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μSR RESEARCH IN SEMICONDUCTORS

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ABSTRACT

Muon and muonium states in semiconductors especially silicon and germanium, have been the subject of μSR research from the birth of the μSR technique until the present. They are now under active investigation at at least three laboratories. Three different electronic states of the muon impurity have been firmly identified in silicon and more tentatively in germanium. This research has produced a significant amount of published literature which, due to the span of time and distance between the various experiments, shows large differences in technique, emphasis and style. I will attempt to present a coherent view of this literature distinghuishing the well-understood effects from those not understood.

INTRODUCTION

The study of the semiconductors silicon and germanium is one of the most interesting, complicated and potentially rewarding fields of muon spin rotation research. The aesthetically simple Breit-Rabi Hamiltonian beautifully describes the energy levels of a muonium atom, and the host is perhaps the purest and best understood of all solid state systems, but the interstitial atom is buffeted by a multitude of forces from electrons, holes, phonons and traps. The complete problem is far from being solved. I will attempt to review here the progress that has been made understanding how the positive muon interacts with its semiconductor host with various dopings and at various temperatures. My emphasis will be on three major themes: 1) In what electronic states does a muon find itself in a semiconductor? 2) What parameters are required to give an accurate description of the time evolution of these states? 3) What experimental techniques can be applied to the determination of the doping and temperature dependence of these parameters?

This field was the subject of a review by Brewer *et al*[1] in 1975, and in what follows, I will concentrate on the more recent experimental results and the ways in which they necessitate a re-evaluation of the older work.

THE ELECTRONIC STATES

Figure one shows two Fourier transforms of μSR data[2] taken in an applied transverse magnetic field of 100 gauss. The quartz transform shows a large peak at low frequency which is due to the precession of "free" muons, or muons in a diamagnetic environment, and a pair of lines at higher frequency from the two-frequency precession of muonium. The splitting of the muonium lines yields a hyperfine frequency for muonium in quartz equal to that in vacuum. A free muon signal and muonium precession is also evident in the silicon data, but the larger splitting of the muonium lines implies a weaker hyperfine interaction. The intermediate-frequency peaks in the Si spectrum are attributable to "anomalous muonium". These three types of signal in Si represent three distinct electronic states of the muon; under varying conditions of doping and temperature they may be observed in-

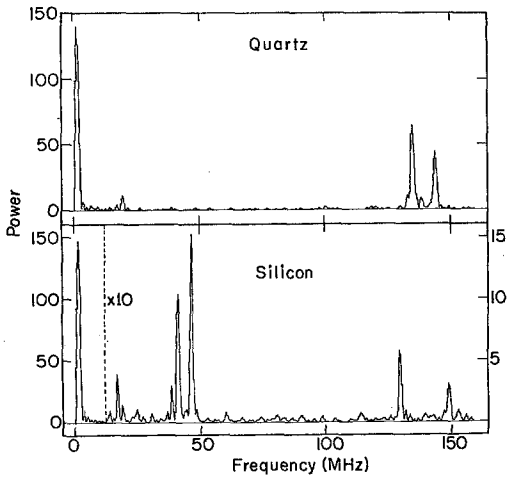

Fig. 1 μSR frequency spectra for fused quartz and p-type Si (5×10^{12} acceptors/cm^3) at 77 K in a transverse field of 100 G. In the lower graph the vertical scale is expanded by a factor of 10 to the right of the dashed line.

dependently. The fact that all three are observed simultaneously in this Si sample (5×10^{12} acceptors/cm^3, 77 K) implies that the three states form simultaneously (ie, within a muonium hyperfine period, 10^{-10} s, of the muon stop). I will follow convention and label these fractions of the total muon polarization "h" for the free (or "hot") fraction, f_{Mu} for the muonium fraction and f_* for the anomalous muonium fraction. A complete accounting of the total muon polarization in Si would imply $h + f_{Mu} + f_* = 1$.

THE PARAMETERS

A description of the energy levels of a state and hence of the observable precession frequencies is given by the parameters of the relevant spin Hamiltonian. For our purposes this means A, the hyperfine frequency. (The electronic and muon g-factors are consistent with values of 2.)

