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# Spin dynamics of transitions among muon states in semiconductors

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**Abstract.** The muon spin rotation ( $\mu$ SR) technique was used to study muonium centers in the elemental semiconductors diamond and silicon, and the compounds CuCl, CuBr and CuI. In diamond, the thermally-activated transition from the isotropic muonium state Mu to the anisotropic muonium state Mu\* is used to determine the sign of the Mu\* hyperfine constants. It is found that the isotropic part of the Mu\* hyperfine interaction is *negative* presumably due to exchange polarization, supporting the bond-center model for Mu\*. Two isotropic muonium states, Mu<sup>I</sup> and Mu<sup>II</sup>, are observed at low temperatures in CuCl and CuBr, and a diamagnetic 'bare' muon state ( $\mu^+$ ) is seen at high temperature. A study was made of the irreversible Mu<sup>I</sup>  $\rightarrow$  Mu<sup>II</sup>  $\rightarrow$   $\mu^+$  transitions in CuCl. Several unusual properties of these muonium centers in the copper halides, when compared with Mu in other tetrahedrally coordinated materials, will be discussed. The low-temperature Mu and Mu\* states in high-purity silicon both become unstable at higher temperature, undergoing irreversible transitions to the  $\mu^+$  state. At the highest temperatures investigated, even this  $\mu^+$  state becomes unstable, indicating *reversible* transitions of the type  $\mu^+ \leftrightarrow$  Mu. A generalized theory which treats the time-dependent muon polarization during transitions among various muon states is presented and applied to the situations mentioned above.

## I. Introduction

A positive muon implanted into an insulator or a semiconductor may bind an electron to form a muonium ( $\mu^+e^-$ ) atom. Since the muon mass is approximately  $\frac{1}{9}$  of the proton mass, muonium may be considered a light isotope of hydrogen [1]. Properties of muonium and hydrogen in vacuum are compared in Table 1. It is expected that these two atoms will remain electronically similar when implanted into a solid. In contrast to the case of hydrogen, which has not been observed in a paramagnetic state in semiconductors, two different muonium states have been observed in semiconductors: i) normal muonium (Mu), which is characterized by a strong isotropic hyperfine (*hf*) interaction, and ii) anomalous muonium (Mu\*), characterized by a weak axially symmetric *hf* interaction. Such muonium states can be studied with the muon-spin-rotation ( $\mu$ SR) method [3, 4]. In this technique, polarized positive muons ( $\mu^+$ ) are stopped in the material to be investigated, and the time-dependent muon polarization is monitored via positrons from the anisotropic muon-decay which are recorded as a function of the elapsed time since a muon stop.

The spin Hamiltonian for normal muonium, which describes the *hf*

Table 1  
Comparison of hydrogen and muonium in vacuum from Ref. 2.

	H	Mu
Mass ( $m_e$ )	1837.15	207.769
Reduced electron mass ( $m_e$ )	0.999456	0.995187
Ground-state radius $a$ (Å)	0.529465	0.531736
Ground-state energy (eV)	-13.5984	-13.5403
Nuclear gyromagnetic ratio $\gamma$ ( $s^{-1} T^{-1}$ )	$2.67520 \times 10^8$	$8.51607 \times 10^8$
Hyperfine frequency $A$ (MHz)	1420.41	4463.30

interaction in an external field  $\vec{B}$  can be written:

$$\mathcal{H} = hA\vec{I} \cdot \vec{S} - g_\mu\mu_\mu\vec{I} \cdot \vec{B} - g_e\mu_B\vec{S} \cdot \vec{B} \quad (1)$$

where  $\vec{I}$  and  $\vec{S}$  are the muon and electron spin operators and  $A$  is the  $hf$  frequency, which is proportional to the electron density at the muon site [2, 5]:

$$A = -\frac{2}{3h}\mu_0g_eg_\mu\mu_B\mu_\mu|\Psi(0)|^2 \quad (2)$$

The energy-level diagram for normal muonium is shown in Fig. 1. In an external magnetic field transverse to the initial muon polarization, the indicated  $\Delta m = \pm 1$  transitions are observed. For Mu in vacuum,  $A_{\text{vac}} = 4463$  MHz, but in semiconductors and insulators  $A$  is in generally much smaller.

In the semiconductors diamond [2] silicon [6, 7], germanium [8], GaP and GaAs [9], an additional muonium state,  $\text{Mu}^*$ , is observed whose  $hf$  interaction has  $\langle 111 \rangle$ -axial symmetry. The  $hf$  interaction of  $\text{Mu}^*$  is strongly anisotropic, with

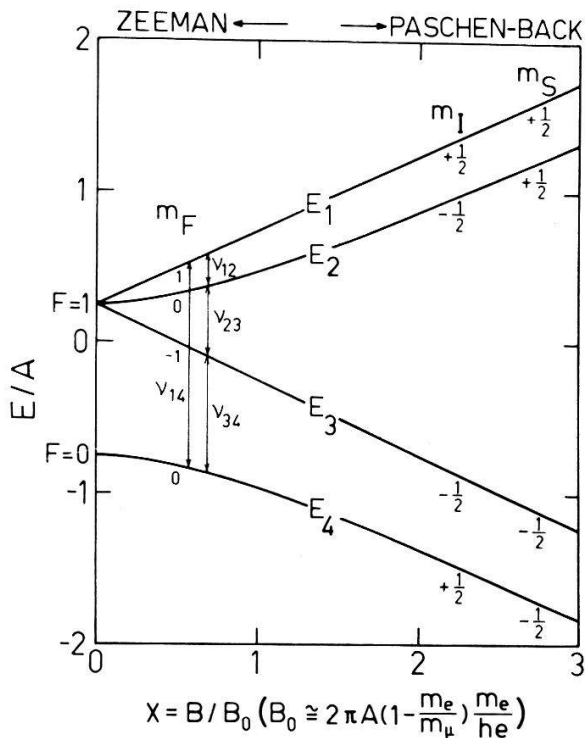


Figure 1  
Energy-level diagram for normal muonium (Mu). The magnetic field  $X$  is measured in units of  $B_0$ . In vacuum,  $B_0(\text{vac}) = 0.15868$  T. The transitions indicated corresponds to the observable  $\mu\text{SR}$  frequencies in a transverse field.

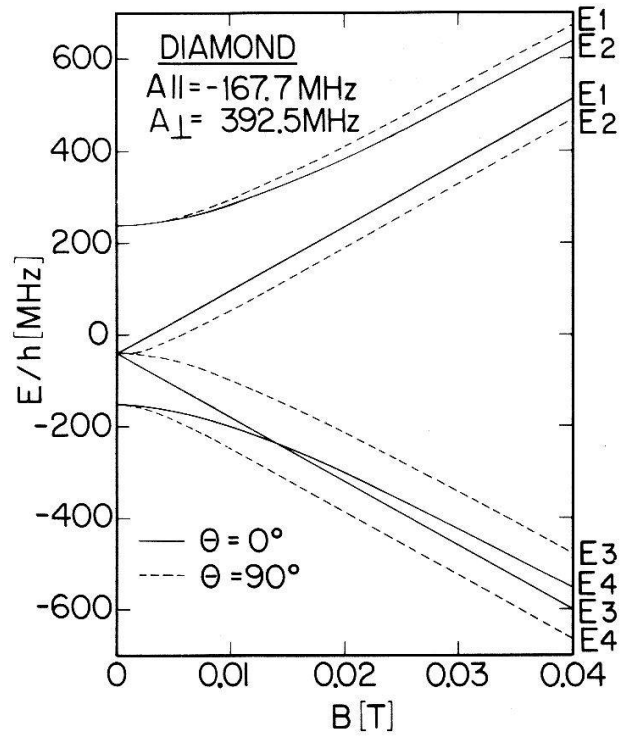


Figure 2

Energy-level diagram for anomalous muonium ( $\text{Mu}^*$ ) in diamond. The eigenvalues of the spin Hamiltonian (equation (3)) depend on the angle  $\Theta$  between the symmetry axis  $\vec{n}$  and the magnetic field  $\vec{B}$ .

coupling constants more than one order of magnitude weaker than that of vacuum  $\text{Mu}$ . The anisotropic spin Hamiltonian for  $\text{Mu}^*$  has the form:

$$\mathcal{H} = hA_{\perp} \vec{I} \cdot \vec{S} + h(A_{||} - A_{\perp})(\vec{I} \cdot \vec{n})(\vec{S} \cdot \vec{n}) - g_{\mu}\mu_{\mu} \vec{I} \cdot \vec{B} - g_e\mu_B \vec{S} \cdot \vec{B} \quad (3)$$

Here  $\vec{n}$  is a unit vector along one of the four equivalent  $\langle 111 \rangle$  axes in the diamond lattice. Figure 2 gives the energy-level diagram for  $\text{Mu}^*$  in diamond, using the hyperfine constants from Ref. 2. The anisotropy of the  $\text{Mu}^*$   $hf$  interaction implies that it is immobile in the host lattice. It is convenient to express the  $\text{Mu}^*$   $hf$  parameters in terms of the isotropic and anisotropic contributions [10]  $A_s$  and  $A_p$ , or in terms of  $\omega_0$  and  $\omega^*$  as in [11]:

$$A_{\perp} = A_s - A_p = \frac{1}{2\pi} \omega_0 \quad (4)$$

$$A_{||} = A_s + 2A_p = \frac{1}{2\pi} (\omega_0 + \omega^*)$$

The measured low-temperature  $hf$  parameters for all muonium states known in the diamond and zincblende semiconductors are summarized in Table 2.

An outstanding problem regarding  $\text{Mu}^*$  is the *sign* of the  $hf$  coupling constants  $A_s$  and  $A_p$  defined in equations (3, 4). Since the electron spin density at the muon is reflected by  $A_s$ , knowledge of its sign is required in order to construct a realistic model of  $\text{Mu}^*$ . For example, a positive spin density might indicate that a single paramagnetic electron occupies an orbital which is centered on the muon, while a negative spin density suggests that initially diamagnetic electrons at the muon are polarized by a more distant paramagnetic electron due to an exchange



Table 2

Low-temperature hyperfine parameters for anisotropic  $\text{Mu}^*$  ( $A_{\parallel}$ ,  $A_{\perp}$ ) and isotropic  $\text{Mu}$  ( $A$ ) in diamond and zinblende semiconductors, the maximum temperatures of their observation and observed transitions among the muon states. Beside some minor corrections the values are taken from Refs. 3, 12.

Sample	$A_{\parallel}$ (MHz)	$A_{\perp}$ (MHz)	$A$ (MHz)	$T_{\text{Mu}^*}^{\text{max}}$ (K)	$T_{\text{Mu}}^{\text{max}}$ (K)	Transitions
C	+167.983(57)	-392.586(55)	3711(21)	$\geq 1000$	405	$\text{Mu} \rightarrow \text{Mu}^*$
Si	16.819(11)	92.59(5)	2006.3(2.0)	165	300	$\text{Mu}^* \rightarrow \mu^+$ $\text{Mu} \leftrightarrow \mu^+$
Ge	27.269(13)	131.037(34)	2359.5(2)	85	120	$(\text{Mu}, \text{Mu}^*) \rightarrow \mu^+$
$\beta$ -SiC				$\geq 22$		$\mu^+ \rightarrow \text{Mu}?$
GaP	219.0(2)	79.48(7)	2914(5)	100	240	
GaAs	217.8(2)	87.74(6)	2883.6(3)	100	300	$\text{Mu}^* \rightarrow \mu^+$
ZnS			3547.8(3)		$\geq 10$	
ZnSe			3456.7(3)		$\geq 13$	
CuCl			1334.24(7) <sup>I</sup>		60 <sup>I</sup>	$\text{Mu}^{\text{I}} \rightarrow \text{Mu}^{\text{II}}$
			1212.75(12) <sup>II</sup>		445 <sup>II</sup>	$\text{Mu}^{\text{II}} \rightarrow \mu^+$
CuBr			1403.70(7) <sup>I</sup>		153 <sup>I</sup>	$\text{Mu}^{\text{I}} \rightarrow \text{Mu}^{\text{II}}$
			1250.79(22) <sup>II</sup>		$\geq 300^{\text{II}}$	$\text{Mu}^{\text{II}} \rightarrow \mu^+?$
CuI			1670.94(23)		102	

interaction. In a standard  $\mu\text{SR}$  experiment only the relative sign of  $A_s$  and  $A_p$  can be determined.

In diamond, zero-field measurements of the temperature-dependent  $\text{Mu}^*$  signal strength in a powder sample demonstrated that a thermally-activated transition occurs from the  $\text{Mu}$  to the  $\text{Mu}^*$  state [2]. Soon after this observation, Meier [11] suggested that single crystal measurements would show a resonant transfer of the muon polarization at particular applied magnetic fields where the  $\text{Mu}$  and  $\text{Mu}^*$  precession frequencies coincide, and that such a resonance could be used to determine the sign of the  $\text{Mu}^*$  hyperfine parameters. Such a measurement was attempted [13], but the sample was rich in nitrogen (type Ia), and rapid  $\text{Mu}$  relaxation, presumably due to impurity trapping, prevented a conclusive sign determination. In the present work, a nitrogen-poor stone (type IIb) was used, resulting in narrow precession lines and a sharp resonance. Furthermore, the elimination of  $\text{Mu}$ -trapping allowed us to follow the transition from the decay of the precursor  $\text{Mu}$  state to the enhancement of the  $\text{Mu}^*$  signal strength, and to describe both processes with a single Arrhenius law. The large temperature region over which  $\text{Mu}$  signals could be observed in this sample (up to 400 K) also permitted a measurement of the temperature-dependence of the  $\text{Mu}$   $hf$  frequency. A preliminary report of these experiments has been presented elsewhere [14].

