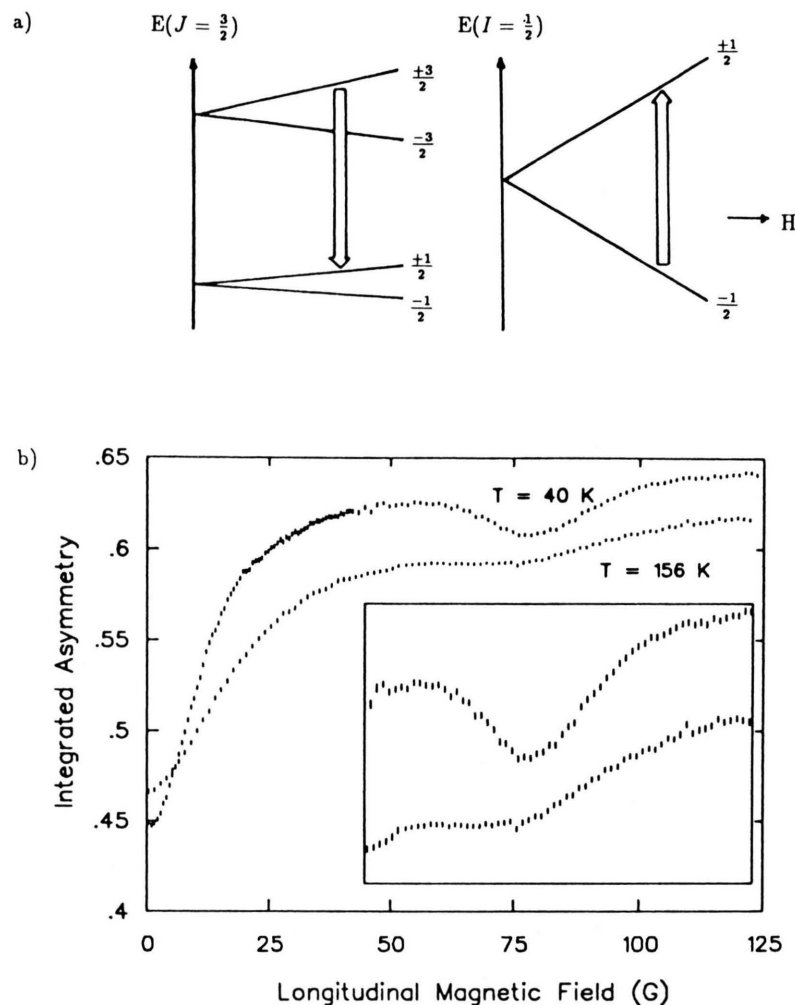


Fig. 1. The principles of muon level crossing resonance, illustrated for muons adjacent to spin $-3/2$ nuclei (a), and experimental data for copper (recorded by Luke et al. [6]) (b). Muon depolarisation occurs by cross relaxation to the Cu nuclei at low fields (comparable with the dipolar local fields) and at the level crossing resonance. The resonance region is shown with the vertical scale expanded in the insert; note the weakening of the signal at temperatures where the interstitial muon becomes mobile in the lattice.