In order to describe the interaction of muonium with its host, Ivanter and Smilga developed a theory[3] in which one assumes that the muonium electron is depolarized or "flipped" at an average rate ν and that the muonium atom as a whole has a "chemical" lifetime τ. It is generally assumed that at the end of the chemical lifetime the muonium atom is either ionized or reacts chemically, placing the muon in a diamagnetic environment.

An additional interaction of a muon or muonium atom with the host is the depolarization due to so-called random local magnetic fields (RLMF) such as those produced by the randomly oriented nuclear moments of the host.

As will be seen, muonium in semiconductors tends to disappear with heavy doping and high temperatures. This could be caused by 1) a decrease in F_{Mu}, 2) a decrease in A, 3) an increase in ν, or 4) a decrease in τ.

THE EXPERIMENTAL TECHNIQUES

If the external magnetic field is oriented perpendicular to the initial muon polarization and if the various electronic states remain undisturbed for a sufficiently long time, their precession at characteristic frequencies may be directly observed as in Fig. 1. Then a Fourier transformation of the data is sufficient to yield h, f_{Mu} and f_* as well as the pertinant hyperfine frequencies A. A careful examination of the time histogram will also yield the relaxation times T_2 of the various states which may be related to RLMF, τ, or ν. Another powerful technique using a weak perpendicular field is the observation of an apparent change of the initial phase of the free muon signal which indicates that a paramagnetic state

such as muonium was formed at time zero and "chemically" reacted to place the muon in a stable diamagnetic environment after a time τ which is longer than a muonium hyperfine period but shorter than a muonium precession period.

The external field may also be oriented parallel to the initial polarization. In this case, it is the polarization along the field axis which is measured. The polarization observed for muonium atoms in zero field is 0.5, corresponding to the M=1 eigenstate, and at higher fields the hyperfine interaction is partially "quenched" resulting in a characteristic increase in the polarization whose form depends on a critical field $H_c \propto A$. If the muonium state is disrupted by a rapid electron depolarization ν, this quenching effect is degraded, but a chemical lifetime τ which is much longer than a hyperfine period will have no effect on the quenching curve. This allows one, for example, to determine the hyperfine frequency of Mu in spite of very fast reactions. The presence of several states with different hyperfine frequencies will appear as several sharp rises in a plot of polarization versus field, although a sharp rise may also signal the point at which the external field exceeds the RLMF. It is important to take into account any longitudinal relaxation with time of the polarization and to correctly extrapolate the signal to time zero. The relaxation time itself also contains physical information, but it may represent an undetermined mixture of the simultaneous relaxation of several states and hence be difficult to interpret.

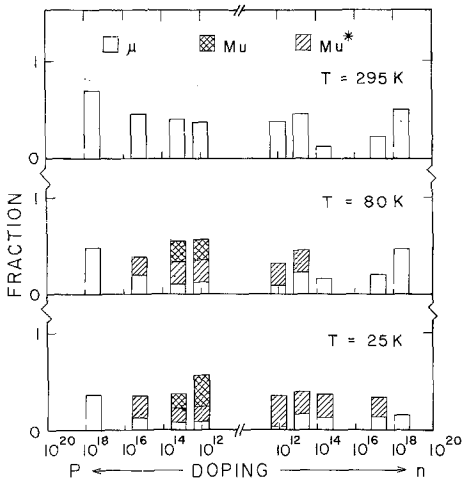

Fig. 2 The measured fractions (h, f_{Mu} and f_*) of the initial muon polarization appearing in the three precession components μ^+, Mu and Mu* as a function of temperature and doping.

EXPERIMENTAL RESULTS: Si

The transverse field measurements of the free muon fraction h by Feher et al.[4], Eisenstein et al.[5] and by the SIN group[6] (Fig. 2) are all in agreement. The large values of h observed at both doping extremes is presumably related to the destruction of muonium by free charge carriers (as in the case of metals) via electrostatic screening. Also noteworthy is the minimum in h at room temperature for intermediate n-doping which may reflect the crossing of a muonium impurity level in the energy gap by the doping-dependent Fermi level. Measurements of the free muon relaxation at 100 G yielded[7] values of T_2 which were strongly correlated with h: the larger h is, the longer T_2 is.