Not only  $\text{Mu}$  in diamond, but *all* muonium states observed to date in semiconductors become unstable above a certain temperature  $T^{\text{max}}$  (see Table 2). At sufficiently high temperatures, only the precession of 'naked muons' ( $\mu^+$ ) in a diamagnetic environment is observed. Low-temperature  $\mu\text{SR}$  measurements in the group I–VII semiconductors [15]  $\text{CuCl}$ ,  $\text{CuBr}$  and  $\text{CuI}$  reveal  $\text{Mu}$  centers with

weak isotropic  $hf$  parameters, approximately  $\frac{1}{3}$  the vacuum value  $A_{\text{vac}}$ . In CuBr and CuCl two distinct Mu centers ( $\text{Mu}^{\text{I}}$  and  $\text{Mu}^{\text{II}}$ ) are observed at low temperatures, whereas in CuI only one Mu center was observed. The temperature dependence of their  $hf$  coupling constants displays unusual characteristics when compared with the other semiconductors.

In a further experiment, the thermally-activated transitions  $\text{Mu}^{\text{I}} \rightarrow \text{Mu}^{\text{II}} \rightarrow \mu^+$  in CuCl have been investigated. In addition, a search was made in CuCl for effects on the  $\mu\text{SR}$  spectra of the structural phase transition [16] from zincblende to wurtzite at 680 K and upon melting at 733 K.

Above room temperature, measurements on high-purity silicon show several interesting features: with increasing temperature, first the Mu signals disappear, then the  $\mu^+$  signal becomes stronger. At still higher temperatures the  $\mu^+$  depolarization rate increases as well. All the data for Mu and for  $\mu^+$  can be described consistently by a  $\text{Mu} \leftrightarrow \mu^+$  transition model. The predicted  $\mu^+$  frequency shift for high transition rates is in good agreement with the observations.

The behavior of the muon polarization during irreversible transitions among muonium states has been described for several simple cases [11, 17–19]. These treatments are insufficient, however, for the more complex transitions seen in CuCl and Si. Here we develop a more generalized theory suggested by Celio [20]. Besides being capable of describing reversible transitions for an arbitrary number of muon states, this theory treats the effect of loss and conservation of the muonium electron polarization during the transition and allows the inclusion of a phenomenological electron spin depolarization of the type discussed by Ivanter and Smilga [17]. This generalized theory permits a consistent description of the experimental data.

The Paper is organized as follows: In Section II we present the generalized theory describing transitions among muon states. The experimental technique and sample-specific details are given in Section III. In Sections IV, V and VI, the experiments performed on diamond, the cuprous halides and silicon are presented. Conclusions are presented in Section VII.

## II. Theory

In this Section we develop a general theoretical model suggested by Celio [20] which adequately describes the transitions among muon states which are of interest in this paper. In our discussion of the individual muon states, only the  $\text{Mu}^*$  case is considered, since Mu and  $\mu^+$  are described by the same spin Hamiltonian (equation (3)) with different  $hf$  parameter values. To simplify the expressions, we follow the notation of [11], where the  $\text{Mu}^*$   $hf$  parameters  $\omega_0$  and  $\omega^*$  are used. Introducing the vectors

$$\begin{aligned}\vec{\omega}_e &= \gamma_e \vec{B} = 2\pi \cdot 28024.21 \text{ MHz}/T \times \vec{B} \\ \vec{\omega}_\mu &= \gamma_\mu \vec{B} = 2\pi \cdot 135.53 \text{ MHz}/T \times \vec{B}\end{aligned}\tag{5}$$

and expressing the spin operators with the Pauli matrices  $\sigma$  and  $\tau$  for the muon and the electron respectively, the  $\text{Mu}^*$  spin Hamiltonian (3) can be rewritten:

$$\mathcal{H} = \frac{1}{4}\hbar\omega_0\vec{\sigma} \cdot \vec{\tau} + \frac{1}{4}\hbar\omega^*(\vec{\sigma} \cdot \vec{n})(\vec{\tau} \cdot \vec{n}) - \frac{1}{2}\hbar\vec{\omega}_\mu\vec{\sigma} + \frac{1}{2}\hbar\vec{\omega}_e\vec{\tau} \quad (6)$$

The  $g$ -factors in the muon and electron gyromagnetic ratios  $\gamma_i = g_i\mu_i/\hbar$  are taken to be isotropic. The spin Hamiltonians for the individual muon states are obtained from equation (6) as follows:

$$\begin{aligned} \text{Mu}^*: \quad & \omega_0 \neq 0, \quad \omega^* \neq 0 \\ \text{Mu}: \quad & \omega_0 \neq 0, \quad \omega^* = 0 \\ \mu^+: \quad & \omega_0 = \omega^* = \omega_e = 0 \end{aligned} \quad (7)$$

(a) *The time-dependent muon polarization in the  $\text{Mu}^*$  state*

The general density matrix for the two-particle system muon-electron is given by

$$\rho = \frac{1}{4}(1 + \vec{p}_\mu \cdot \vec{\sigma} + \vec{p}_e \cdot \vec{\tau} + p^{jk}\sigma_j\tau_k). \quad (8)$$

where

$$\begin{aligned} \vec{p}_\mu &= \text{Tr}(\rho\vec{\sigma}) \\ \vec{p}_e &= \text{Tr}(\rho\vec{\tau}) \\ p^{jk} &= \text{Tr}(\rho\sigma_j\tau_k) \end{aligned} \quad (9)$$

are the muon, electron and mixed polarizations. Using the commutation relations

$$\begin{aligned} [\sigma_j, \sigma_k] &= 2i\epsilon_{jkl}\sigma_l \\ [\sigma_j\tau_m, \sigma_k\tau_n] &= 2i(\delta_{jk}\epsilon_{mnr}\tau_r + \delta_{mn}\epsilon_{jkl}\sigma_l) \end{aligned} \quad (10)$$

the equation of motion for the density matrix  $\rho$

$$i\hbar \frac{d\rho}{dt} = [\mathcal{H}, \rho] \quad (11)$$

leads to the following set of 15 coupled differential equations for the polarizations

$$\begin{aligned} \dot{p}_\mu^j &= \epsilon_{jkl} \left[ \frac{\omega_0}{2} p^{lk} + \frac{\omega^*}{2} n_k n_m p^{lm} - \omega_\mu^k p_\mu^l \right] \\ \dot{p}_e^j &= \epsilon_{jkl} \left[ \frac{\omega_0}{2} p^{kl} + \frac{\omega^*}{2} n_k n_m p^{ml} + \omega_e^k p_e^l \right] \\ \dot{p}^{jk} &= \epsilon_{nlm} \left[ \delta_{jm} \delta_{kn} \frac{\omega_0}{2} (p_\mu^l - p_e^l) - \delta_{jn} \left( \frac{\omega^*}{2} n_m n_k p_\mu^l - \omega_\mu^m p^{lk} \right) \right. \\ &\quad \left. + \delta_{kn} \left( \frac{\omega^*}{2} n_j n_l p_e^m + \omega_e^l p^{jm} \right) \right] \end{aligned} \quad (12)$$

describing the time evolution in the undisturbed  $\text{Mu}^*$  state. With the vector

$$\vec{P} = \begin{pmatrix} \vec{P}_\mu \\ \vec{P}_e \\ p^{jk} \end{pmatrix} \quad (13)$$

this set of equations may be written as

$$\dot{P}_\alpha = M_{\alpha\beta} \cdot P_\beta \quad (14)$$

If  $U$  denotes the unitary matrix which diagonalizes  $M$  ( $U^{-1}MU = D$ ), we obtain

$$P_\alpha(t) = U_{\alpha n} U_{n\beta}^{-1} P_\beta(0) \exp(D_{nn}t) \quad (15)$$

where  $U$  and  $M$  are  $15 \times 15$  matrices. For an undisturbed state, the purely imaginary elements of the eigenvector matrix  $D$  are oscillation frequencies. For later reference, equation (15) may be rewritten as:

$$\vec{P}(t) = \exp(Mt) \cdot \vec{P}(0) \quad (16)$$

The disturbance represented by an exchange of spin between the bound electron and the surroundings can be taken into account by adding to the right-hand side of equation (12) relaxation terms of the form

$$\begin{aligned} \dot{p}_e^j &= \dots - 2\nu_{\text{ex}} \cdot p_e^j \\ \dot{p}^{jk} &= \dots - 2\nu_{\text{ex}} \cdot p^{jk} \end{aligned} \quad (17)$$

where for the moment  $\nu_{\text{ex}}$  is a phenomenological spin exchange rate. Such a disturbance has been studied in [17] and [21].

This set of equations can in certain cases be reduced. The muon polarization in the  $\text{Mu}^*$  state depends on three vectors: (i) the direction of the external field  $\vec{B}$  (taken to be the  $z$  axis), (ii) the unit vector  $\vec{n}$  parallel to one of the four equivalent  $\langle 111 \rangle$  directions in the crystal and (iii) the initial beam polarization  $\vec{p}_\mu(0)$ . The system of equation (12) and (17) can be separated into two subsystems, if  $\vec{n} \perp \vec{B}$  or  $\vec{n} \parallel \vec{B}$ . One subsystem involves only the component of the muon and the electron polarizations along the magnetic field (longitudinal subsystem), and the other contains only the perpendicular components (transverse subsystem). For the isotropic state  $\text{Mu}$ , such a separation into subsystems is always possible [17, 22].

In the Appendix, reduced sets of coupled differential equations are summarized for  $\vec{n} \perp \vec{B}$  and  $\vec{n} \parallel \vec{B}$  for the longitudinal and transverse subsystems.

### (b) *Spin dynamics of transitions among muon states*

In the investigated systems, the muon polarization may be carried over from one state to another (see Table 2). We are now concerned with the transformation of a state described by the spin Hamiltonian  $\mathcal{H}_1$  (equation (6)) into a state described by the Hamiltonian  $\mathcal{H}_2$  which has the same form but different  $hf$  parameters. Such a transformation is denoted by  $\mathcal{H}_1 \rightarrow \mathcal{H}_2$ . We assume that

$\mathcal{H}_1 \rightarrow \mathcal{H}_2$  occurs with the rate  $\Lambda_{12}$ , and we include the possibility of the inverse process  $\mathcal{H}_2 \rightarrow \mathcal{H}_1$  with the rate  $\Lambda_{21}$ . Consider first the case where the electron polarization is conserved during the transitions. This is a reasonable assumption in view of ESR experiments on radical termination reactions [23].

Celio [20] has suggested an elegant method to treat such transformations. The total polarization in state 1 at time  $t$  is given by (i) those muonium atoms which are in state 1 at time zero and remain there until time  $t$ , plus (ii) the muonium atoms which undergo a transition from  $2 \rightarrow 1$  at time  $t' < t$ , plus (iii) two transitions ( $1 \rightarrow 2 \rightarrow 1$ ), etc:

$$\begin{aligned} \vec{P}_1(t) = & \exp[(M_1 - \Lambda_{12})t] \cdot \vec{P}_1(0) \\ & + \Lambda_{21} \int_0^t dt' \exp[(M_1 - \Lambda_{12}) \cdot (t - t')] \exp[(M_2 - \Lambda_{21})t'] \cdot \vec{P}_2(0) \\ & + \Lambda_{12}\Lambda_{21} \int_0^t dt' \int_0^{t'} dt'' \exp[(M_1 - \Lambda_{12}) \cdot (t - t')] \\ & \times \exp[(M_2 - \Lambda_{21}) \cdot (t' - t'')] \exp[(M_1 - \Lambda_{12})t''] \cdot \vec{P}_1(0) \\ & + \dots \end{aligned} \quad (18)$$

The same holds for  $\vec{P}_2(t)$ , which is obtained by exchanging the indices 1 and 2. The *total* polarization  $\vec{P}^{\text{tot}}(t)$  is given by the sum:

$$\vec{P}^{\text{tot}}(t) = \vec{P}_1(t) + \vec{P}_2(t) \quad (19)$$

For the special case where only one jump is considered ( $\Lambda_{21} = 0$ ) we regain the expressions obtained by Percival and Fischer [18] and by Meier [11].

The integral expressions in equation (18) are equivalent to the following set of two coupled differential equations

$$\begin{pmatrix} \dot{\vec{P}}_1 \\ \dot{\vec{P}}_2 \end{pmatrix} = \begin{pmatrix} M_1 - \Lambda_{12} & \Lambda_{21} \\ \Lambda_{12} & M_2 - \Lambda_{21} \end{pmatrix} \cdot \begin{pmatrix} \vec{P}_1 \\ \vec{P}_2 \end{pmatrix} \quad (20)$$

Note that the matrices  $M_1$  and  $M_2$  in equation (20) determine the polarization evolution in the individual states 1 and 2 and that the 'off-diagonal' terms  $\Lambda_{12}$  and  $\Lambda_{21}$  are responsible for the polarization transfer.