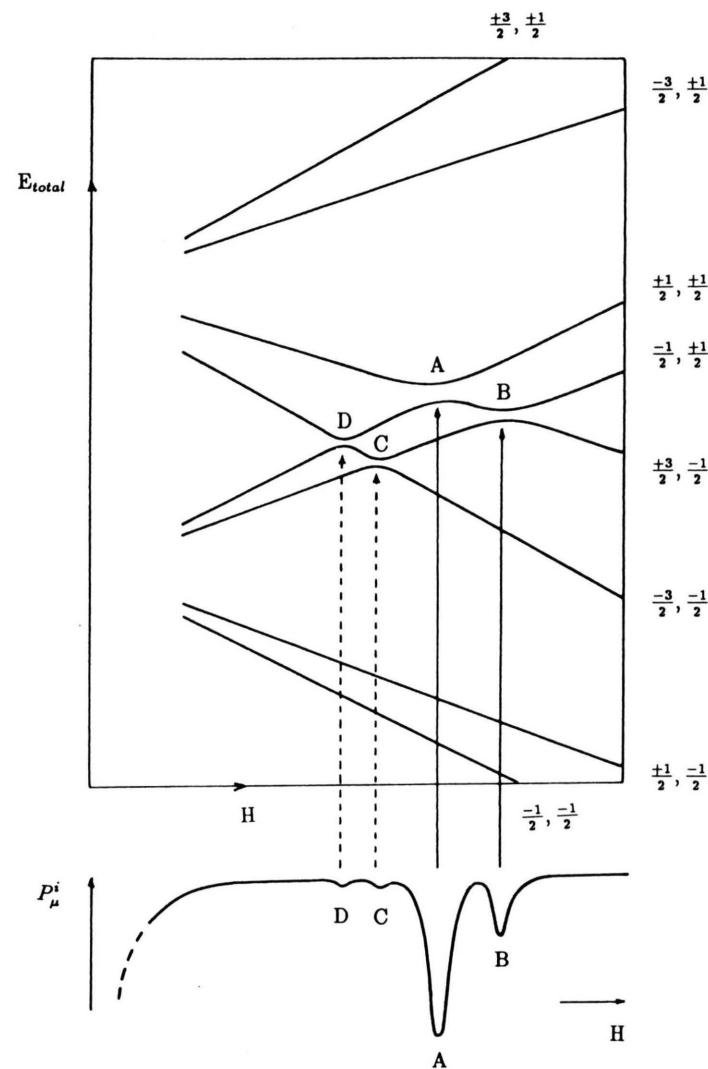


Fig. 2. Total energy level scheme for a spin $J_n = 3/2$ with electric quadrupole interaction plus a spin $I_\mu = 1/2$, coupled by the magnetic dipole interaction (a). (The diagram is qualitative, sketched for a fictitious ratio $\gamma_\mu/\gamma_n \approx 7$. Resonant depolarisation of the probe spin I_μ sketched in (b), arises where level crossings are avoided notably at A and (except for overall axial geometry) B.

4. Conditions for Detection

A necessary condition for cross-relaxation to occur is that the Zeeman energy of the muon probe is equal – to within a dipolar linewidth – to the combined quadrupolar and Zeeman energy of the nucleus in question. Fortunately the gyromagnetic ratio of the muon happens to be greater than that for all other nuclei – in fact about three times that of the proton ($\gamma_\mu = 2\pi \times 13.6 \text{ kHz/Gauss} = 3.18\gamma_p$) – so that it should always be possible to meet such a condition [4]. The required magnetic field is given approximately by

$$H_{\text{res}} \simeq |\Omega_q|/(\gamma_\mu - \gamma_n). \quad (1)$$

Here $\Omega_q/2\pi$ is the quadrupole splitting (in units of frequency and referred to zero field). The precise value of the field for resonance will vary slightly with the orientation of the applied field relative to the quadrupole tensor axes.

While the electric quadrupole interaction determines the position of the resonance, it is the magnetic dipole-dipole interaction which drives the cross-relaxation, i.e. which permits the resonance to be detected and determines its intensity. This coupling is not apparent in Fig. 1a, where the two spin systems are depicted separately. Its effects may be seen in the energy level diagram for the *total* system, drawn in Fig. 2 for the case of one $J=3/2$ nucleus (e.g. Cu, ^{11}B , etc.) plus one $I=1/2$ probe (i.e. muon or proton). The dipolar interaction mixes the pure spin states and removes degeneracy between the relevant levels of the total system, where these levels would cross in the absence of such a coupling. For this reason, the term *avoided level crossing* or ALC is also to be found in the literature. Pedantic as this may be, it is a necessary condition for the detection of the resonance, and the residual separation of the levels is a measure of its strength. The estimates given in the Appendix make it clear that the muon must also be quite close to the quadrupolar nucleus in question: in most cases this will mean nearest neighbour in a lattice or molecule, since the dipolar coupling falls off rapidly with distance, as $1/r^3$ [10].

The principal resonance results from the admixture of spin states at the point marked A in Figure 2. In the special case that the electric field has axial symmetry, and that this axis, the internuclear vector and the applied magnetic field are all in line, this is in fact the only level crossing which is avoided, the admixture of states being due to flip-flop terms in I^+J^- and I^-J^+

in the dipolar Hamiltonian [10]. More generally, for other geometries and orientations, the misalignment of the quadrupole tensor axis and the external magnetic field, together with the non-secular terms in the dipolar Hamiltonian, result in a complicated admixture of states and the appearance of subsidiary resonances where other level crossings are avoided. Marked B, C and D in Fig. 2, their relative positions and intensities vary with orientation. The individual resonances have not yet been resolved in copper metal (where each muon has not one but six Cu neighbours, the muons adopting octahedral interstitial sites in the fcc lattice, and also the two Cu isotopes have slightly different quadrupole moments), but the overall line-shape is sufficient to infer that the quadrupole interaction energy must be negative in this system [6].

The similarity between μLCR and cross-relaxation methods in NQR is evident, but there are some noteworthy differences in the preparation and monitoring of the probe-spin polarisation. The intrinsic polarisation of the incoming muon beam can be as high as 100%, obviating the need for any polarising field, and the muon decay provides a form of trigger detection of the resonance, allowing the evolution of muon polarisation to be monitored however low the working field. Field cycling is therefore unnecessary: *preparation* of the resonance is taken care of by the muon production process and the *evolution* and *detection* phases proceed simultaneously.