The hyperfine frequency for muonium in Si was determined[8] by Andrianov et al. in a classic longitudinal field quenching experiment at room temperature which yielded the result A(Si)/A(vac) = 0.41 ± 0.03 (see Fig. 3). The quenching of Mu is also apparent in the earlier longitudinal field data of Eisenstein et al.[5] (see Fig. 4), but they were unable to correctly interpret this data due to their failure to account for the time-dependence of the polarization. The hyperfine frequen-

cy was later measured in transverse field at low temperature by Brewer et al.[2] with the result A(Si)/A(vac) = 0.45 ± 0.02. Measurements at SIN[7] have shown that this hyperfine frequency remains unchanged in a p-type sample (3 x 10^{13} acceptors/cm^3) from 33 K to 247 K.

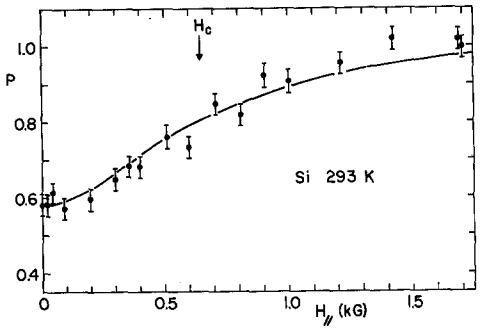

Fig. 3 The residual muon polarization extrapolated to zero time vs. the longitudinally applied magnetic field for p-type Si (1.6 x 10^{13} acceptors/cm^3) at room temperature. The data are consistent with the quenching of Mu with a critical field H_C=643 G (solid curve).

The doping dependence of f_{Mu} for three temperatures is shown in Fig. 2. It is interesting to note that although Mu is not observed in transverse field at room temperature or in n-type samples, it is clearly in evidence there in the longitudinal field data of Eisenstein et al. This indicates that the mechanism for Mu disappearance in Si involves a chemical lifetime τ. Andrianov et al. conclude from their quenching curve that ν is negligibly small, and they find that the entire muon polarization is accounted for ($h + f_{Mu} = 1$) for p-type Si (1.6 x 10^{13} acceptors/cm^3) at room temperature.

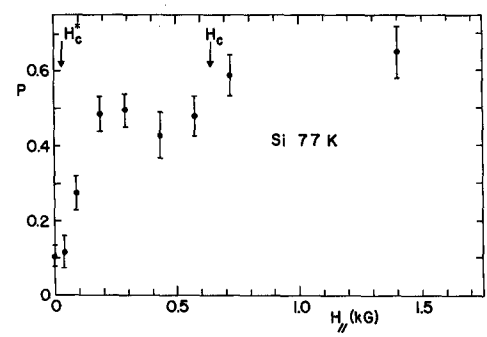

Fig. 4 The approximate residual muon polarization vs. the longitudinally applied field for n-type Si (4 x 10^{13} donors/cm^3) at 77 K. The data simultaneously indicate quenching behaviour for Mu (H_C=643 G) and perhaps for Mu^* ($H^*_C \approx 30$ G).

The longitudinal field quenching data of Eisenstein et al.[5] at low temperature (Fig. 4) show a significant rise in the polarization at a critical field $H^*_C < H_C$. Although possibly due to the RLMF from Si^{29} nuclei, this is tantalizing evidence for an additional electronic state with a further reduced hyperfine interaction which approximates the effect of RLMF via an anisotropic Hamiltonian. This suspicion was confirmed by the discovery[2] of anomalous muonium precession by Brewer et al. They showed that Mu^* was indeed anisotropic and that it was characterized by a hyperfine frequency 50 times smaller than the vacuum value, in fair agreement with the H^*_C observed by Eisenstein et al.

Transverse field measurements of f_* (Fig. 2) are in striking qualitative agreement with the Mu^* fraction one can deduce from the longitudinal field data of Eisenstein et al. This agreement leads one to conclude that the disappearance of Mu^*, unlike that of Mu, is not related to a chemical lifetime effect. The observation by Andrianov et al. that $h + f_{Mu} = 1$ at room temperature suggests that the disappearance of Mu^* is simply due to a decrease in f_*.

