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Muonium states and dynamics as a model for hydrogen in semiconductors

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Abstract

An atomistic picture of interstitial hydrogen in semiconductors involves, as it does for hydrogen in metals, determination of the lattice sites and configurations adopted and the mechanisms of diffusion. An additional dimension is added in semiconductors, namely the possibility of examining different charge states of the defect centre—positive, neutral and negative—respectively the diamagnetic proton, the paramagnetic hydrogen atom and diamagnetic hydride ion. Muon spectroscopy has been successful in modelling all these states, determining their local structure, their different stabilities, mobilities and interactions with charge carriers. In semiconductors doped heavily to metallic conductivities, only diamagnetic states are observed, though still with a rich variety of mobilities and trapping sites. Studies of the interaction and pairing with dopant atoms, simulating the important process of passivation, also appear promising. This short review is illustrated with recent results for the elemental semiconductors Si and Ge and the compounds GaAs and InP.

Keywords: Hydrogen; Semiconductors; Passivation; Muonium; Diffusion

1. Introduction: the positive muon as a proton analogue

The study of hydrogen in semiconductors has a shorter history and a less extensive bibliography than that of hydrogen in metals but is receiving increasing attention [1]. This interest stems from the realization that, even as a trace impurity, hydrogen can have a profound effect on the electronic properties of semiconductors. The major and best known effect is the passivation of dopants, whereby hydrogen destroys the electronic function of donors or acceptors by forming chemical complexes with them, removing their electrically active levels from the energy gap. In addition, interstitial hydrogen displays an electrical activity of its own and can act as a deep-level donor, acceptor or recombination centre, depending on the material and the interstitial lattice site adopted. The studies focus on the determination of local geometrical and electronic structure, both for the isolated centres and for those in combination with other defects or impurities. Compared with metal–hydrogen systems, there are no issues pertaining to hydrogen storage or containment, and little attention to mechanical properties such as embrittlement, but there is considerable common ground concerning aspects of solubility, diffusion and impurity-trapping. Hydrogen is often incorporated during production of the material (e.g. during deposition from the hydride gases) and can also be introduced at various stages of processing, notably etching. Our own studies address the nature of the interaction with charge carriers induced thermally, optically and by doping; they also reveal very different mobilities for the different charge-states and show that, under certain conditions, the diffusion of hydrogen in semiconductors may be controlled by charge-state transitions coupled to local configurational changes.

This article describes progress in building up an atomistic picture of all these processes by studying not the hydrogen states themselves, but their counterparts formed by implanting positive muons, used as proton analogues. In contrast to the situation in metals, the density of mobile conduction electrons in semiconductors is always insufficient to screen a defect charge. A positive muon can therefore bind a single unpaired electron to form a neutral paramagnetic centre. The vacuum-state version resembles atomic hydrogen and is known as muonium, $Mu=\mu^+e^-$; in fact its Bohr radius and ionization potential are so similar to that of protium that it can legitimately be considered as a light isotope ($m_{Mu}/m_H \approx 1/9$). Our studies rely on the supposition that the solid state chemistry of protium and muonium are sufficiently similar that the same crystallo-

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graphic sites are preferred and—with due regard for differences in zero-point energy—the local lattice relaxations and electronic structures are essentially identical. More careful attention must be paid to the large isotopic mass ratio when it comes to interpreting interstitial diffusion rates; this is well known in comparative studies of muons and protons in metals, where indeed it is exploited as a rigorous test of dynamical models [2].

The various muon and muonium states in semiconductors may be detected and characterized by the spectroscopy known as μSR, standing for muon spin rotation, relaxation or resonance. These techniques have a good deal in common with conventional magnetic resonance, combining aspects of ESR for the electronically paramagnetic muonium states and of proton NMR in the study of the electronically diamagnetic muon states. Their advantage over the conventional spectroscopies is a remarkable sensitivity and selectivity, arising from the unique properties of muon production and decay [3,4].