The loss of the electron polarization during the transition may thus be introduced by multiplying these off-diagonal terms by a matrix  $\mathcal{A}$

$$\begin{aligned} \mathcal{A}_{ij} &= \delta_{ij} \quad \text{if } i, j = 1, 2, 3 \\ \mathcal{A}_{ij} &= 0 \quad \text{if } i, j = 4 \dots 15 \end{aligned} \quad (20)$$

This prevents the electron polarization from being carried over from one state to the other. If the polarization is conserved in the transition, matrix  $\mathcal{A}$  is the  $15 \times 15$  unity matrix.

Consider now the special case where two identical states are involved ( $M_1 = M_2 = M$ ), where both transformation rates are equal ( $\Lambda_{12} = \Lambda_{21} = \Lambda$ ) and where the electron polarization is lost during the transition. The equations of

motion for the time-dependent polarizations are then given by:

$$\dot{\vec{P}}^{\text{tot}} = [M - \Lambda \cdot (1 - \mathcal{A})] \cdot \vec{P}^{\text{tot}} \quad (22)$$

This is exactly the same expression as equation (17). The rate  $\nu_{\text{ex}}$  assumes the meaning of a transition rate for a muon jumping between equivalent sites and replacing its bound electron each time by a randomly polarized electron from the surroundings.

The extension of equation (20) to  $N$  muon states results in the following set of equations:

$$\dot{\vec{P}}_k(t) = \left( M_k - \sum_{l \neq k}^N \Lambda_{kl} \right) \cdot \vec{P}_k(t) + \sum_{l \neq k}^N \Lambda_{lk} \mathcal{A} \vec{P}_l(t) \quad (23)$$

with

$$\vec{P}^{\text{tot}}(t) = \sum_{k=1}^N \vec{P}_k(t) \quad (24)$$

The solution of this set of equations proceeds in a similar fashion to that for the individual  $\text{Mu}^*$  state (equations (14, 15)), but aside from a few special cases, it cannot be performed analytically. The limit of complexity for such problems is set by the computer. The muon polarization is given by the sum

$$p_\mu^\alpha(t) = \sum_{k=0}^{N-1} \left[ \sum_{l, \beta=1}^{15 \cdot N} U_{15 \cdot k + \alpha, l} U_{l, \beta}^{-1} P_\beta(0) \exp(D_u t) \right] \quad (25)$$

with  $\alpha = 1, 2, 3$  denoting the  $x$ ,  $y$  and  $z$  components of the muon polarization.

### (c) The transition from $\text{Mu}$ to $\text{Mu}^*$

An example of the transformation model which can be solved analytically is the transition from an isotropic muonium state to an anisotropic muonium state with  $\vec{n} \perp \vec{B}$  ( $\text{Mu} \rightarrow \text{Mu}^*(90^\circ)$ ) in the absence of relaxation effects ( $\nu_{\text{ex}} = 0$ ). Here we denote by  $\Lambda = \Lambda_{12}$  the transition rate, by  $\mathcal{H}$  the spin Hamiltonian for  $\text{Mu}$  (equation (1)) and by  $\tilde{\mathcal{H}}$  the Hamiltonian for  $\text{Mu}^*$  (equation (6)). We take  $E_n$  to be the energy eigenvalue of the eigenstate  $|n\rangle$  of  $\mathcal{H}$  ( $\mathcal{H}|n\rangle = E_n|n\rangle$ ). The muon polarization then oscillates at frequencies  $\omega_{mn}$  given by the energy differences:

$$\omega_{mn} = 2\pi\nu_{mn} = (E_m - E_n)/\hbar. \quad (26)$$

For  $\text{Mu}^*(90^\circ)$ , the four transition frequencies observed in a transverse field experiment are given by

$$\begin{aligned} \omega_{14} &= 2\pi\nu_{14} = \frac{1}{2}[\omega_0 - \frac{1}{2}\omega^* \csc(2\psi) + (\omega_0 + \frac{1}{2}\omega^*) \csc(2\chi)] \\ \omega_{12} &= 2\pi\nu_{12} = \frac{1}{2}[\omega_0 - \frac{1}{2}\omega^* \csc(2\psi) - (\omega_0 + \frac{1}{2}\omega^*) \csc(2\chi)] \\ \omega_{23} &= 2\pi\nu_{23} = \omega_{14} - \omega_0 \\ \omega_{34} &= 2\pi\nu_{34} = \omega_{12} - \omega_0 \end{aligned} \quad (27)$$



where the angles  $\chi$  and  $\psi$  are defined by

$$\begin{aligned}\tan(2\psi) &= \frac{-\frac{1}{2}\omega^*}{\omega_e - \omega_\mu} \\ \tan(2\chi) &= \frac{\omega_0 + \frac{1}{2}\omega^*}{\omega_e + \omega_\mu}\end{aligned}\quad (28)$$

The time-dependent, 15-component polarization  $\vec{P}$  for such an irreversible process can be obtained from equations (18, 19) by setting  $\Lambda_{21} = 0$ . In the absence of relaxation effects, however, it is unnecessary to follow all 15 components, and the total muon polarization  $\vec{p}_\mu^{\text{tot}}(t)$  can be written in the following form:

$$\vec{p}_\mu^{\text{tot}}(t) = \vec{p}_\mu(t) \exp(-\Lambda t) + \vec{p}_\mu^{\text{tr}}(t) \quad (29)$$

where  $\vec{p}_\mu(t)$  is the muon polarization in an undisturbed Mu state and where

$$\vec{p}_\mu^{\text{tr}}(t) = \Lambda \int_0^t dt' \exp(-\Lambda t') \text{Tr} \{ \exp[-i\tilde{\mathcal{H}}(t-t')/\hbar] \rho(t') \exp[i\tilde{\mathcal{H}}(t-t')/\hbar] \cdot \vec{\sigma} \} \quad (30)$$

If the muon polarization is carried over from one state to the other but the electron polarization is lost, the density matrix at the time of the reaction  $t'$  is given by:

$$\rho(t') = \frac{1}{4}[1 + \vec{p}_\mu(t') \cdot \vec{\sigma}] \quad (31)$$

On the other hand, if the electron polarization is conserved during the transition, then  $\rho(t')$  is given by:

$$\rho(t') = \exp(-i\mathcal{H}t'/\hbar) \rho(0) \exp(i\mathcal{H}t'/\hbar) \quad (32)$$

Integrating over all transition times  $t'$ , one obtains

$$\begin{aligned}\vec{p}_\mu^{\text{tot}}(t) &= \sum_{m,n,\tilde{m},\tilde{n}} [\langle m | \rho(0) | n \rangle \langle n | \vec{\sigma} | m \rangle - \vec{\mathcal{P}}_{\tilde{m},\tilde{n}/m,n} \exp(i\alpha_{mn}^{\tilde{m}\tilde{n}})] \\ &\quad \times \exp[-(i\omega_{mn} + \Lambda)t] \\ &\quad + \sum_{m,n,\tilde{m},\tilde{n}} \vec{\mathcal{P}}_{\tilde{m},\tilde{n}/m,n} \exp(-i\tilde{\omega}_{\tilde{m}\tilde{n}}t + i\alpha_{mn}^{\tilde{m}\tilde{n}})\end{aligned}\quad (33)$$

where

$$\vec{\mathcal{P}}_{\tilde{m},\tilde{n} | m,n} = \langle \tilde{m} | m \rangle \langle m | \rho(0) | n \rangle \langle n | \tilde{n} \rangle \langle \tilde{n} | \vec{\sigma} | \tilde{m} \rangle \cos \alpha_{mn}^{\tilde{m}\tilde{n}} \quad (34)$$

and

$$\tan \alpha_{mn}^{\tilde{m}\tilde{n}} = \frac{\tilde{\omega}_{\tilde{m}\tilde{n}} - \omega_{mn}}{\Lambda}. \quad (35)$$

Two points should be noted: (i) the damping rate of the precursor Mu precession signals (at frequencies  $\omega_{mn}$ ) is simply the transition rate  $\Lambda$ . (ii) The amplitudes of the final state Mu\* signals ( $\tilde{\omega}_{\tilde{m}\tilde{n}}$ ) are determined by the angle  $\alpha$  and show a maximum for  $\alpha = 0$  (i.e. for  $\tilde{\omega}_{\tilde{m}\tilde{n}} = \omega_{mn}$ ).

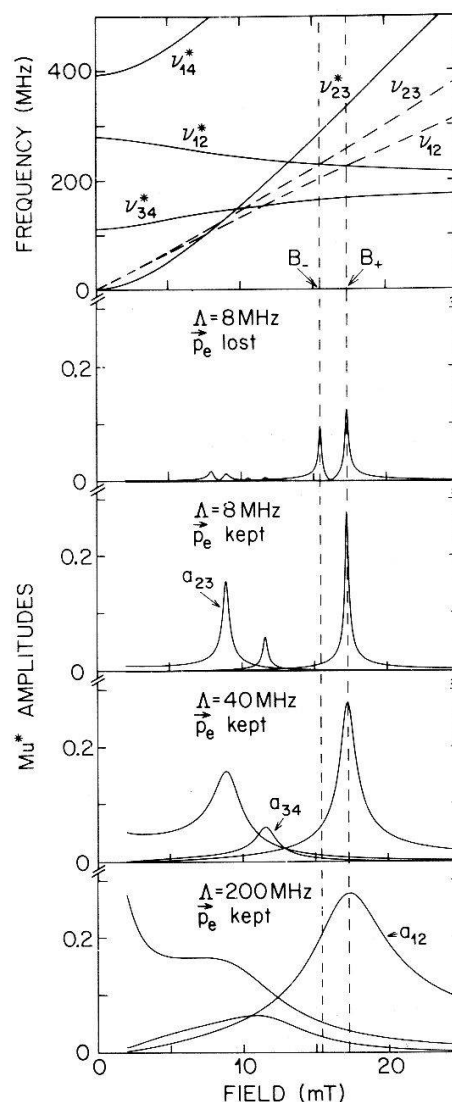


Figure 3

Upper section: expected  $\text{Mu}^*$  and  $\text{Mu}$  precession frequencies for the magnetic field along the  $\langle 110 \rangle$  axis in diamond, which coincide at particular fields  $B_-$  and  $B_+$ . Lower sections: the theoretically predicted  $\text{Mu}^*$  amplitudes resulting from a  $\text{Mu} \rightarrow \text{Mu}^*(90^\circ)$  with  $A_s(\text{Mu}^*)/A(\text{Mu}) > 0$  for various transition rates  $\Lambda$  under the assumption of the loss ( $\vec{p}_e$  lost) and conservation ( $\vec{p}_e$  kept) of the electron polarization.

We can now apply this description to the experimentally investigated case of a  $\text{Mu} \rightarrow \text{Mu}^*(90^\circ)$  transition in diamond [2, 13] with conservation of the electron polarization. With the  $\text{Mu}$  and  $\text{Mu}^*$   $hf$  parameters determined for diamond, the  $\text{Mu}^*$  frequency 1–2 as function of the applied field crosses the triplet muonium frequencies at the field values  $B_- = 15.4 \text{ mT}$  and  $B_+ = 17.2 \text{ mT}$  (see equation (27) and Fig. 3). If the  $\text{Mu}$   $hf$  interaction is taken to be positive (by analogy with vacuum  $\text{Mu}$ ), then a resonantly large fraction of the muon polarization will be carried over from  $\text{Mu}$  to  $\text{Mu}^*$  at either  $B_-$  or  $B_+$ , depending upon whether  $A_s(\text{Mu}^*)/A(\text{Mu})$  is less than or greater than zero. The  $\text{Mu}^*$  3–4 signal precesses in the opposite sense and thus does not show a resonance.

The existence of a *single* resonant field follows from the assumption that the electron polarization is *conserved* during the transition. Due to the smallness of the  $\text{Mu}^*$   $hf$  coupling constants, the  $\text{Mu}^*$  electron spin is decoupled from the muon spin at magnetic fields greater than  $\sim 10 \text{ mT}$ . For a positive  $A_s$ , the  $\text{Mu}^*$  1–2 signal then corresponds to a muon spin flip with the electron spin up, and for a negative  $A_s$  to the electron spin down. Furthermore, the  $\text{Mu}$  hyperfine states  $|1\rangle$



and  $|3\rangle$  are also eigenstates of the electron spin  $S_z$  with the electron spin up and down, respectively. The factors  $\langle \tilde{m} | m \rangle$  and  $\langle n | \tilde{n} \rangle$  in equation (34) thus imply that a coincidence between  $\tilde{\omega}_{12}$  and  $\omega_{12}$  ( $\tilde{\omega}_{12}$  and  $\omega_{23}$ ) will cause a resonant polarization transfer for  $A_s$  positive (negative). In the *absence* of electron spin conservation, this selection does *not* occur, and an enhanced transfer of muon polarization is expected at *both*  $B_-$  and  $B_+$ .