Brewer et al. gave a description of Mu* which treated its anisotropy by employing an effective isotropic hyperfine interaction whose strength depended upon the orientation of the crystal in the field. This approach required an electronic g-factor with the improbable value of 13. Recent work at SIN has shown[9] that a much more consistent description is possible with an anisotropic hyperfine interaction with axial symmetry about any one of the four [111] axes. The spin Hamiltonian has the form:

$$\mathcal{H}^* = A_{\perp}(I_x S_x + I_y S_y) + A_{||} I_z S_z - g_e \mu_B \vec{S}\cdot\vec{H} - g_\mu \mu_\mu \vec{I}\cdot\vec{H} ,$$

where z corresponds to a [111] axis and the constants have the values:

$$|A_{\perp}| = 92.1 \pm 0.3 \text{ MHz},$$

$$|A_{||}| = 17.1 \pm 0.3 \text{ MHz},$$

$A_{\perp}$ and $A_{||}$ have the same sign,

$$g_\mu = 2.01 \pm 0,01,$$

$$g_e = -2.2 \pm 0.2.$$

The resulting comparison of theory and experiment is shown in Fig 5.

Except for the room temperature experiment by Andrianov et al. on a p-type sample, $h + f_{Mu} + f_* < 1$. A possible way out of this dilemma is suggested by an observation made by the Berkeley group[1] of a rapidly relaxing ($T_2 \sim 30$ ns) free muon signal superimposed on the longer-lived h fraction in cold n-type Si at high applied field. This observation, which has been tentatively confirmed[7] at SIN appears to imply the existence of yet another possible fate for the incoming muon. It has been suggested that this "f_+ fraction" represents muons which after thermalizing in a diamagnetic environment capture electrons to form Mu or Mu* on a time scale of 30 ns.

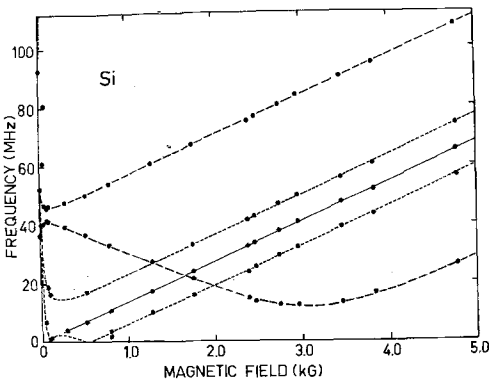

Fig. 5 Observed precession frequencies in Si as a function of the applied field along the [111] direction. Theoretical curves are included for the μ^+ component (solid line) and for the Mu* components. The light (heavy), broken curves correspond to Mu* centers whose symmetry axes make an angle θ=0 (70.5) with the field. The Mu frequencies are not shown.

EXPERIMENTAL RESULTS: Ge

The fact that Si and Ge have identical crystal structures and very similar electronic band structures would lead one to expect similar μSR phenomena in the two hosts. Free muon (h) and muonium (f_{Mu}) precession have both been observed in Ge, and there is some evidence that an anomalous state (f_*) similar to that in Si may also form in Ge.

Transverse field measurements of the temperature-dependence of h and the free

muon T_2 in Ge by Feher et al.[4], Eisenstein et al.[5] and Andrianov[10] et al. are consistent with similar measurements performed in Si up to a point. The fraction h decreases with decreasing temperature except in a heavily doped n-type sample where it remains close to unity. The same sample showed no relaxation at any temperature. Behaviour quite different from that observed in Si was apparent for a p-type sample (10^{14} acceptors/cm^3) measured by Andrianov et al. which showed no relaxation between 80 K and room temperature and a T_2 which dramatically decreased as the temperature was raised further to 370 K. Temperatures above room temperature have not yet been investigated for Si, but the qualitative behaviour is consistent with the Si data.

Muonium precession in transverse field was observed at 77 K by Andrianov et al.[10] who determined that $h + f_{Mu} = 1$ and by Gurevich et al.[11] who employed the two-frequency precession technique to determine that $A(Ge)/A(vac) = 0.56 \pm 0.01$. Very large Mu signals were observed in both of these experiments, a result which has not been attained by other groups[7,13]. Longitudinal field data of Eisenstein et al. at 293, 77 and 10 K do not show muonium quenching for an n-type sample (10^{15} donors/cm^3); the large doping presumably causes either a small f_{Mu} or a large ν.