5. Passivation of Boron in Silicon by Hydrogen or Muonium

Another spin $\frac{3}{2}$ nucleus for which μLCR would be of considerable interest is ^{11}B , the abundant isotope of boron, in the situation depicted in Figure 3. This concerns the phenomenon of *passivation* in semiconductors, in which hydrogen pairs with donor or acceptor impurities, substantially modifying the electronic properties by removing electrically active levels from the energy gap. For the case of acceptors, e.g. boron in silicon, the proton is believed to adopt a position immediately adjacent to the substitutional impurity¹, but no study of the microscopic structure by any of the nuclear probe spectroscopies has yet been reported.

¹ The experimental and computational situations are summarised by Maric et al. [11].

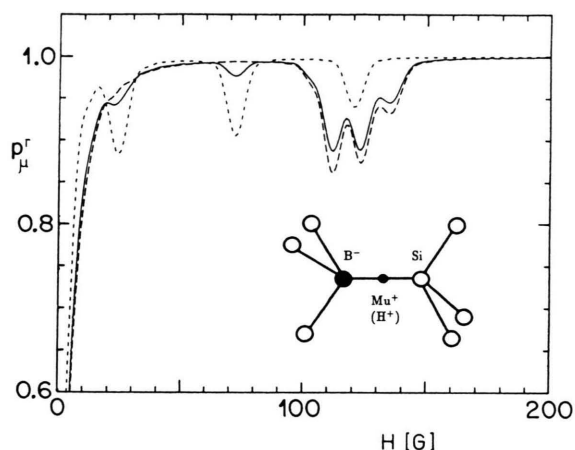


Fig. 3. Simulated μ LCR spectrum for B-Mu passivation complexes in Si (due to Maric et al. [11]). Integrated muon polarisation P_μ^r (defined in the Appendix) is calculated as a function of field along the $\langle 111 \rangle$ direction. The dashed line represents resonances with ^{11}B , the dotted line those with ^{10}B ; the full line combines these according to the natural abundances. The expected "bond-centre" site for the muon, immediately adjacent to a substitutional impurity, is drawn in the insert.

With muons in the place of protons (implanted in p-type silicon), these complexes should be particularly amenable to study by μ LCR. Figure 3 shows simulated spectra due to Maric et al. [11]. Here the electric field gradient at the boron nucleus obtained from *ab initio* cluster calculations has been used to predict the positions of the resonances, so that their observation would confirm the microscopic and electronic structure of the passivation complexes. The expected contribution from the ^{10}B isotope ($J=3$, 20% abundant) may also be seen in Figure 3. This distinctive signature of the B-Mu passivation complexes has not yet been detected in preliminary experiments, however. Either the complexes are not formed within the muon lifetime, or the resonance is washed out by some rapid reorientation of the structure (e.g. by tunnelling of the muon between the four equivalent bond centres). This is disappointing, but it would be well worth persevering with the search, in case conditions of temperature or doping favourable to detection of the spectrum can be found.

Also a conventional NQR experiment on highly doped Si(B, H) would be well worth while attempting: detection of cross-relaxation to the protons using a field-cycling technique – at mixing fields about 3 times higher ($\gamma_\mu/\gamma_p=3.18$) than those for the muon resonances predicted in Fig. 3 – should be just feasible.

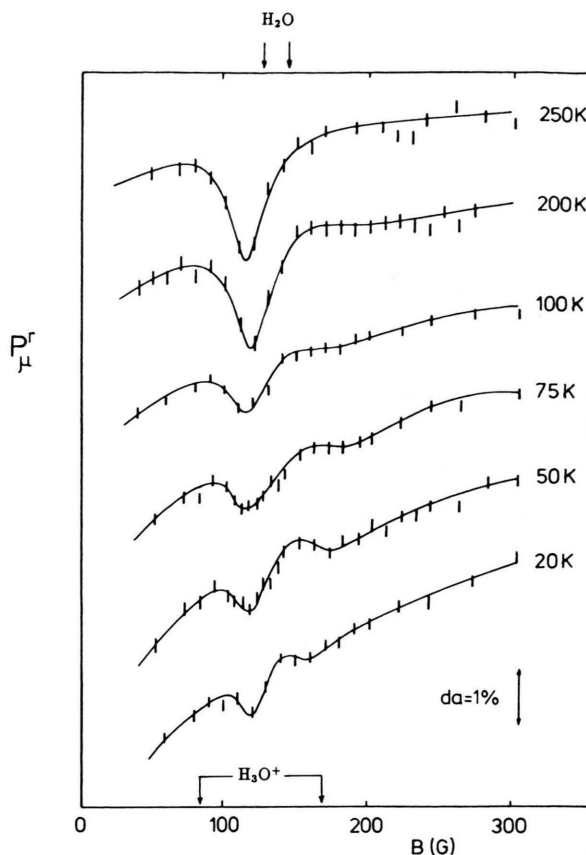
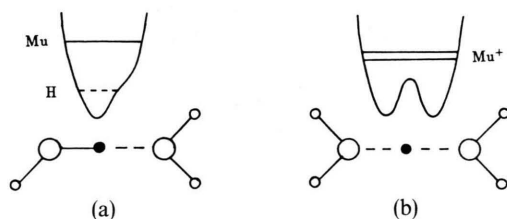