2. Neutral paramagnetic states: an example of metastability

In intrinsic or lightly doped semiconductors, the muonium spin-states are sufficiently long-lived to permit the local distribution of (electron) spin density to be mapped fully: the muon–electron hyperfine tensor is determined via characteristic frequencies in the muon spin rotation spectra [5] and the near-neighbour nuclear hyperfine interactions are determined by level crossing resonance [6]. Early μSR experiments made the surprising and important discovery that muonium centres are formed in two distinct paramagnetic states at low temperatures in Si, Ge, GaAs and GaP. Each state carries a magnetic moment of one Bohr magneton. However, whereas one of these has major spin density centred on the muon (as expected for a ''trapped atom'' state located in an interstitial cage) the other has it divided between two neighbouring host atoms, with the muon squeezed into the chemical bond between them, at or near a node of the unpaired electron wavefunction [7]. We denote the two states as Mu^0_T and Mu^0_{BC}, with the superscript denoting the neutral charge-state and the subscript the tetrahedral cage-centred and bond-centred sites respectively. These are illustrated in Fig. 1.

This coexistence is a remarkable example of metastability. Prior to the μSR studies, no isolated hydrogen defect centre was known and the bond-centred state was quite unanticipated; in experimental and theoretical work prompted by the μSR findings, H^0_{BC} has since been detected in ESR spectra [8] and ab initio calculations which allow for lattice relaxation have found that it is the ground state of interstitial hydrogen in Si. The energy difference between the two sites proves to be rather small and it may be that H^0_T is the ground-state in other materials, such as Ge or GaAs [9].

In the tetrahedrally coordinated semiconductors, Mu^0_T is highly mobile; measurements in GaAs in fact provided the first example of quantum diffusion for the neutral muonium atom, showing a striking minimum in mobility around 90 K [10]. The low elastic distortion and absence of drag from a screening cloud of conduction electrons make an interesting comparison with Mu^+ diffusion in fcc metals [11,12]; this is illustrated in Fig. 2. The Mu^0_{BC} state is immobile in Si and GaAs, locked in place by the large local distortion (the Si–Si bond, for instance, must be stretched by about 40% of its intrinsic length to accommodate the muon). By implication, neutral hydrogen diffuses only via the tetrahedral cage sites. This may not be the case in other semiconductors: our own experiments on muonium diffusion in Ge, together with a re-examination of old μSR linewidth data, suggest that the energy barrier between the T and BC sites is low for this material, so that

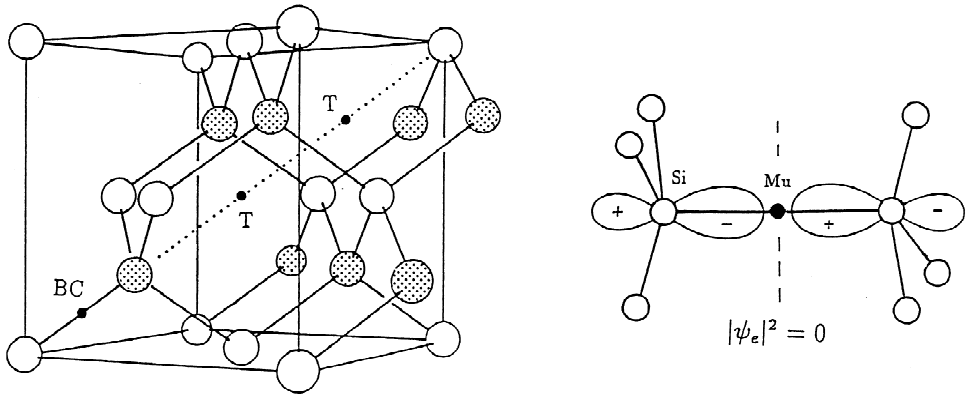

Fig. 1. Definition of the cage-centre (T) and bond-centre (BC) sites in the tetrahedrally coordinated lattice. Two inequivalent cage-centre sites (T_{III} and T_V) exist in the compound III–V semiconductors. The Mu^0_T state resembles a trapped hydrogen atom in materials with large band-gap but hybridises increasingly with the host atoms as band-gap decreases [4]; the Mu^0_{BC} wavefunction resembles an antibonding Si–Si function but is non-bonding on the muon (insert) [7].