(d) *Transitions between two similar Mu states*

High-field experiments on the cuprous halides [15] show transitions between  $\text{Mu}^{\text{I}}$  and  $\text{Mu}^{\text{II}}$ , two isotropic states with almost equal  $hf$  constants. To apply our transformation model to this case, we begin by writing the precession frequencies for an undisturbed Mu state as

$$\begin{aligned}\omega_1 &= 2\pi\nu_1 = \frac{1}{2}[\omega_0 + \omega_e - \omega_\mu - \omega_0 \csc(2\chi)] \\ \omega_2 &= 2\pi\nu_2 = \omega_1 - \omega_0 \\ \omega_3 &= 2\pi\nu_3 = \frac{1}{2}[\omega_0 + \omega_e - \omega_\mu + \omega_0 \csc(2\chi)] \\ \omega_4 &= 2\pi\nu_4 = \omega_3 - \omega_0\end{aligned}\quad (36)$$

with

$$\tan(2\chi) = \frac{\omega_0}{\omega_e + \omega_\mu} \quad (37)$$

We write the  $hf$  constants of the two states as

$$\omega_0^{\text{I/II}} = \omega_0 \pm \Delta\omega_0 \quad (38)$$

We assume that the following conditions hold: (i) the  $hf$  constants are similar ( $\Delta\omega_0 \ll \omega_0$ ), (ii) we are dealing with the transverse subsystem ( $\vec{p}_\mu(0) \perp \vec{B}$ ), (iii) the electron polarization is conserved in the transition and (iv) there is no electron exchange ( $\nu_{\text{ex}} = 0$ ). Under these circumstances, the transition model yields analytical solutions. We expect in general 8 precession lines

$$\lambda_n^\pm \cong \frac{1}{2}\{i(\omega_n^{\text{I}} + \omega_n^{\text{II}}) - (\Lambda_{12} + \Lambda_{21}) \pm \sqrt{[i(\omega_n^{\text{I}} - \omega_n^{\text{II}}) - (\Lambda_{12} - \Lambda_{21})]^2 + 4\Lambda_{12}\Lambda_{21}}\} \quad (39)$$

where  $n = 1, \dots, 4$ .  $\omega_n^i$  with  $i = \text{I, II}$  are the oscillation frequencies for the undisturbed Mu states with the  $hf$  constants given by equation (38). Note that the real part of  $-\lambda_n^\pm$  represents a relaxation rate, while the imaginary part is an oscillation frequency. The time-dependent muon polarization is given by:

$$\begin{aligned}p_\mu(t) &= \frac{1}{2} \sum_{n=1}^4 \left\{ W_n \frac{\Lambda_{12} + a_n}{\Lambda_{12}\Lambda_{21} + a_n^2} [a_n p_\mu^{\text{I}}(0) + \Lambda_{21} p_\mu^{\text{II}}(0)] \exp(\lambda_n^+ t) \right. \\ &\quad \left. + W_n \frac{\Lambda_{21} - a_n}{\Lambda_{12}\Lambda_{21} + a_n^2} [\Lambda_{12} p_\mu^{\text{I}}(0) - a_n p_\mu^{\text{II}}(0)] \exp(\lambda_n^- t) \right\}\end{aligned} \quad (40)$$

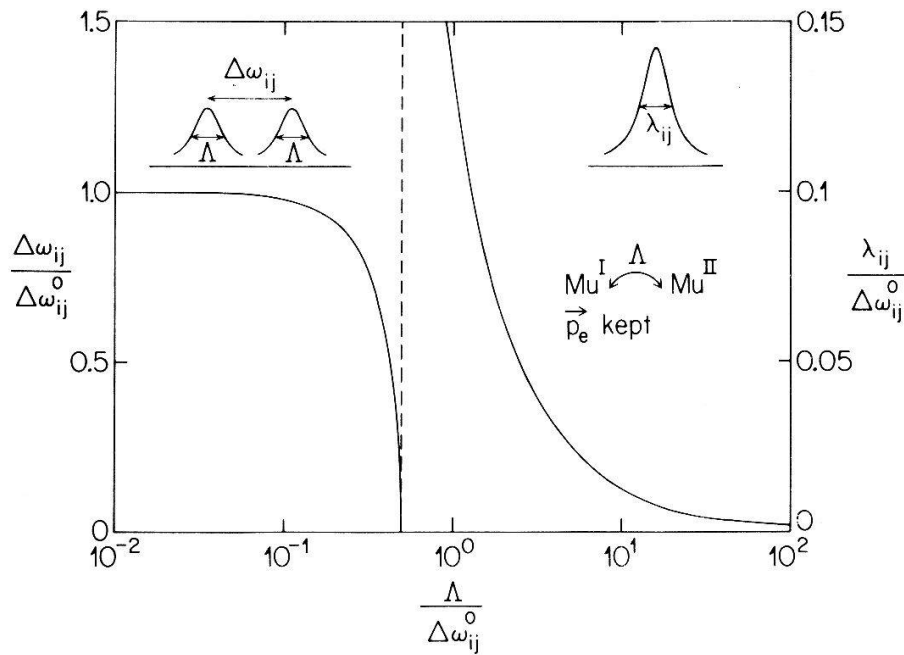


Figure 4

'Universal' plot of the rate-dependent line separation  $\Delta\omega_n$  and linewidth  $\lambda_n$  for Mu hopping between sites with different but similar  $hf$  frequencies. The quantities are normalized to the linewidth separation without jumps  $\Delta\omega_n^0$  and plotted against the normalized jump rate  $\Lambda/\Delta\omega_n^0$ .

where

$$a_n = \lambda_n^+ - (i\omega_n^{\text{II}} - \Lambda_{21}) \quad (41)$$

$$W_n = (\cos^2 \chi, \cos^2 \chi, \sin^2 \chi, \sin^2 \chi)$$

$p_\mu^{\text{I}}(0)$  and  $p_\mu^{\text{II}}(0)$  denote the initial muon polarizations in states I and II, respectively. Note that in the high field limit only contributions with  $n = 1, 2$  are expected. The irreversible case  $\text{Mu}^{\text{I}} \rightarrow \text{Mu}^{\text{II}}$  is obtained by setting  $\Lambda_{21} = 0$ ; we then obtain a relaxed precursor state and an undamped final state.

When both transition rates are equal ( $=\Lambda$ ), the discriminant in equation (39) is real and, depending on its sign, a splitting occurs in the relaxation rates (if positive) or in the oscillation frequencies (if negative). In the first case (small  $\Lambda$ ), two distinct muon states are visible. A plot of the frequency splitting  $\Delta\omega_n$ , normalized to the difference  $\Delta\omega_n^0 = \omega_n^{\text{I}} - \omega_n^{\text{II}}$  for  $\Lambda = 0$ , is plotted in Fig. 4. For rates  $\Lambda$  larger than  $\Delta\omega_n^0/2$ , the frequency splitting vanishes, and a single line  $\omega_n$  is seen corresponding to a Mu state with the  $hf$  constant equal to the averaged value  $\omega_0$ . Each frequency now appears twice, with different relaxation rates. With increasing  $\Lambda$ , one of the damping rates decreases (see Fig. 4), while the other approaches asymptotically  $2\Lambda$ .

### III. Experimental details

#### (a) The $\mu\text{SR}$ -technique

The high-intensity accelerators, the so-called meson factories, make it possible to use positive muons as unique microscopic probes in solid-state physics.

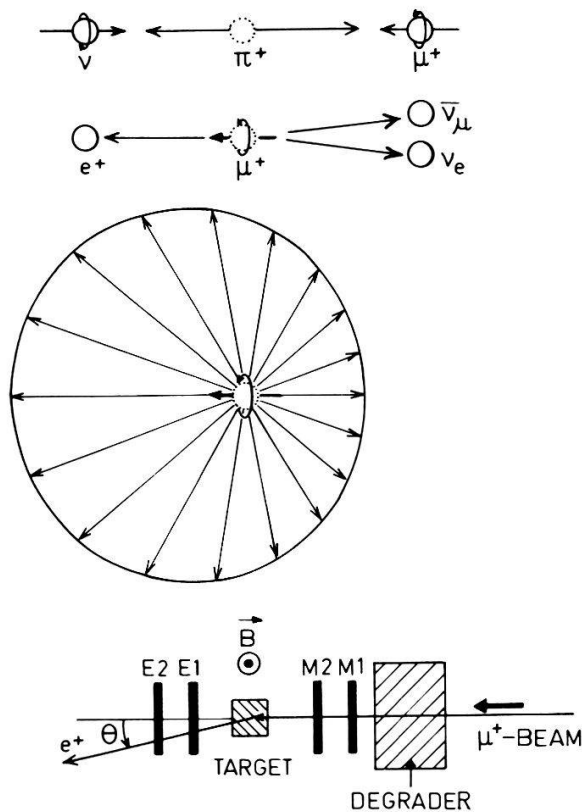


Figure 5

Upper part: the  $\pi^+$  and  $\mu^+$  decay. Center part: the angular distribution of the decay positrons with respect to the  $\mu^+$  spin. Lower part: a simplified diagram of the counter arrangements in a  $\mu$ SR experiment. The scintillation counters M1 and M2 register the incoming muons and E1 and E2 the decay positrons.

The muon is a spin- $\frac{1}{2}$  particle and belongs to the family of leptons. Its mass is 207 times the electron mass or  $\frac{1}{9}$  of the proton mass. A feature of the muon which is vital to its use in solid state experiments is its parity-violating decay (with a mean lifetime of  $2.2 \mu\text{s}$ ) into a positron and two neutrinos with the positron emitted *preferentially along the muon spin direction* (see Fig. 5). This fact makes it possible to monitor the time evolution of the muon polarization.

In a muon-spin-rotation ( $\mu$ SR) experiment [3, 24], polarized positive muons are stopped in the material to be investigated, and the decay positrons are recorded as a function of the time after a muon stop. In the short time of thermalization ( $\sim 10^{-12}$  s) the muon maintains its polarization. When a magnetic field  $\vec{B}$  is applied perpendicular to the initial muon polarization, a free muon precesses with the Larmor frequency  $\omega_\mu$  (see equation (5)). Due to the anisotropic muon decay, the exponential muon decay, as monitored in a particular direction in the plane of precession, is modulated at the frequency  $\omega_\mu$ . If muonium ( $\mu^+e^- = \text{Mu}$ ) is formed in a solid, precession components are observed at frequencies which correspond to transitions between the hyperfine levels of the spin Hamiltonian given in equations (1, 3). The upper limit for the rate at which data can be collected in a  $\mu$ SR experiment is given by the requirement that no more than one muon be present in the sample at given time, since the parent muon of a decay positron must be uniquely identified.

### (b) Experimental setups

All the present measurements were performed at the Swiss Institute for Nuclear Research (SIN). Two different  $\mu$ SR spectrometers were used, depending on the type of experiment and on sample size.

For measurements on thin (down to  $30 \text{ mg/cm}^2$ ) samples a  $\mu\text{SR}$  spectrometer specially designed for surface muons ( $p_\mu = 29 \text{ MeV/c}$  from pion decay at rest) was used. Surface muons are 100% backward polarized, and their range is approximately  $150 \text{ mg/cm}^2$ . Therefore thin windows of  $\approx 130 \mu\text{m}$  made from Kapton and  $\approx 20 \mu\text{m}$  Cu-Be alloy were used for the cryostat and the oven, respectively. The typical sample area was  $0.5 \text{ cm}^2$ . Rotatable Helmholtz coils could produce magnetic fields up to  $0.4 \text{ T}$ , and the earth's field was compensated by three pairs of 'zero-field' coils to better than  $2 \mu\text{T}$ . A He gas-flow cryostat and a hot-finger oven enabled measurements in the temperature range  $6\text{--}800 \text{ K}$ . Below  $300 \text{ K}$ , the sample temperature was measured with platinum and carbon resistors. In the oven the temperature was measured with a Ni-NiCr thermocouple. Two independent sets of positron counters allowed either large-acceptance forward-backward counting for zero field and longitudinal field experiments or up-down counting for transverse field experiments. By replacing the thin incident muon counter with a thicker one, this  $\mu\text{SR}$  apparatus could be used as well with conventional muons ( $p_\mu > 50 \text{ MeV/c}$ ).