Fig. 4. Experimental μ LCR spectra for ice, enriched to 45% in H_2^{17}O , recorded at various temperatures. The curved baselines subsume details of the spin-lattice relaxation of the various muonium states. The fields for resonance predicted from the quadrupole frequencies for unsubstituted H_2O and H_3O^+ in ice are indicated; note especially the isotope shift for the substituted species HMuO .

6. μ LCR Studies in Ice

More successful have been studies of muons implanted in H_2O ice [12, 13]. Here the sample is enriched with H_2^{17}O to provide a quadrupolar nucleus for resonance. New data for this system [14], showing how the spectra evolve with temperature, are reported in Figure 4. The $J(^{17}\text{O})=5/2$ system provides two main resonances at frequencies which differ by a factor 2 when the field gradient tensor has axial symmetry ($\eta=0$, as for ionic species such as H_3O^+ or OH^-) but which become nearly equal for large anisotropy ($\eta \simeq 1$, as for the neutral H_2O unit in the Ih structure) [15].

The single dominant resonance detected above 200 K may therefore be assigned with confidence to the isotopically substituted unit, HMuO. The ^{17}O quadrupole coupling constant is then found to be significantly smaller than for the unsubstituted H_2O unit. This is the first example of a quadrupole isotope effect induced by muon substitution. It may be ascribed to the larger zero-point energy of the lighter particle, together with the high degree of anharmonicity in the hydrogen bond potential (sketch a). Higher polarisation and more nearly tetrahedral bonding in the vicinity of the HMuO unit may be envisaged, resulting in a lowering of the electric field gradient at the oxygen nucleus [13].



Assignment of the minor resonance which appears at lower temperatures is less certain, but a likely candidate is the ionic species $\text{H}_2\text{O}-\text{Mu}^+-\text{OH}_2$. Here the muon is envisaged as trapping between two oxygens where the usual hydrogen bond is absent – a favourable site for a positive charge – converting an orientational (Bjerrum-L) defect into an ionic defect [13]. The unusual *increase* of a quadrupole coupling constant with temperature, apparent in the new data, may be taken as supportive of this model: it implies that the muon has access to energy levels separated by as little as 0.01 eV, which could correspond to tunnelling states within the symmetric double well potential (sketch b).

The scope for μLCR studies of other hydrogen-bonded systems is manifest; it is particularly interesting that the muon is able to probe a more anharmonic region of the hydrogen bond than is the heavier proton or deuteron.

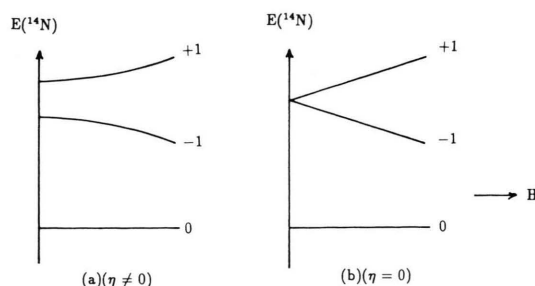
7. μSR and μLCR Studies of High- T_c Superconductors

^{17}O resonance has also been chosen for a remarkable study of the crystallographic sites adopted by muons implanted in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [16]. Knowledge of these sites is valuable in interpreting μSR measurements of internal fields in this and similar materials (a

massive body of data is now available ranging from studies of magnetic flux penetration in the superconductors themselves to magnetic order and fluctuation in related phases) [17]. The spectrum recorded by Brewer et al. [16] is reproduced in Figure 5a. Pairs of lines may be assigned to $(\text{OMu})^-$ species fundamentally similar to hydroxyl groups, so that the implanted muons “stick” to O^{2-} ions as anticipated. The potential complexity of the problem may be appreciated from Fig. 5b, but the spectrum suggests that only two main inequivalent sites are involved. A full analysis due to Noakes [19] reveals rather small electric field gradients at ^{17}O compared with normal OH^- groups, and surprisingly large departures from axial symmetry, which may indicate some structural distortion when this material is protonated.