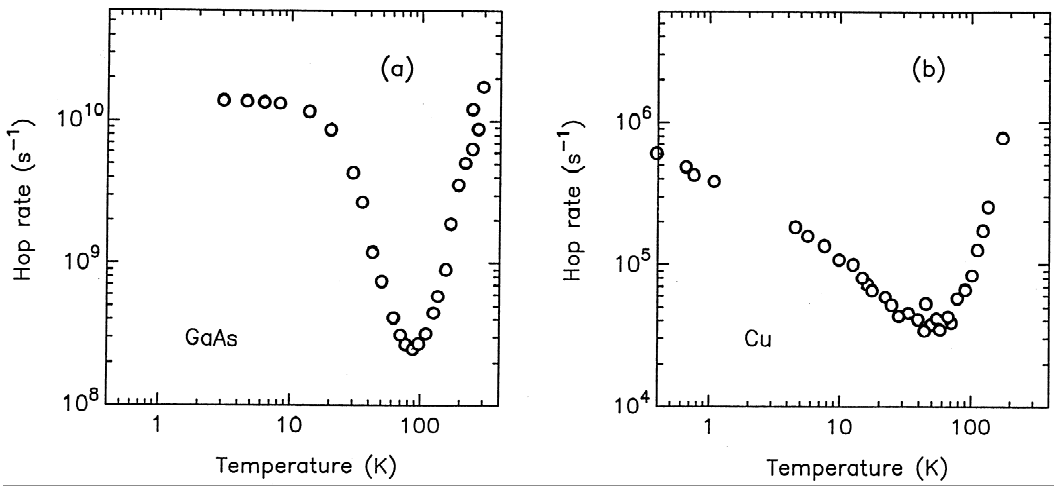

Fig. 2. Temperature-dependences of mobility for (a) the neutral muonium atom in GaAs, replotted from Kadono et al. [10], and (b) the small polaron state of positive muons in Cu metal, replotted from Luke et al. [12]. The very different magnitudes and low-temperature slopes reflect the absence of coupling to conduction electrons in the semiconductor.

both may be visited in the course of diffusion of the neutral state [13].

3. Charged diamagnetic states: an example of bistability

For the ionic states, the site preferences are much more pronounced. In the elemental semiconductors Si and Ge, the positively charged defect should be located at the bond centre, denoted Mu_{BC}^{+}, that is, the interstitial muon (or proton) seeks out the region of high electron density provided by the spin-paired valence electrons. The negatively charged centre ($Mu^{-}=\mu^{+}e^{-}e^{-}$, analogous to the hydride ion) cannot exist in this location but is repelled to the cage-centre, denoted Mu_{T}^{-}. This is a fine example of bistability in a defect centre.

The paramagnetic muonium centres correspond to singly-occupied energy levels within the forbidden gap between valence and conduction band [14–16]. Lowering the Fermi energy by heavy p-type doping therefore favours ionization of the neutral centres, creating Mu_{BC}^{+}, while raising it by heavy n-type doping favours double occupation, i.e., capture of a second electron to create Mu_{T}^{-}. Fig. 3 confirms the existence of this latter state in GaAs by level crossing resonance, a technique which exploits the presence of quadrupolar nuclei; this spectrum provides the strongest evidence for hydride ions in semiconductors. A similar identification of Mu_{BC}^{+} in p-type material is a high priority for the immediate future.

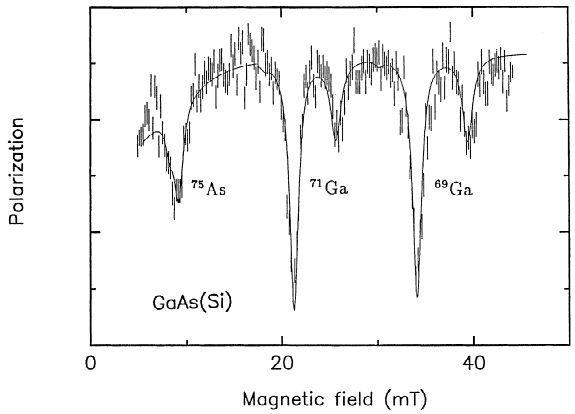

Fig. 3. Level crossing resonances for the Mu_{T}^{-} state in metallic GaAs:Si [17]. Their positions determine the electric field gradients induced at neighbouring nuclei, providing a test of models of electronic structure.