For experiments which require a high time-resolution and a large applied magnetic field, a dedicated  $\mu\text{SR}$  spectrometer was developed [15] (see Fig. 6). The object of the high magnetic field was to quench the nuclear hyperfine interaction of muonium [25] to produce narrow precession lines, thus allowing measurements of muonium in non-metals with a high concentration of nuclear moments. The resulting Mu precession frequencies lie in the GHz region. During

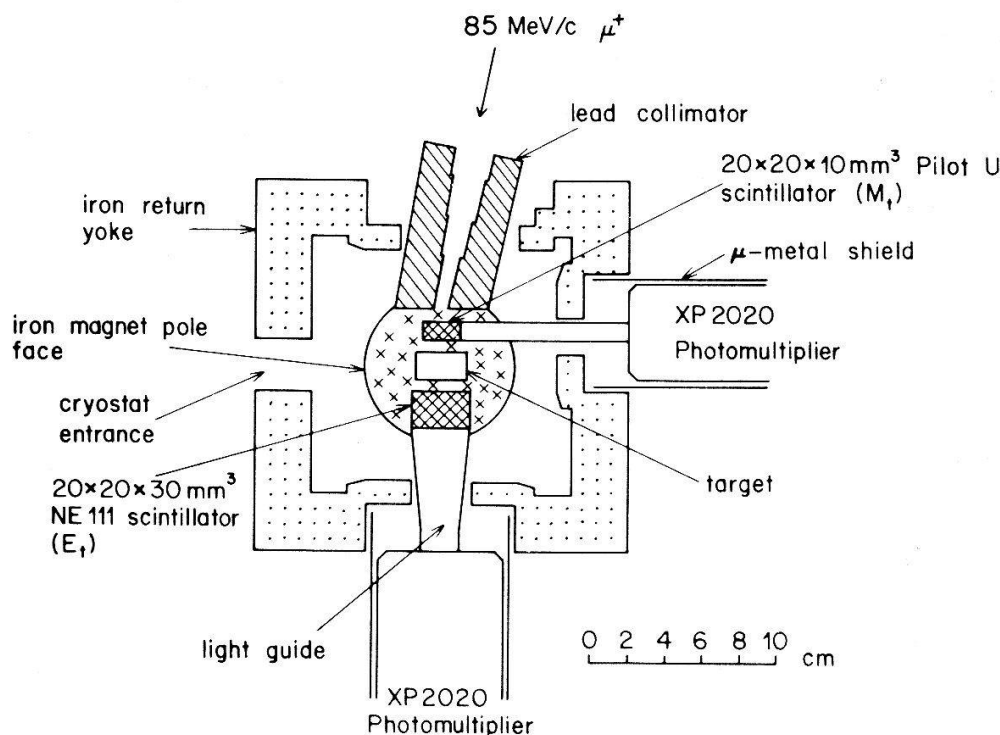


Figure 6

Schematic diagram of the high timing resolution (220 ps FWHM) apparatus used to resolve precession frequencies in a large (1.2 T) transverse magnetic field. The return yoke of the compact iron-core electromagnet reduces the magnetic stray field and thus permits the use of short light guides between the fast plastic scintillators and photomultipliers.

the experiments on the copper halides, muons polarized in the forward direction were used with a momentum of 85 Mev/c. Due to kinematic depolarization, the experimentally-determined muon polarization was reduced to approximately 80%. The range width for this momentum is approximately  $2 \text{ g/cm}^2$ . A compact iron-core electromagnet with return yoke allowed measurements in transverse fields from 0.01 up to 1.2 T. The stray field of the magnet was less than  $10 \mu\text{T}$  10 cm from the magnet center. This allowed the use of short light guides from the scintillation counters to the field sensitive photomultipliers – a requirement for achieving a high time-resolution. With fast scintillators, quartz light guides, selected XP-2020 photomultiplier tubes and bases, special coaxial signal cables, constant fraction discriminators and temperature-regulated electronics, this apparatus achieves a time resolution of 220 ps (FWHM) [15]. This allowed measurements of frequencies up to approximately 2.3 GHz. The sample, with a typical size of  $14 \times 16 \times 24 \text{ mm}^3$  was cooled and heated in a He gas flow cryostat and hot finger oven, respectively.

### (c) Electronics and data-acquisition

A diagram of the electronics used for the high-field, high-timing resolution apparatus is shown in Fig. 7. The anode pulses from the detectors are discriminated by Ortec 583 constant fraction differential discriminators and, if in coincidence with the appropriate logic signals, are fed into the start and the stop inputs of a time-to-amplitude converter (TAC). A logic box and pile-up gate were

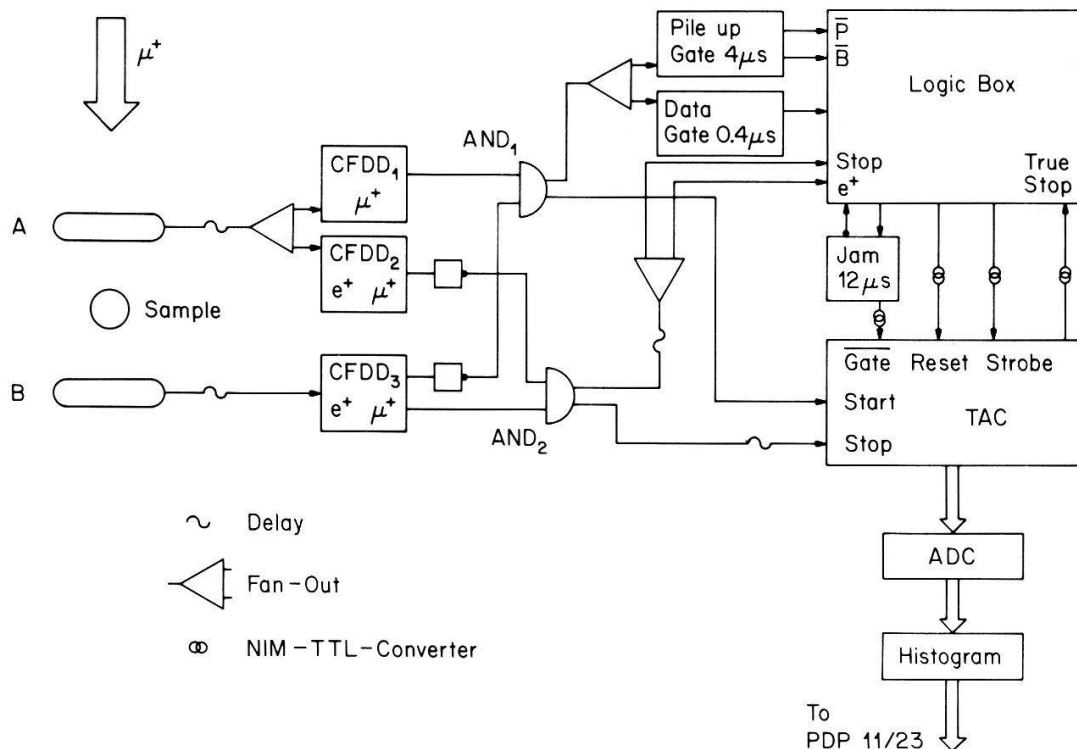


Figure 7  
Electronic setup used for the high-field, high-timing resolution apparatus shown in Fig. 6.

used to reject events resulting from two detected positrons or two stopped muons during one measuring cycle. The TAC was coupled to a 8000-channel analog-to-digital (ADC) converter (LeCroy model 3512). A TAC setting of 45 ps/channel was necessary to resolve the high Mu frequencies, and this limited the length of the time spectra to 400 ns. Calibration of the TAC was performed with a 100 MHz quartz time calibrator that produced lines in the time spectrum with a well-defined separation of  $10 \text{ ns} \pm 10 \text{ ppm}$ . The direct coupling of the ADC to a histogramming memory (HM) module (LeCroy model 3588) permitted data taking at a high rate with the computer free for other tasks.

If no high frequencies were expected ( $< 500 \text{ MHz}$ ), a LeCroy model 4202 time-to-digital (TDC) converter based on a quartz clock, and again directly coupled to the HM, was used instead of the TAC and ADC. The 8 k spectrum could be divided into several subspectra (e.g. forward, backward).

A data acquisition system was developed based on an LSI-11/23 computer coupled to a CAMAC crate. The memory size of the LSI was 256 KB, and a 10 MB winchester drive was installed. The subroutines to drive the CAMAC controller were written in Assembler, while Fortran was used for the rest of the program. A Fast-Fourier Transformation allowed an on-line analysis of the data. Using a video display driver, a second television screen could display the time spectrum updated by the LSI from the HM every few seconds. A ROAD C interface in CAMAC permitted automated setting of the applied magnetic field at the sample.

#### (d) *Data analysis*

The general form of a  $\mu\text{SR}$  spectrum consists of an exponential decay, modulated by a sum of damped sinusoidal oscillations corresponding to the time-dependent muon polarization:

$$N(t) = N_0 e^{-t/\tau_\mu} [1 + X(t)] + B \quad (42a)$$

$$X(t) = \sum_{j=1}^n a_j R_j(t) \cos(2\pi\nu_j t + \Phi_j) \quad (42b)$$

$N_0$  is a normalization constant,  $\tau_\mu$  is the muon lifetime ( $2.2 \mu\text{s}$  for positive muons) and  $B$  is a time-independent background. The parameters  $a_j$ ,  $\nu_j$ , and  $\Phi_j$  are the amplitudes, precession frequencies, and initial phase angles of the  $n$  different contributions to the muon polarization. The relaxation functions  $R_j(t)$  are assumed to be exponential

$$R_j(t) = \exp(-\lambda_j t) \quad (43)$$

or Gaussian

$$R_j(t) = \exp(-\sigma_j^2 t^2) \quad (44)$$

To determine the number  $n$  of significant signals and their approximate frequencies, the modulation spectra  $X(t)$  were Fourier-transformed. Least-square



fits of the time spectra to equation (42a) were then performed. It was often found to be advantageous, particularly if there were a large number of weak signals, to perform least-square fits of the Fourier transform of equation (42b) to the complex *Fourier* spectra. A comparison showed that the two methods yielded identical results.

For high frequencies, the effects of the finite time resolution [5] of the particle detection system must be considered. If one assumes a Gaussian resolution function with a FWHM of  $\Delta t$ , then the observed amplitude  $a_{\text{obs}}$  of a signal at frequency  $\nu$  is given by:

$$a_{\text{obs}} = a_{\text{theo}} \exp \left[ -\frac{(\pi \nu \Delta t)^2}{4 \ln 2} \right] \quad (45)$$

where  $a_{\text{theo}}$  is the expected amplitude. The time resolution  $\Delta t$  could be calibrated using observations of the two high field Mu precession frequencies.

To obtain absolute amplitude values, the measured precession amplitudes, after correction for finite time resolution, were normalized to the maximum experimental amplitude, taken from the free-muon precession in a metal such as copper.

#### (e) *Sample specific details*

1. *Diamond*. The diamond experiments were performed using 28 MeV/c muons on a single crystal sample with no evidence of nitrogen impurities in its infrared absorption spectrum. The diamond was in a high-vacuum hot finger oven with the applied magnetic field along  $\langle 110 \rangle$ . Fine orientation adjustments of the crystal were made based on the  $\text{Mu}^*$  line splitting. In this orientation, two  $\langle 111 \rangle$  symmetry axes were at  $\theta = 90^\circ$ , and the other two at  $\theta = 35.26^\circ$  with respect to the external field. The measurements were performed in the temperature region 300–600 K, and magnetic fields up to 25 mT were applied. The uncertainty of the sample temperature was less than 0.1 K, and that of the field was less than 0.4%. To minimize background, muon decay positrons were detected perpendicular to the incoming beam. Our time resolution of approximately 900 ps FWHM allowed the observation of frequencies up to 500 MHz. In each run,  $2 - 5 \times 10^6$  good muon decay events were accumulated in each of two time histograms, of which approximately 20% were from muons which stopped in the copper target holder. The precession frequencies, their amplitudes and their relaxation rates were extracted by multi-frequency fits to the  $\mu\text{SR}$  time histograms. The transition model (equations (33–35)) was fitted to the weighted average of the amplitudes from both histograms. In the analysis, account was taken of the temperature dependence of the  $\text{Mu}^*$  hyperfine constants [2].

2. *Cuprous halides*. All measurements on the cuprous halides were performed in the high-field (1.2 T), high-timing resolution apparatus using 85 MeV/c muons. Below room temperature, single crystals of CuCl, CuBr and CuI were investigated, which had been cut from rods grown from the melt by C. Schwab using a traveling-heater technique [26]. The dimension of the crystals was

approximately 12 mm in diameter by 12 mm long. The crystals were oriented ( $\langle 111 \rangle \parallel \vec{B}$ ) in the case of CuCl and CuBr, but not in the case of CuI, and cooled in a He-float cryostat. The measurements above room-temperature were performed in a hot finger oven on a polycrystalline CuCl sample in a glass ampoule of approximately 8 mm in diameter and 12 mm length. Up to 445 K, high-frequency Mu signals were observed, and therefore the high-resolution setting of 45 ps/channel was used on the TAC. Above 445 K, only the slow  $\mu^+$  precession was observed, and the setting was changed to 200 ps/channel. For the muonium runs, up to  $15 \times 10^6$  good muon decay events were accumulated, and for the  $\mu^+$  runs typically  $2.5 \times 10^6$ . Approximately 90% of the incoming muons stopped in the crystals, but this fraction was reduced to 75% for the polycrystalline sample due to its smaller size. Correction for this difference was made by assuming equal muonium formation probabilities in the two samples. The timing resolution  $\Delta t$ , obtained from measurements on a crystalline quartz sample at room temperature, was 205(13) ps and 271(15) ps for the low-temperature and high-temperature experiments, respectively.

3. *High-purity silicon.* For these measurements, surface muons (28 MeV/c) were used which were spin-rotated upstream of the experiment with a Wien-filter by an angle of  $65^\circ$  relative to the muon momentum. A single counter perpendicular to the incoming beam detected the decay positrons. In this way, background due to beam contaminants was reduced to a minimum, and bending of the muon beam was avoided, since the applied field was parallel to the incoming beam.