8. Other Nuclei, and Future Prospects

The above examples concern nuclei with half-integral spin ($3/2$, $5/2$). A potential difficulty arises for those with integral spin, which is illustrated for the case of ^{14}N ($J=1$, 100% abundant) in sketch (a). For arbitrary symmetry of the electric field gradient, all degeneracy of the ^{14}N energy levels is lifted in zero field. In consequence, these levels have horizontal tangents at the origin of their field dependence, that is, the magnetic moment of the nucleus is effectively quenched at low fields. It recovers only as the quantity $Z/(1+Z^2)^{1/2}$, where Z is the ratio of the nuclear Zeeman energy to the non-axial component of quadrupole energy ($Z = \gamma_N \hbar H / K \eta$, with $K = \frac{1}{4}(e^2 q Q / \hbar)$) [20]. The cross relaxation rate varies as the same quantity so that level crossing resonance may be undetectably weak if the asymmetry parameter η is large.



In principle, the problem is overcome by choosing species with axial symmetry at the nitrogen atom (i.e. with $\eta = 0$), so that the full ^{14}N magnetic moment is effective (sketch b). This should be the case for species

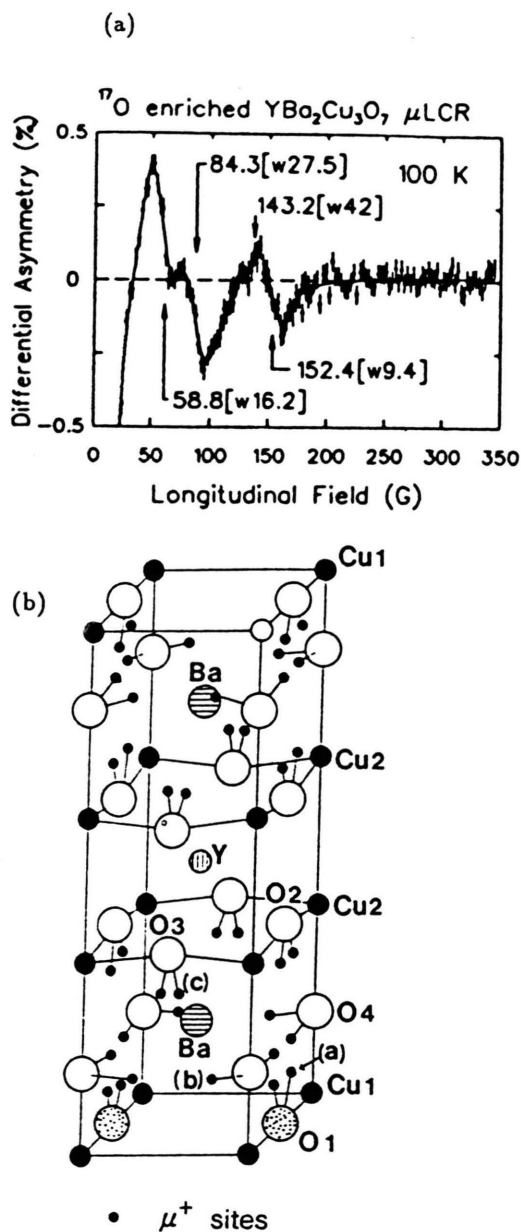


Fig. 5. μLCR spectrum of ^{17}O -enriched $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (a), (recorded by Brewer et al. [16]), and the candidate muon sites to be considered (b), (according to Nishida and Miyatake [18]).

such as $\text{R}_3\text{N}:\text{Mu}^+$ where the muon is envisaged as adding to a tertiary amine in a process analogous to protonation. Strangely, no μLCR spectrum could be detected from muons implanted in frozen triethylamine however [21]. It seems likely that muonic ion

has a charge distribution at the nitrogen atom so close to tetrahedral symmetry that the quadrupole interaction is small and the resonance buried in the low-field cross-relaxation [22].

Nuclei with half-integral spin therefore seem most promising for further studies, Kramers' theorem guaranteeing that their full magnetic moment is effective for cross-relaxation. The scope for further investigations with ^{11}B and ^{17}O is considerable, and there is a good number of other nuclei for which μLCR experiments should be feasible. ^{27}Al (5/2, 100% abundant) seems a particularly promising candidate in a variety of situations, both as the metal (suitably irradiated or doped to provide trapping sites to suppress the muon diffusion, which is intrinsically rapid in this metal [9]), as a dopant in semiconductors [11], or in inorganic compounds. Trapping at vacancies and impurities in metals is a problem of perennial interest [1, 3, 9] but, surprisingly, μLCR has yet to be exploited as a means of studying the defects or muon-impurity pairs. In this connection ^{23}Na (3/2) and ^{55}Mn (5/2) also look interesting, as well as (if the resonances are not too broad) the higher spin nuclei ^{45}Sc (7/2), ^{51}V (7/2), ^{59}Co (7/2), ^{93}Nb (9/2), ^{181}Ta (7/2), etc., and various rare earth metals. In semiconductors, ^{69}Ga (3/2, 60%) and ^{71}Ga (3/2, 40%) together with ^{75}As (3/2) provide ample opportunity for further studies, notably for the identification of the diamagnetic or ionised muonium state: it should be possible to use μLCR spectra to distinguish between Mu^+ , which is believed to be stable at a bond-centre site, and Mu^- , believed stable at the tetrahedral interstitial site. This information is eagerly awaited by those concerned with the location, stability and mobility of the various charge states of hydrogen in semiconductors. In muonium chemistry, it has often proved difficult to identify products of reactions where muonium is incorporated in a closed-shell molecule. This was one motivation for the μLCR experiment in ice, which has provided spectral characteristics of the elusive diamagnetic states, and the most direct evidence for formation of the isotopically substituted species HMuO [12, 13]. Further possibilities are manifest, among which the halogens ^{35}Cl (3/2, 76%), ^{79}Br (3/2, 51%) and ^{127}I (5/2), which must have an affinity for muonium almost identical with that for hydrogen, certainly deserve attention [22].