4. Charge-state and site transitions

Fig. 4 shows the results of measurements on ultrapure germanium, in which the evolution of muon polarization is recorded in a longitudinal magnetic field, i.e., a field applied parallel to the initial (muon beam) polarization. A strong depolarization sets in around 200 K which represents rapid trapping and detrapping of conduction electrons by the muon, i.e., repeated formation and ionization of muonium. The variation of this relaxation rate with applied magnetic field determines the muon–electron hyperfine interaction and thereby identifies the active muonium state. The fitted curves in Fig. 4 assign the initial peak near room temperature to charge-state cycles at the bond-centre, expressed in Eq. (1), and the broader maximum around 800 K to coupled charge and site transitions, with Mu^{0} at the cage-centre, as in Eq. (2) [13,18]. In Si, for comparison, a single broad maximum is seen, dominated by cycle (2); no separate peak attributable to cycle (1) is discernible [19].

$$Mu_{BC}^{0} \overset{\pm e}{\leftrightarrow} Mu_{BC}^{+} \quad (1)$$

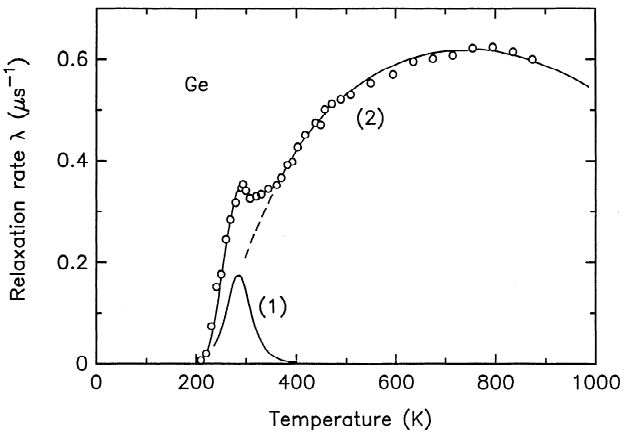

Fig. 4. Temperature-dependence of the muon depolarization rate in semi-insulating Ge, measured at ISIS in a longitudinal field of 10 mT. This is muon spin relaxation; an exponential relaxation function is fitted to extract a relaxation rate, λ, analogous to a spin–lattice relaxation rate T_1^{-1} in proton NMR. The drawn curves are fits to the two contributing charge–exchange cycles, Eqs. (1) and (2).

$$\mathrm{Mu}_{\mathrm{T}}^{0} \overset{\pm e}{\leftrightarrow} \mathrm{Mu}_{\mathrm{BC}}^{+}. \quad (2)$$

Yet another cycle dominates in n-type GaAs, namely the successive capture of electrons and holes, expressed in Eq. (3) [18,20]. By implication, cage-centred hydrogen acts as a recombination centre in this material.

$$\mathrm{Mu}_{\mathrm{T}}^{-} \overset{+h,+e}{\leftrightarrow} \mathrm{Mu}_{\mathrm{T}}^{0}. \quad (3)$$

5. Illumination

The effects of optical illumination promise to be another valuable source of information and the first observations in Si and Ge have recently been reported [21,22]. In our own experiments, we find the response in Si to be confined to p-type material, with lightly and heavily doped samples showing similar behaviour. This is illustrated in Fig. 5. The temperature-dependence of the light-induced depolarization implies involvement of a T to BC site-change, consistent with a suggestion made by Kadono et al. [21]. However, in apparent contradiction to another report [22], we find no response in n-type Si, whether lightly (10^{12} cm^{-3}) or more heavily (10^{14} cm^{-3}) doped. Further studies are required in this area to clarify the nature of the interaction of hydrogen centres with photo-generated carriers and to distinguish and characterize (e.g. with wavelength resolution) any direct photostructural transitions. Such experiments should establish whether hydrogen impurity influences photoconductivity or other opto-electronic functions.