The silicon sample used was a float-zone single crystal with a resistivity of 13500  $\Omega\text{-cm}$  and a specified concentration of electrically active impurities of  $\sim 10^{12} \text{ cm}^{-3}$  (*p*-type). The crystal was oriented with the  $\langle 110 \rangle$  axis perpendicular to the applied field. Measurements were performed in the temperature region 40–700 K in applied fields of 10.6 and 287.1 mT. Depending on the temperature region, a He-flow cryostat or a hot finger oven was used. The uncertainty of the sample temperature was less than 0.2 K, and that of the external field was 45  $\mu\text{T}$ . During the temperature scan at 10.6 mT,  $2 \times 10^6$  good muon decay events were accumulated for each run in a single histogram with 7400 usable channels, each 625 ps wide. The rate of accumulated events was  $800 \text{ s}^{-1}$  at a muon stop rate of  $6200 \text{ s}^{-1}$ . The timing resolution was obtained from measurements on crystalline quartz  $\text{SiO}_2$  at various fields and found to be  $\Delta t = 1.44(4) \text{ ns}$ . The precession amplitudes were corrected for finite timing resolution and normalized to the maximum experimental asymmetry taken to be the free-muon precession amplitude in brass.

#### IV. The Mu and Mu\* states in diamond

##### (a) *Sign determination of the Mu\* hyperfine parameters*

The first evidence for a Mu to Mu\* transition in diamond came from zero-field powder measurements [2]. Three Mu\*  $\mu\text{SR}$  signals are expected in



zero-field. By measuring the temperature dependence of the  $\text{Mu}^*$  signal strength, Holzschuh et al. [2] observed increases in the three amplitudes which occur at different temperatures. The explanation was found to be a  $\text{Mu} \rightarrow \text{Mu}^*$  transition with the electron spin conserved during the transition. Meier [11] treated the zero-field case, and predicted as well that a determination of the sign of the  $\text{Mu}^*$  hyperfine parameters would be possible in experiments with a single crystal oriented in an external magnetic field.

With the electron polarization conserved during the transition, a field scan at constant temperature should yield a 1–2  $\text{Mu}^*$  precession amplitude with a resonant maximum at either  $B_-$  or  $B_+$ , depending on the sign of  $A_s$  (see Section II.(c)). The width of this resonance is a function of the transition rate and therefore temperature-dependent; a definitive sign determination requires a narrow resonance and hence a measurement at as low a temperature as possible.

A first experiment [13] on a nitrogen-rich crystal showed the predicted resonance, but a sign determination was not possible due to relaxation broadening. It is believed that Mu trapping at the nitrogen impurities was the source of this broadening. In the present measurements, a nitrogen *poor* diamond (type IIb) was used, resulting in narrow precession lines and a sharp resonance.

Field scans were performed at 454 and 494 K, and the field was applied parallel to  $\langle 100 \rangle$  and was varied from 7.8 mT to 25.7 mT in the vicinity of the frequency crossing. Note that with the applied magnetic field along  $\langle 110 \rangle$ , there are two  $\text{Mu}^*$  centers with  $\vec{n} \perp \vec{B}$  ( $\text{Mu}^*(90^\circ)$ ) and therefore the same precession frequencies. Combined fits of the transition model equations (33–35) to the amplitudes of both  $\text{Mu}^*$  lines  $\nu_{12}(90^\circ)$  and  $\nu_{34}(90^\circ)$  were made under the assumptions that a temperature-independent ‘prompt’  $\text{Mu}^*$  fraction  $f_1$  is always present and that a Mu fraction  $f_2$  is a precursor for  $\text{Mu}^*$ . Such a ‘prompt’  $\text{Mu}^*$  fraction can be explained by almost instantaneous  $\text{Mu}^*$  formation for a particular fraction of the incoming muons. This leads to total four contributions which must be added in phase.

The amplitude of the 1–2  $\text{Mu}^*$  line showed a single resonance at  $B_-$  (see Fig. 8), establishing that the electron polarization is conserved during the transition (see Fig. 3) and that the isotropic part  $A_s$  of the  $\text{Mu}^*$  hyperfine interaction is *negative*. It is known from  $\mu\text{SR}$  experiments that  $A_s$  and  $A_p$  have the opposite sign in diamond [2]. For comparison, the dot-dashed curve in Fig. 8 shows the expected results for a positive  $A_s$  and negative  $A_p$  and unchanged values for the other fit parameters. The fitted transformation rate  $\Lambda$  was found to be  $46(5) \times 10^6 \text{ s}^{-1}$  at 454 K and  $142(12) \times 10^6 \text{ s}^{-1}$  at 494 K.

#### (b) *Temperature dependence of the Mu to $\text{Mu}^*$ transition rate*

As mentioned in Section II.(c), in the absence of additional depolarization such as from trapping at impurities, the damping rate of the precursor Mu state is equal to the  $\text{Mu} \rightarrow \text{Mu}^*$  transition rate  $\Lambda$ . The temperature dependence of the Mu relaxation rate was studied in the range 300 K to 400 K in an applied field of 1.25 mT. At this low field, the Mu precession frequencies  $\nu_{12}$  and  $\nu_{23}$  are centered

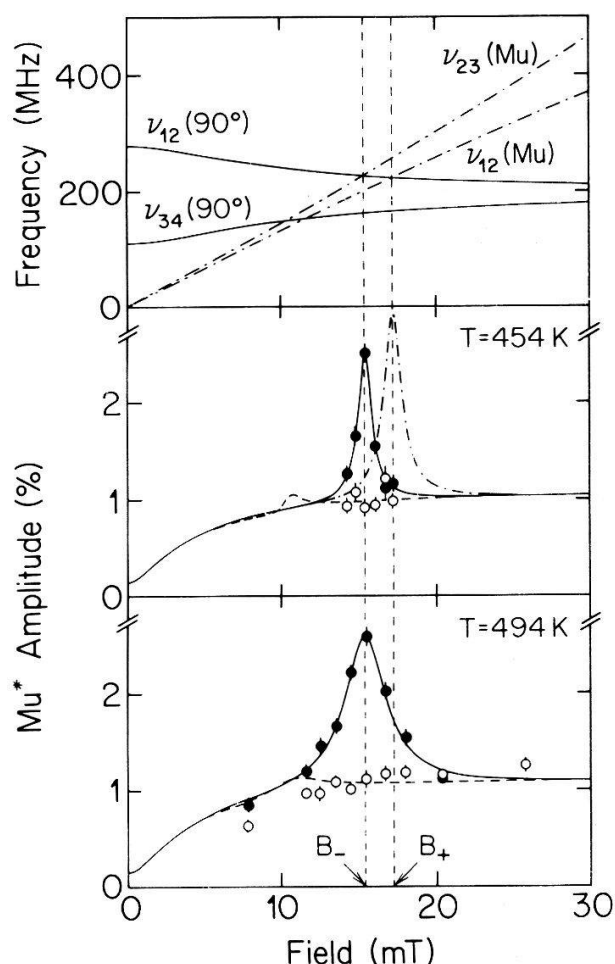


Figure 8

Expected Mu and Mu\* precession frequencies for the magnetic field along the  $\langle 110 \rangle$  axis in diamond. Also shown are the measured and fitted amplitudes of the Mu\* precession signals 1–2 (solid circles, solid curves) and 3–4 (open circles, dashed curves) as a function of the applied field at 454 K and 494 K. The resonant maximum at the field  $B_- = 15.4$  mT establishes that  $A_s(\text{Mu}^*)/A(\text{Mu}) < 0$ . For comparison, the dot-dashed curve shows the expected resonance at  $B_+$  for the opposite sign ( $> 0$ ).

at 17.1 MHz with an unresolved splitting of  $\sim 0.18$  MHz. With account taken of the splitting, a fit of the Mu relaxation rate  $\lambda$  to the Arrhenius law

$$\lambda(T) = \Lambda(T) + \lambda_0 = \Psi \exp(-U/kT) + \lambda_0 \quad (46)$$

yielded the dot-dashed curve in Fig. 9.  $\lambda_0$  denotes a temperature-independent background.

At still higher temperatures, the transition rate  $\Lambda$  can be determined from the temperature-dependent increase of the Mu\* amplitude (see Fig. 10). Such measurements were performed from 300 K to 660 K in an applied field of 16.5 mT, i.e. between the crossover fields  $B_-$  and  $B_+$ . At 373 K, strongly damped Mu signals are still visible. The measured Mu\*(90°) precession amplitudes as function of temperature are presented in Fig. 9. The constant value for  $T < 400$  K corresponds to the prompt Mu\* fraction  $f_1$ . The shift of the rise in the 3–4 amplitude to higher temperatures is a consequence of its opposite sense of precession (see equation (27)). A second increase of the Mu\* amplitudes, from the transfer of the Mu precession components 1–4 and 2–3, at frequencies higher than 3 GHz, is expected above 670 K. The solid and dashed curves in Fig. 9 are the results of a fit to the transition model (equations (33–35)) assuming an Arrhenius law for the transition rate  $\Lambda$ .

Values of  $\Lambda(T)$  are thus available from three different sources: i) from the

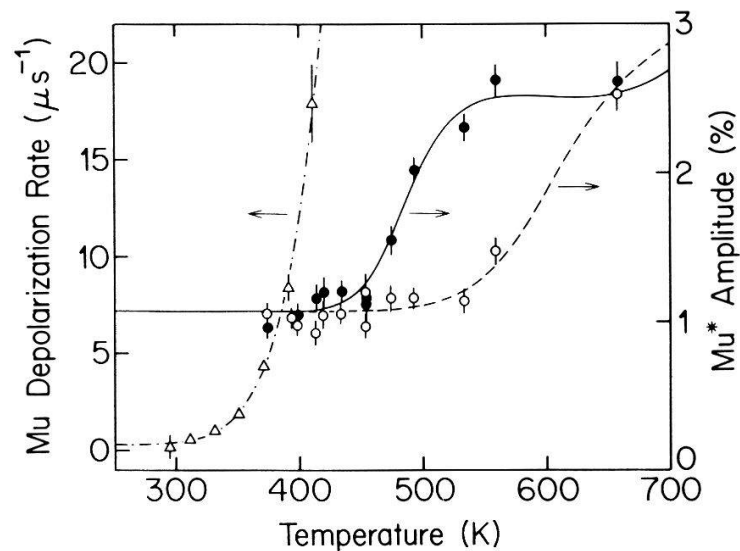


Figure 9

Mu damping rate of diamond for a field of 1.25 mT (triangles and left-hand scale) as a function of sample temperature. The dot-dashed curve is a fit to an Arrhenius law. Also shown are the measured amplitudes of the 1–2 (solid circles) and 3–4 (open circles) precession signals for  $\text{Mu}^*(90^\circ)$  centers in a field of 16.5 mT (right-hand scale). The solid and dashed curves are fits to the Mu to  $\text{Mu}^*$  transition model assuming an Arrhenius law for the transition rate.

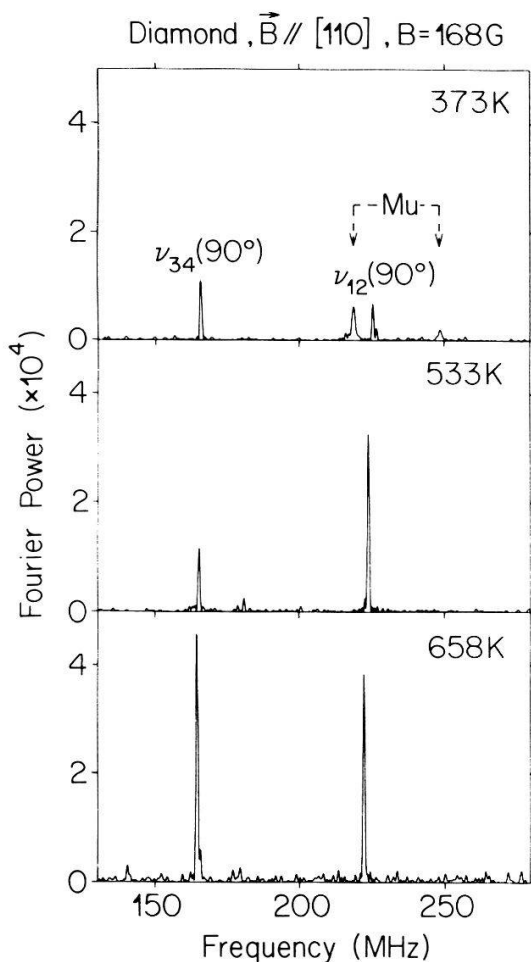


Figure 10

The  $\mu\text{SR}$  frequency spectra in a type-IIb diamond with  $\vec{B} \parallel \langle 110 \rangle$  in a transverse magnetic field of 16.8 mT for different temperatures. The shift of the rise in the  $\text{Mu}^*$  3–4 signal strength to higher temperatures is a consequence of its opposite sense of precession. Note that rapidly damped Mu lines are still observed at 373 K.