A combination of the μLCR technique as described above with RF irradiation would further increase the scope of the experiments. This is as yet untried but promises to give more detailed spectroscopic infor-

mation on the muon states, by analogy with RF decoupling and dipolar heating techniques in conventional NQR, and in particular to provide pure quadrupole resonance spectra in zero field.

It may be hoped that the identification of species by muon level crossing or quadrupolar resonance will help extend muonium chemistry from the organic to the inorganic and metallo-organic realms.

Acknowledgements

I wish to record my thanks to J.A.S Smith for suggestions and discussions which have proved invaluable to the development of a μ LCR programme at ISIS, also to T.L. Estle and A.N. Garroway for helpful comments on this paper.

Appendix

Strength of the Resonance

Since the initial muon polarisation on implantation is well defined, there is in principle an oscillatory exchange of polarisation between the muon and a single quadrupolar neighbour, which would continue *ad infinitum* in the absence of spin-lattice relaxation and if the muon did not decay. The amplitude of this oscillation is only significant in the vicinity of a resonance (where the admixture of states is appreciable) and its frequency corresponds to the separation in energy of the mixed states (and therefore to the energy gap between them on resonance – see Figs. 2, 6, and 7). This may be thought of as the nutation of the muon spins about an effective field which at resonance reduces to some transverse component of the dipolar field from the neighbour and cannot be “tuned out” by an external magnetic field. These nutational frequencies are therefore of the same order as dipolar linewidths in NMR, i.e. at most tens of kHz, which is slow on the timescale of the muon lifetime ($\tau_\mu = 2.2 \mu\text{s}$). Only a fraction of a nutational period is executed and only a correspondingly small net depolarisation of the muons observed in practice. In his original paper [4], Abragam estimates the size of the effect by considering the muon polarisation effectively turned through an angle

$$\alpha = \gamma_\mu H_l \tau_\mu. \quad (2)$$

For a typical local field H_l of 1 Gauss, this is about 10 degrees and corresponds to a longitudinal depolar-

isation of order 1%. The situation in copper metal, with the muon squeezed close to several Cu nuclei, is especially favourable and Fig. 1b shows a somewhat larger effect. The estimate is valid as long as the residence time of the muon at a given site is not much less than τ_μ . Diffusion interrupts the coherence of the oscillatory exchange, which must begin afresh with each new partner, and may be seen in Fig. 1b to affect resonant and non-resonant cross relaxation alike. In the case of rapid hop rates $W \gg \tau_\mu^{-1}$ (and equally for the case of large widths W of the quadrupolar transition), an estimate of depolarisation can be made by replacing τ_μ in expression (2) by the quantity $\sqrt{\tau_\mu/W}$ [4]. (More elaborate treatments of motional effects are given by Kreitzman [23] and by Luke et al. [7].)

Cross-relaxation is therefore the bottleneck which determines the muon depolarisation rate even in the case that spin-lattice relaxation of the host spins is rapid. As a general rule, since the off-diagonal terms responsible for cross relaxation also make a partial contribution to the NMR linewidth of the probe spin, the resonant cross-relaxation rate cannot exceed the overall spin-spin relaxation rate T_2^{-1} of the probe [24]. This contrasts with the situation in paramagnetic systems, as explained below.

Time Domain Measurements

Expressions or simulations for the detailed time evolution of the muon polarisation are given by various authors [25, 26, 11], with worked examples given for Cu by Vogel et al. [25] and for Si(B, Mu) by Maric et al. [11]. Figure 6a displays its oscillatory nature, calculated for a static muon interacting with a single neighbour. The extension to the case of several neighbours has also been tackled [25, 26].

Experimentally, the polarisation function $P(t)$ may be extracted from the time-dependent asymmetry in the muon decay in the usual fashion [1, 3]. Examples at and near resonance in Cu are given by Kreitzman [23], Celio [26], and Luke et al. [7]. Figure 6b shows the results for a phenomenological cross-relaxation rate fitted to such data.