6. Diffusion and trapping

The neutral paramagnetic muonium states are not detectable in all semiconductors; in InP, for instance, calculations suggest that $\mathrm{Mu}_{\mathrm{BC}}^{0}$ should ionize spontaneously [23]. No fewer than four distinct diamagnetic states are found in this material, however, according to temperature and dopant-type. Summarising a rather intricate assignment [24], $\mathrm{Mu}_{\mathrm{T_V}}^{+}$ coexists with $\mathrm{Mu}_{\mathrm{BC}}^{+}$ at low temperature, that is, the positive ion can exist within an interstitial cage defined by Group-V anions as well as at the bond centre; the $\mathrm{Mu}_{\mathrm{T_V}}^{+}$ state has not been identified in GaAs, but appears to play a role in the more ionic InP. A narrowing of the μSR linewidth between 150 and 200 K signals the onset of

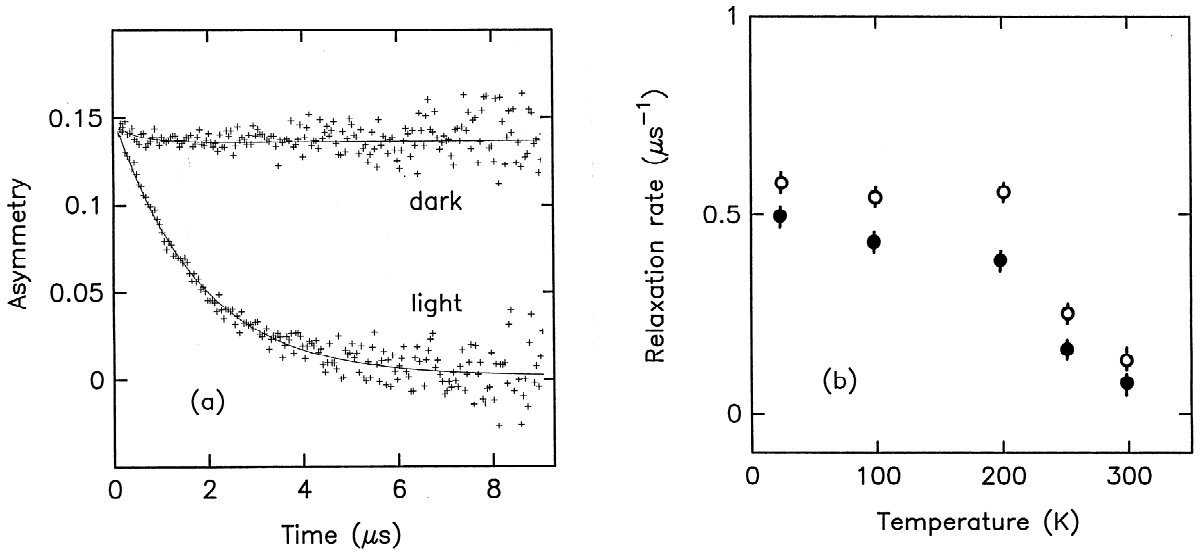

Fig. 5. Muon depolarization in lightly doped p-type Si, with and without illumination by a Xe flashlamp synchronized to the ISIS beam pulse (a) and the temperature-dependences of the optically induced depolarization rates (b) for two levels of doping—approximately 10^{11} cm^{-3}, filled circles, and 10^{13} cm^{-3}, open circles.