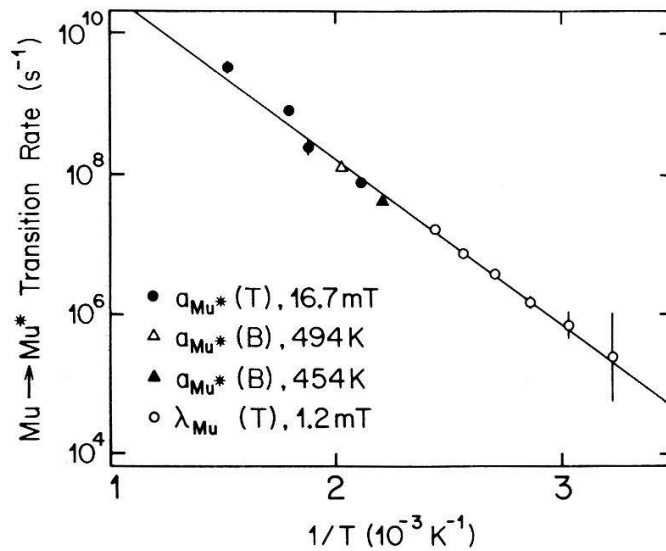


Figure 11

Experimental values of the temperature-dependent  $\text{Mu} \rightarrow \text{Mu}^*$  transition rate  $\Lambda$  obtained from various experiments as explained in the text. The solid line is a fit to an Arrhenius law.

field-dependent  $\text{Mu}^*$  amplitude at 454 K and 494 K ii) from the temperature-dependent  $\text{Mu}$  relaxation rate (minus the temperature-independent term  $\lambda_0$ ) iii) from the temperature-dependent  $\text{Mu}^*$  amplitudes. A global fit to these values was performed to an Arrhenius law with the resulting values

$$\begin{aligned}\Psi &= 1.14(28) \cdot 10^{13} \text{ s}^{-1} \\ U &= 0.476(9) \text{ eV}\end{aligned}\tag{47}$$

and the results are shown in Fig. 11. Note that a single Arrhenius law describes the available data over more than 5 orders of magnitude in  $\Lambda$ .

The entire muon polarization in the type-IIb diamond at room temperature could be accounted for by the prompt  $\text{Mu}^*$  fraction  $f_1 = 25(2)\%$  and the precursor  $\text{Mu}$  fraction  $f_2 = 75(6)\%$ . Any missing fraction was less than 6%. The temperature-independent quotient  $f_1/f_2$  obtained as a weighted average from all the measurements was 0.328(12).

### (c) Temperature dependence of the $\text{Mu}$ hyperfine parameter

The temperature dependences of the  $\text{Mu}$  hyperfine parameter  $A$  in Si and Ge have been accurately measured with the zero-field, high time-resolution technique [5]. No measurement of  $A(T)$  for  $\text{Mu}$  in diamond has yet been reported. In our type-IIb sample,  $\text{Mu}$  precession was observed at the frequencies  $\nu_{12}$  and  $\nu_{23}$  up to 410 K (see Fig. 9) in fields up to 45.3 mT. Together with the precession frequency  $\nu_\mu = 135.54 \text{ MHz/T} \times B$  of the free muon, these measurements yield the  $\text{Mu}$  hyperfine frequency  $A$  according to

$$A = 2 \left[ \frac{\nu_{12}\nu_{23} + \nu_\mu(\nu_{12} + \nu_{23} + \nu_\mu)}{\nu_{23} - \nu_{12}} \right].\tag{48}$$

Table 3

The hyperfine coupling constant  $A$  and electronic  $g$ -factor  $g_e$  for isotropic Mu in diamond as a function of temperature.

$T$ (K)	$A$ (MHz)	$g_e$
6 <sup>a</sup>	3711(21)	-2.0034(17)
293.0	3710.9(1.0)	-1.9971(56)
373.5	3693.0(8.6)	-1.9972(57)
398.5	3568(69)	-2.005(12)

<sup>a</sup>) Taken from Ref. 2.

In addition, the electronic  $g$ -factor  $g_e$  can be obtained from the relation:

$$g_e = -g_\mu \frac{m_e}{m_\mu} \left[ \frac{\nu_{12} + \nu_{23}}{\nu_\mu} + 1 \right]. \quad (49)$$

The experimental values for  $A$  and  $g_e$  are summarized in Table 3. Because of the limited data available, it is not possible to discriminate between the Debye and the Einstein model for  $A(T)$  discussed in Refs. 2 and 27.

#### (d) Discussion

Our study of the  $\text{Mu} \rightarrow \text{Mu}^*$  transition in diamond clearly establishes that the isotropic part of the  $\text{Mu}^*$  hyperfine interaction is *negative*. This implies that  $\text{Mu}^*$  is not simply a distorted version of isotropic Mu, since this would imply a positive electron spin density at the muon. A more promising model of  $\text{Mu}^*$  is a paramagnetic complex similar to a molecular radical with the unpaired electron removed from the muon. The weak negative spin density at the muon is then the result of an 'exchange polarization' mechanism. The  $\text{Mu}^*$  hyperfine constants  $A_s$  and  $A_p$  have been studied previously in diamond, silicon and germanium as a function of temperature [28]. Although in that work the incorrect sign for  $A_s$  was assumed, in view of the similar behavior for the three materials, it was convincingly argued that the same sign assignments for  $A_s$  and  $A_p$  should apply. A further result of the present investigation is that the thermally-activated transition from Mu to  $\text{Mu}^*$  in diamond proceeds without loss of the electron polarization.

At room temperature, Mu and  $\text{Mu}^*$  are observed simultaneously in the  $\mu\text{SR}$  spectra; both are formed promptly upon muon implantation. The thermally-activated conversion of Mu to  $\text{Mu}^*$ , together with the fact that  $\text{Mu}^*$  is observable [2] in diamond up to at least 1100 K establishes that  $\text{Mu}^*$  is the more stable state. In Si and Ge,  $\text{Mu}^*$  disappears above 165 and 85 K, respectively, perhaps under the influence of free carriers [29, 30].

While normal muonium is generally accepted to be at a tetrahedral interstitial site in the diamond lattice [31–38], the site of  $\text{Mu}^*$  is still uncertain. The anisotropic  $hf$  interaction of  $\text{Mu}^*$  implies that it is immobile. Of the many models that have been suggested for  $\text{Mu}^*$ , the two which are being most seriously developed are (i) muonium which occupies a host-ion vacancy [39–43] and (ii)



muonium situated near the center of a host bond [44–48]. Both of these models appear consistent with  $A_s < 0$ , but the high Arrhenius prefactor  $\Psi \approx 10^{13} \text{ s}^{-1}$  for the  $\text{Mu} \rightarrow \text{Mu}^*$  transition rate  $\Lambda(T)$  is incompatible with a model where the precursor Mu searches for a preexisting lattice vacancy in order to become  $\text{Mu}^*$ . This value for  $\Psi$  is comparable to an optical phonon frequency in diamond and hence is approximately the maximum possible jump rate for Mu, implying that only a *single jump* is required by Mu to form  $\text{Mu}^*$ . A cluster calculation [46, 48] of the potential energy surface traversed by muonium from the tetrahedral interstitial site to the center of a strongly stretched C–C bond in diamond reproduces our observation that the Mu state is metastable, but it apparently overestimates the true barrier height. Further support of the bond-centered model for  $\text{Mu}^*$  has been provided by the observation of its resolved nuclear hyperfine structure in Si [49], and with a single Ga and a single As in GaAs [50].

## V. The $\text{Mu}^{\text{I}} \rightarrow \text{Mu}^{\text{II}} \rightarrow \mu^+$ transition in CuCl

### (a) The muonium hyperfine parameters for $\text{Mu}^{\text{I}}$ and $\text{Mu}^{\text{II}}$

The muon-spin rotation frequency spectra for CuCl, CuBr and CuI in a transverse magnetic field of 1.2 T are shown in Fig. 12. The two pairs of lines  $\nu_i^{\text{I}}$  and  $\nu_i^{\text{II}}$  (see equation (36)) observed in CuBr and CuCl at low temperatures are attributed to different muonium centers  $\text{Mu}^{\text{I}}$  and  $\text{Mu}^{\text{II}}$ . In CuI only a single pair of lines is observed. The frequencies are independent of crystal orientation, indicating that the hyperfine interaction for these centers is isotropic. The  $hf$  coupling constant  $A = \omega_0/2\pi$  is thus simply given by  $\nu_1^i + \nu_2^i$ , for  $i = \text{I}, \text{II}$  (see equation (36)). The temperature dependence of the  $hf$  parameters for all three samples is shown in Fig. 13. Except for the  $\text{Mu}^{\text{II}}$  center in CuBr, the last data point plotted corresponds to the highest temperature at which the state can be seen (see Table 2). At higher temperatures, the signals were rapidly damped.

In CuI only one muonium center is observed with decreasing  $hf$  parameter as a function of temperature. In CuCl and CuBr the muonium center with the larger  $hf$  coupling constant ( $\text{Mu}^{\text{I}}$ ) is only observed at low temperatures.

The temperature-dependence of the  $hf$  parameters for CuBr and CuCl are very similar. In contrast to Mu in other semiconductors, their  $hf$  parameters generally *increase* with increasing temperature. At low temperatures, a Debye model [2, 15] was fitted to the measured  $hf$  parameters in the Cu halides. Such a model assumes that the temperature variation in the  $hf$  parameter is due to muonium interaction with a Debye spectrum of acoustic phonons, and predicts an  $A(T)$  of the form:

$$A(T) = A(0) \left[ 1 - \kappa \left( \frac{T}{\Theta_e} \right)^4 \int_0^{\Theta_e/T} \frac{x^3}{e^x - 1} dx \right] \quad (50)$$

where  $A(0)$  is the  $hf$  parameter extrapolated to 0 K,  $\Theta_e$  is the effective Debye temperature and  $\kappa$  is a coupling constant. Fits to the low temperature values

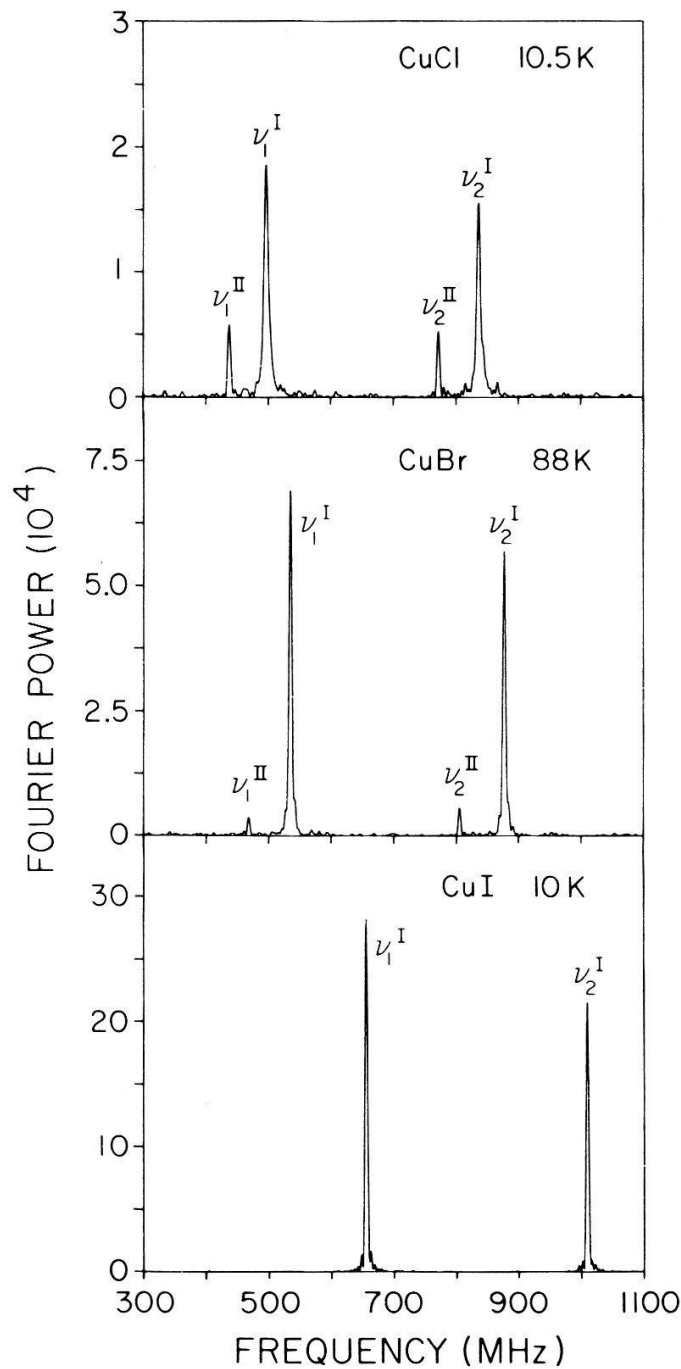


Figure 12

$\mu$ SR spectra in the Cu halides in a transverse magnetic field of 1.156 T. In CuCl and CuBr, two distinct isotropic muonium centers ( $\text{Mu}^{\text{I}}$ ,  $\text{Mu}^{\text{II}}$ ) are observed.