Only the initial part of the function $P(t)$ is displayed within a few muon lifetimes. Fortunately, the detailed form of this function is not always required. For instance, the quantity

$$P_\mu^r = \int_{t_1}^{t_2} dt p(t) \quad (3)$$

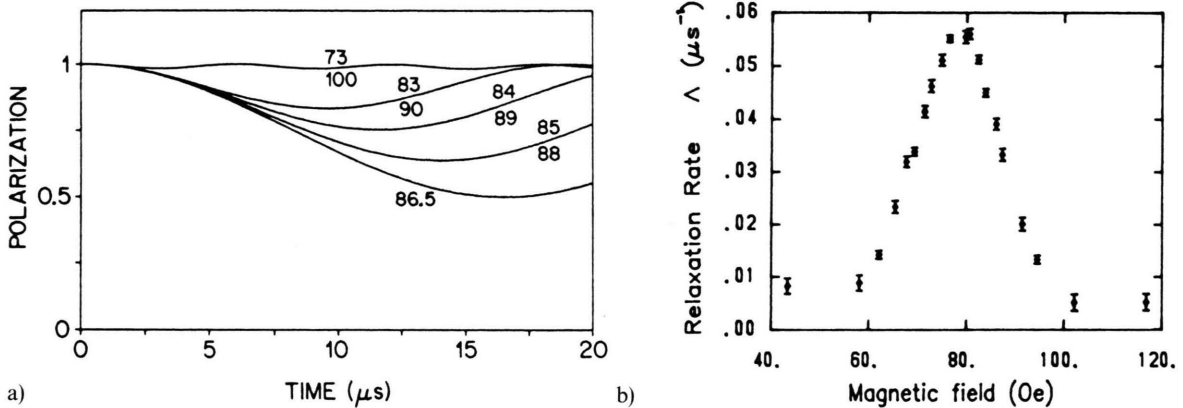


Fig. 6. Simulations of the muon polarisation function at and near resonance, due to Vogel et al. [25], showing the oscillatory of polarisation with a single neighbour (a), and the results of fits of a suitably defined cross-relaxation rate to the data for Cu [23] (b) (compare Figure 1 b).

gives a measure of residual polarisation, averaged over a time window $t_1 \rightarrow t_2$ which is delayed relative to muon implantation ($t = 0$), allowing some time for the cross relaxation to develop. Such measurement is particularly convenient at a pulsed muon source such as that at ISIS (Oxfordshire, U.K.), and this quantity (with $t_1 = 3 \mu\text{s}$ and $t_2 = 10 \mu\text{s}$) is displayed in the data of Fig. 4, for instance, and in the simulations of Figure 3.

Integral Counting

At continuous muon sources, time domain measurements impose a limit on the rate at which data may be accumulated [1, 3]. The full intensity available at sources such as TRIUMF (Vancouver) and PSI (Zurich) and potentially also the powerful low duty cycle at LAMPF (Los Alamos) can be exploited by the so called *integral counting* method, however. This makes use of the total “forward” and “backward” positron counts within a given interval, yielding the quantity

$$P_\mu^i = \int_0^\infty dt p(t) \exp(-t/\tau_\mu). \quad (4)$$

This measurement weights the data heavily to early times, but the estimate given by expression (2) applies, and integral counting is certainly sufficient to allow the positions and widths of the resonances to be determined, as in the data of Figure 1 b [7].

Resolution

The widths of the resonances will normally be determined by the local dipolar fields, by the intrinsic spread of quadrupolar splitting, or by motional effects. In integral counting experiments, the muon lifetime itself imposes a limit on resolution, however. Converted to units of field, this intrinsic width is of order

$$2/(\gamma_\mu \tau_\mu) \simeq 10 \text{ Gauss (FWHM)}. \quad (5)$$

The muon lifetime being known to high precision, this contribution to the overall linewidth can generally be de-convolved. The deconvolution is in fact automatically achieved in the display of time-domain data, where the muon decay is compensated either mathematically or by constructing “forward-backward” asymmetry. The fascinating consequences of other forms of lifetime broadening are explored below.

Adiabatic Passages and Mode Locking?