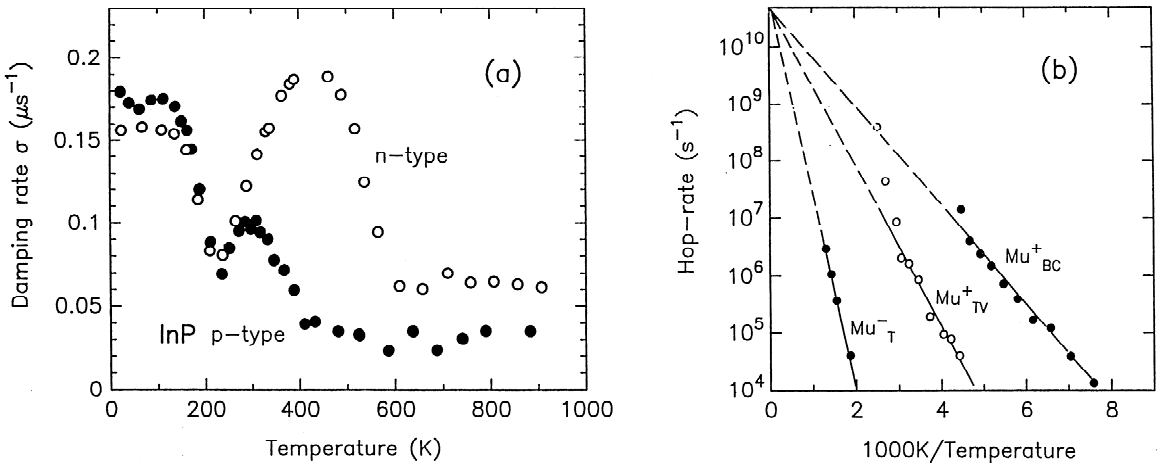

Fig. 6. Temperature-dependence of the transverse-field relaxation rate for diamagnetic muon states in InP, recorded at ISIS (a). This describes the damping of Larmor precession signals, analogous to T_2^{-1} linewidths in proton NMR, and displays motional narrowing and trapping. Hop rates (from zero-field data) for the three isolated states [24] are given in (b).

motion of these states and a peak at higher temperatures indicates that deeper traps can be found when the muons are able to explore the lattice. Fig. 6(a) shows that the high-temperature trapping site differs between n- and p-type material. The most likely candidates are Mu_T^- for n-type and a muon–acceptor pair, i.e., a passivation complex, for p-type. Zero-field experiments provide a full characterization of the diffusion rates, revealing a common prefactor but widely activation energies (Fig. 6b).

7. Neutral diamagnetic states: passivation complexes?

Fig. 7 shows relaxation data for heavily doped p-type GaAs, recorded in null external field at ISIS [25]. The temperature-dependence is indicative of muons moving from abundant shallow traps at low temperature to scarcer deep traps populated between about 400 and 600 K. The low-temperature state is almost certainly the positive ion located at intrinsic bond-centre sites, Mu_{BC}^+. The high temperature trapping peak, like that of Fig. 6(a), is another excellent candidate for muonium paired with acceptor atoms. This remains to be confirmed, e.g., by muon level crossing resonance, in which case dynamical information (on the formation and break-up of these complexes) as well as structural information should be available.

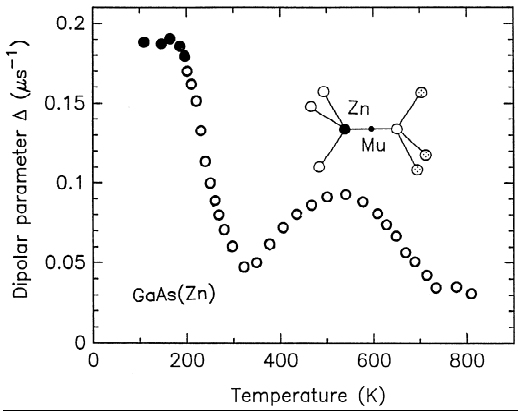

Fig. 7. Temperature-dependence of the zero-field relaxation parameter for p-type GaAs(Zn) doped at approximately 10^{19} cm^{-3} [25]. This parameter (a Gaussian decrement) is a measure of the rms dipolar interaction with neighbouring nuclei. Motional narrowing between 200 and 300 K signals diffusion from a low-temperature site; the trapping peak around 500 K could indicate formation (and, above 600 K, the break-up) of a Mu–Zn pair.

8. Conclusions

Building on earlier spectroscopic studies, predominantly of the neutral muonium states, these more recent results imply a remarkable interplay between charge-state and crystallographic location for hydrogen in semiconductors. This carries two major implications for the functional properties of these materials. The first is that we may be close to identifying the elusive transport states of hydrogen in semiconductors and we suggest that these switch from the positive ion (proton) to the neutral interstitial atom to the negative (hydride) ion, according to temperature and to the type and level of doping. In pure or lightly doped material at high temperatures we suggest that the diffusion is controlled by changes of site and lattice configuration, coupled to charge-state transitions; i.e., diffusion is linked to the interaction with charge carriers. The second is that interstitial hydrogen can act as a centre for electron trapping and detrapping, or electron–hole recombination. Work on Si has reached the stage where all these properties of the isolated states can be accounted for in terms of a consistent sets of energy levels and barriers [15,16]. Our future work is aimed at obtaining a similarly complete set of parameters for each material of importance, and achiev-

ing a more detailed understanding of the pairing with dopant atoms. A spectroscopic determination of the local electronic structure of the passivation complexes would be another major scoop for μSR!

Acknowledgments

On the occasion of the retirement of Erik Karlsson, SFJC wishes to dedicate this paper to him, thanking him for a welcome to the CERN μSR Collaboration in the early eighties.

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