In a study of Ge (unspecified doping) in large longitudinal fields, Gurevich et al. observed[12] a striking relaxation which, due to its strong dependence on the applied field, must be connected with muonium formation. Their T_1 increases with increasing field (as would be expected from the decoupling effect of the field on muonium) and which also increases with increasing temperature. Using a somewhat complex analysis, the authors determine that the relaxation is due to the depolarization of the muonium electron at a rate ν. If it is assumed that $\nu \ll A$, they find a value for A at 233 K which is in fair agreement with that found with two-frequency precession at 77 K, but their corresponding value at 267 K is then 60% larger than the vacuum value. They reject the possibility of $A(Ge) > A(vac)$, although it is known[14] that interstitial hydrogen has a hyperfine frequency in many solids which is larger than its vacuum value. In any case, it is difficult to accept such a strong temperature dependence of A. The assumption that $\nu \gg A$ again results in a temperature-dependent A, but this time one which is 20 to 30 times weaker than the vacuum value.

In their analysis, Gurevich et al. assumed that τ, the chemical lifetime of Mu in Ge is effectively infinite. That this is not the case is elegantly demonstrated by measurements performed in transverse field by Kudinov et al.[15,16]. These authors observed phase shifts (see Fig. 6) of the free muon signal of up to 50° as a function of applied field and temperature which are only compatible with a muonium-like state of short lifetime τ. They found that the agreement between theory and experiment could be improved by including the effects of the depolarization of the muonium electron with a rate ν. Interestingly, the product $\nu\tau$ always turned out to be close to unity, and assuming the constancy of $\nu\tau$ allowed them to extract values of τ from polarization data at temperatures too high for the phase shift method to be usable. The authors proceeded to compare the temperature-dependent values of τ with a theoretical expression involving a barrier height for the muonium reaction, and they were able to cleanly connect the results of the two methods. The resulting barrier height was approximately 0.18 eV.

Does Mu* exist in Ge? One of the cases considered by Gurevich et al[12] in their longitudinal field experiment required the existence of a muonium-like state in Ge with a hyperfine frequency 20 to 30 times smaller than the vacuum value. This is very reminiscent of the Mu* state observed in Si. Again, it is distasteful to allow the hyperfine frequency of such a state to vary 36% in 34 K as Gurevich would like. ($A_*(Si)$ is unchanged[7] from 33 K to 130 K.) It is also difficult to understand how this state has escaped detection[13] in transverse field experiments at low temperatures. A probable clarification of this point is imminent in a recent report from SIN[17] that weak Mu* precession similar to that observed in Si has been detected in Ge.

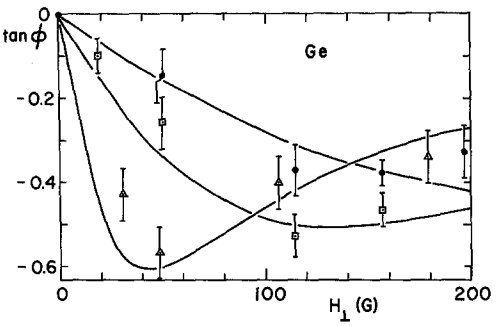

Fig. 6. Measurements of the phase shift ϕ of the free μ^+ signal vs. the applied transverse field for an n-type Ge sample (10^{14} donors/cm^3). The circles, squares and triangels are for temperatures of 198, 187 and 177 K respectively, and the solid curves are calculated from the theory of muonium depolarization.

It is unknown whether or not a rapidly relaxing diamagnetic component similar to the f_+ fraction is present in Ge.

CONCLUSIONS

Given the range of effects and the variety of techniques used to study them, it is physically significant when two or more experiments of different types agree. I believe there is agreement about the following: 1) The hyperfine parameters for Mu and Mu* are accurately known and at least for the case of Si are fairly stable against changes in doping and temperature. 2) The disappearance of the muonium-like states in transverse field experiments at high levels of doping and at high temperatures is due to various distinct causes: for Mu in Si, a shortening of the "chemical" lifetime τ, for Mu* in Si, a decrease in the formation probability f_* and for Mu in Ge, a simultaneous increase in the electron depolarization rate ν and a decrease in the chemical lifetime τ.

Outstanding problems include: 1) The entire initial muon polarization is seldom accounted for. 2) The observed changes in strength and relaxation time of the free muon signal with temperature and doping are not understood. 3) Convincing physical models are lacking for the various electronic states and the transitions between them.

I would like to close with the thought that although the complete solution of these problems will be difficult, it will probably be well worth the trouble in order to understand the simplest impurity problem in systems where the manipulation of impurities is of prime economic importance.

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