Some amusing further generalities are illustrated with a two-state system in Figure 7. Field dependent energy levels $E_1(H)$ and $E_2(H)$ are shown crossing in the absence of coupling in (a). Mixing of the states by some off-diagonal element B results in new eigenvalues λ described by the determinant

$$\begin{vmatrix} E_1 - \lambda & B \\ B^* & E_2 - \lambda \end{vmatrix} = 0 \quad (6)$$

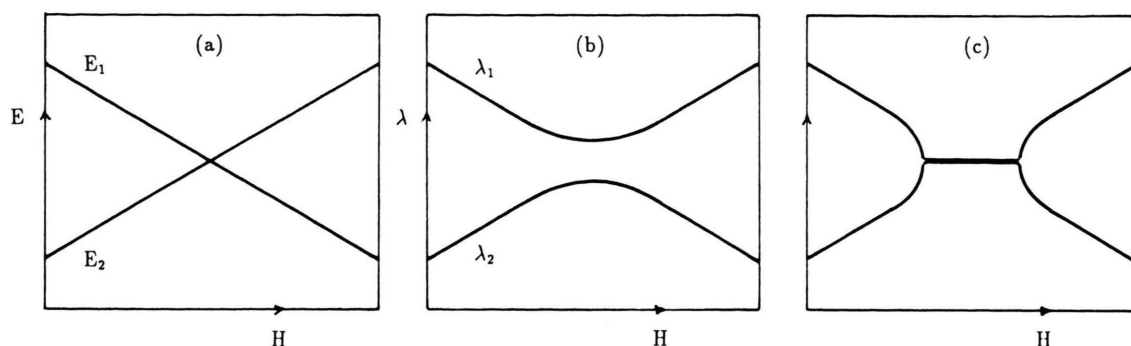


Fig. 7. Schematic energy level diagrams illustrating (a) independent modes, (b) mode-coupling and (c) (for certain conditions of damping) mode-locking.

leading to a minimum energy difference or gap of $\delta E = 2\sqrt{BB^*}$ (see also Fig. 5/6 in [3]).

Normally the resonance is displayed by slowly stepping the magnetic field, monitoring the polarisation of “new” muons at each point. Figure 7b inspires the notion that a larger signal might be obtained by sweeping through resonance *within the lifetime of each muon*, since an adiabatic passage would result in full reversal of muon polarisation. The usual adiabatic condition [10] requires the variation of field to be slower than the muon spin precession at each instantaneous value of effective field, however. Unfortunately $\tau_\mu = 2.2 \mu\text{s}$ is far too short for this condition to be realised. (The prospects are more favourable in paramagnetic systems, as explained below.)

The effect of lifetime broadening of the levels can be represented by replacing the energies in (6) with complex quantities $E_1 + i\Gamma_1$ and $E_2 + i\Gamma_2$ (a respectable mathematical trick which can be justified by a rigorous treatment [27]), leading to a reduced energy gap at resonance of

$$[4BB^* + i^2(\Gamma_1 - \Gamma_2)^2]^{1/2} = [4BB^* - (\Gamma_1 - \Gamma_2)^2]^{1/2}. \quad (7)$$

This can vanish if the widths Γ_1 and Γ_2 are sufficiently disparate, i.e. differ by as much as the coupling. Far from avoiding each other, the two levels then pull together, as in Figure 7c. Well known in classical systems, this phenomenon of mode-locking is presently being explored by Bugg for its application to quantum and nuclear systems [27]. It would be fun to seek an example in μLCR ! The widths Γ_1 and Γ_2 must represent inverse lifetimes, rather than inhomogeneous (e.g. static local field) broadening. Korringa relaxation, which is much faster for host metal nuclei than for the light interstitial muon, might fit the bill. So also would

a chemical reaction, which commonly limits the lifetime of particular muon states in non-metallic systems, e.g. semiconductors or molecular materials.

Paramagnetic Systems

This paper is concerned with the measurement of quadrupole interactions, in systems in which the muons reach diamagnetic states in the host media, i.e. those in which they have no interaction with unpaired electronic spins. It is worth mentioning that this is far from being the only application of μLCR , and that similar methods have also been extremely fruitful in the study of paramagnetic systems, namely organic radicals [28–30] and defect centres in semiconductors [31–33]. Here the measurement is of hyperfine interactions, with the muon effectively mapping out spin density in its vicinity. There are some noteworthy differences with the diamagnetic situation. An energy match is obtained, again by tuning the external magnetic field, between the combined Zeeman and hyperfine energy of the muon, and that of a nearby (dipolar) nucleus. The cross relaxation can often be detected with much more distant nuclei than in the diamagnetic case, since it is mediated by the electronic spin, and is effective over the whole range of the singly occupied molecular orbital. It is also much faster, so that several periods of the oscillatory exchange of polarisation can be followed in favourable cases [28]. This corresponds to the precession of the muon spin about some transverse component of hyperfine field, leading to frequencies of tens of MHz rather than tens of kHz. The prospects for reversal of muon polarisation by adiabatic passage are therefore somewhat im-

proved in such systems, although a rather fierce field modulation would be required! Certainly the average depolarisation measured by an integral counting experiment is enhanced in this situation by spin-lattice relaxation [29] (a rare example in magnetic resonance

of resonances being *increased* in intensity by relaxation effects). A comprehensive bibliography covering this area is to be published in a forthcoming review by Kiefl and Kreitzman [34].

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