(solid curves) and their extensions to higher temperatures (dashed curves) are plotted in Fig. 13. Note that for higher temperatures the data deviate systematically from the fitted Debye model. The fitted parameters are summarized in Table 4, together with the ratios of the electron and muon  $g$  factors obtained from the expression:

$$\frac{g_e}{g_\mu} = \frac{m_e}{m_\mu} \cdot \frac{2\nu_1\nu_2 + (\nu_1 + \nu_2)\nu_\mu}{\nu_\mu(\nu_1 + \nu_2 + 2\nu_\mu)} \quad (51)$$

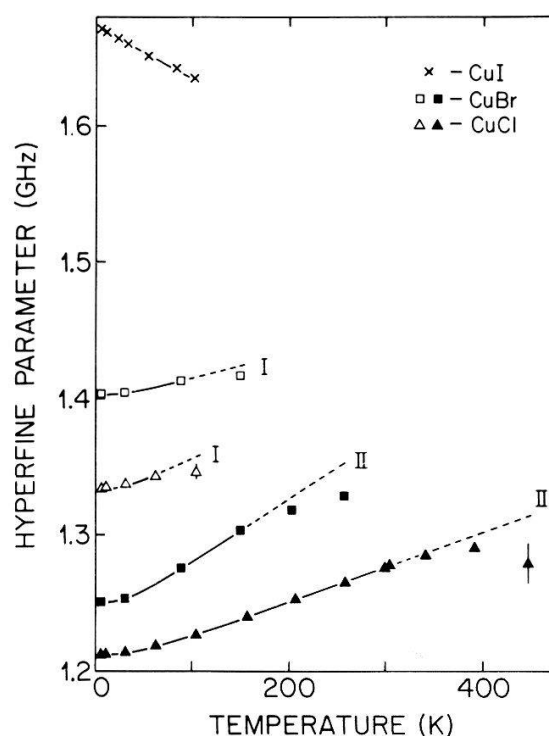


Figure 13

Measured  $hf$  frequencies of the isotropic muonium states in the Cu halides as function of temperature. The solid lines together with extrapolations to higher temperatures (dashed curves) were calculated using equation (50). The corresponding fit parameters are given in Table 4.

Note that the values of  $g_e/g_\mu$  are 2–3% higher than for muonium in vacuum. The fitted Debye temperatures are compared with literature values  $\Theta_D$  obtained from low-temperature specific heat data [51]. The observed value for  $\Theta_e$  in CuI is approximately one order of magnitude less than the specific heat result.

At the highest temperatures,  $A(T)$  for  $\text{Mu}^{\text{I}}$  and  $\text{Mu}^{\text{II}}$  in CuCl and CuBr appear to bend over. A similar non-monotonic behavior has been observed for Mu in silicon [5]. This has been attributed to the rapid hopping of Mu among two different sites with  $hf$  parameters differing by  $\delta\nu_0$ . The observed  $hf$  frequencies are then an average with the occupation of each site given by the Boltzmann factor. A fit to such a model fails for the Cu halides due to the limited data available.

Table 4

Debye model parameters as defined in equation (50) describing the low-temperature dependence of the  $hf$  parameter of  $\text{Mu}^{\text{I}}$  and  $\text{Mu}^{\text{II}}$  in the Cu halides. Debye temperatures  $\Theta_D$  derived from specific-heat data are given for comparison, and the ratio between the electron and muon  $g$  factors for  $\text{Mu}^{\text{I}}$  at 5 K and for  $\text{Mu}^{\text{II}}$  at 150 K are also included.

Center	$A(0)$ (MHz)	$\kappa$	$\Theta_e$ (K)	$\Theta_D^a$ (K)	$g_e/g_\mu^b$
$\text{Mu}^{\text{I}}\text{-CuCl}$	1334.24(7)	-0.083(75)	109(47)	164(4)	1.0292(40)
$\text{Mu}^{\text{II}}\text{-CuCl}$	1212.75(12)	-0.1016(23)	158(3)	164(4)	1.0335(36)
$\text{Mu}^{\text{I}}\text{-CuBr}$	1403.70(7)	-0.0470(82)	118(13)	161(2)	1.0207(15)
$\text{Mu}^{\text{II}}\text{-CuBr}$	1250.79(22)	-0.1311(88)	115(6)	161(2)	1.027(16)
$\text{Mu}^{\text{I}}\text{-CuI}^b$	1670.94(23)	+0.0080(2)	11.4(2)	168(1)	1.0313(24)

a) Taken from Ref. 51.

b) Taken from Ref. 15.



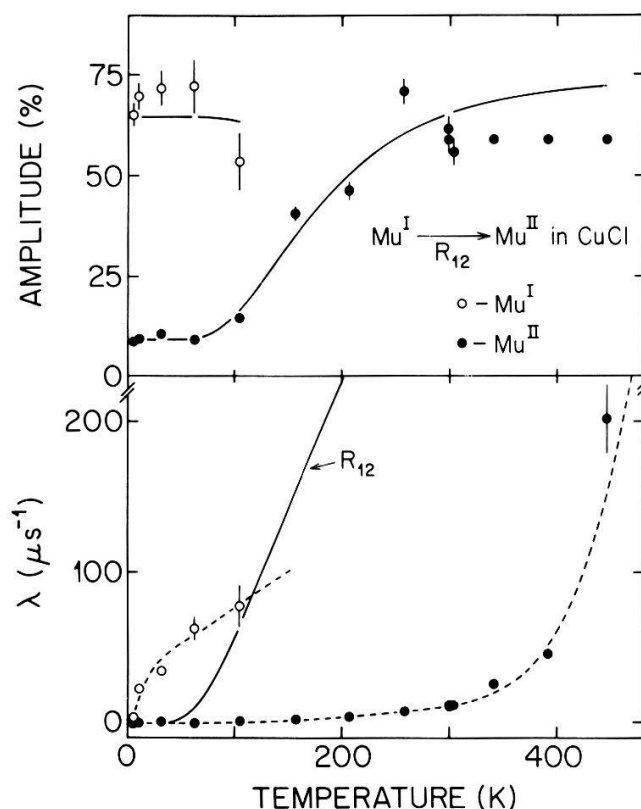


Figure 14

Normalized precession amplitudes and depolarization rates of the two isotropic muonium centers in CuCl as function of temperature. The behavior of the amplitudes indicates a  $\text{Mu}^{\text{I}} \rightarrow \text{Mu}^{\text{II}}$  transition. The theoretical curves are described in the text.

It should be remembered that these copper halides are the least stable of all zincblende materials, implying that lattice expansion, anharmonic vibrational properties, or details of the acoustic phonon spectrum may be more important in the cuprous halides than in other materials. A further interesting point is the possibility that, with increasing temperature, the  $hf$  parameters for  $\text{Mu}^{\text{I}}$  and  $\text{Mu}^{\text{II}}$  approach or even cross one another. Such a crossing would have important consequences for a transition from  $\text{Mu}^{\text{I}}$  to  $\text{Mu}^{\text{II}}$ .

(b) *The thermally activated  $\text{Mu}^{\text{I}} \rightarrow \text{Mu}^{\text{II}} \rightarrow \mu^+$  transition*

The temperature dependence of the precession amplitudes and depolarization rates of the CuCl Mu centers are shown in Fig. 14. The plotted amplitudes are the sum of the contributions from  $\nu_1$  and  $\nu_2$ . Below 65 K, the amplitudes for both centers are temperature-independent, and the formation probability for  $\text{Mu}^{\text{I}}$  is approximately 7 times that for  $\text{Mu}^{\text{II}}$  (see Table 5). With account taken of the fraction precessing as bare muons, found to be 16(4)%, the resulting missing fraction for CuCl is 7.0(4.5)%.

With increasing temperature, the  $\text{Mu}^{\text{I}}$  signals become unobservable due to rapid depolarization. At higher temperatures, the  $\text{Mu}^{\text{II}}$  amplitude increases monotonically and at 250 K approaches the total low-temperature precession

Table 5

Model parameters describing the thermally-activated transitions from  $\text{Mu}^{\text{I}}$  to  $\text{Mu}^{\text{II}}$  to the bare muon state ( $\mu^+$ ).  $p_0^i$ , with  $i = \text{I} - \text{III}$ , are the formation probabilities for the  $\text{Mu}^{\text{I}}$ ,  $\text{Mu}^{\text{II}}$  and the  $\mu^+$  state for  $T > 700$  K, respectively. The transition rates  $\Lambda_{12}$  and  $\Lambda_{23}$  are assumed to follow an Arrhenius law (equation (46)) defined by the parameters  $\psi$  and  $U$ .

Method	$p_0^{\text{I}}$ (%)	$p_0^{\text{II}}$ (%)	$p_0^{\text{III}}$ (%)	$\psi_{12}$ ( $10^9 \text{ s}^{-1}$ )	$U_{12}$ (meV)	$\psi_{23}$ ( $10^9 \text{ s}^{-1}$ )	$U_{23}$ (meV)
Weighted average: $T < 70$ K for $\text{Mu}^{\text{I}}$ $T > 710$ K for $\mu^+$	67(8)	9.2(5)	79(2)				
$\text{Mu}^{\text{I}} \rightarrow \text{Mu}^{\text{II}}$ $\text{Mu}^{\text{II}} \rightarrow \mu^+$	64(2)	9.0(5)	84(4)	0.88(15)	23(4)	670(300)	256(19)

amplitude observed for both centers combined. Above room temperature, the  $\text{Mu}^{\text{II}}$  amplitude was fixed at the averaged room-temperature value of 58.7(1.8)% and is therefore plotted in Fig. 14 without error bars. The  $\text{Mu}^{\text{II}}$  depolarization rate increases slowly in the temperature region below 300 K, followed by a sharp increase above 370 K, and the state is unobservable above 445 K. The  $\mu^+$  amplitude plotted in Fig. 15 has been corrected for a contribution from the sample holder and oven walls by subtracting the low-temperature value of 34.5(3)%. Above 450 K, the free muon amplitude rises to a plateau value of

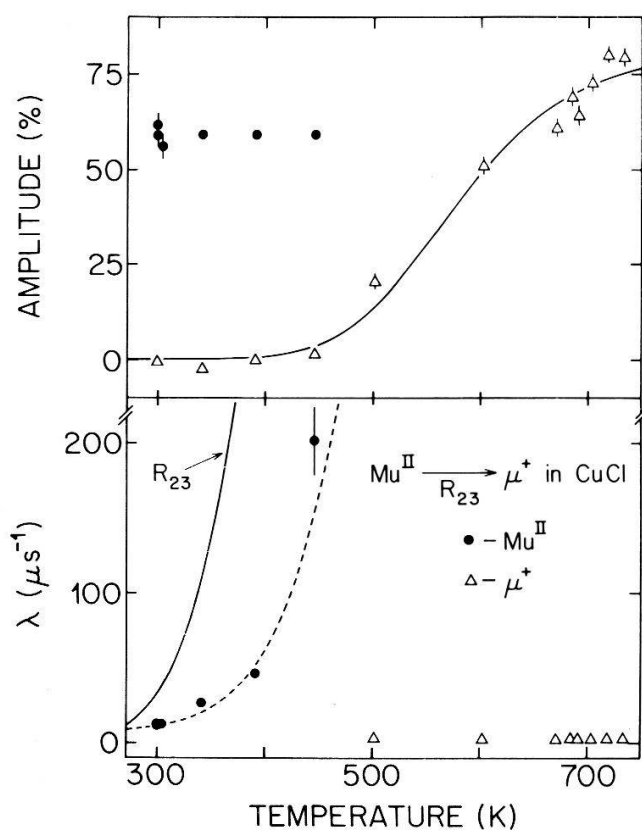


Figure 15

Normalized precession amplitudes and depolarization rates of the isotropic muonium center  $\text{Mu}^{\text{II}}$  and the diamagnetic center ( $\mu^+$ ) in CuCl as function of temperature. The behavior of the  $\mu^+$  signal strength indicates a  $\text{Mu}^{\text{II}} \rightarrow \mu^+$  transition. The theoretical curves are described in the text.

76.7(1.4)% above 700 K. The depolarization rate of the bare muon remained approximately zero up to 733 K, the highest temperature investigated.

These facts strongly suggest the occurrence of a thermally-activated process of the form:



with corresponding transition rates  $\Lambda_{12}$  and  $\Lambda_{23}$ . Since the maxima in the amplitudes of  $\text{Mu}^{\text{II}}$  (at 250 K) and  $\mu^+$  (at 700 K) are the same and approximately equal to the total low-temperature muonium amplitude, we may treat the two processes  $\text{Mu}^{\text{I}} \rightarrow \text{Mu}^{\text{II}}$  and  $\text{Mu}^{\text{II}} \rightarrow \mu^+$  separately.

1. *The transition from  $\text{Mu}^{\text{I}}$  to  $\text{Mu}^{\text{II}}$ .* The expressions for a  $\text{Mu}^{\text{I}} \rightarrow \text{Mu}^{\text{II}}$  transition are obtained from equations (39–41) by setting  $\Lambda_{21} = 0$ . Since all measurements were performed in the high-field region, only the components at the frequencies  $\nu_1$  and  $\nu_2$  need be considered, and they have approximately the same amplitude. In the high-field limit the resulting expression for the  $\text{Mu}^{\text{I}}$  amplitude has the form:

$$a^{\text{I}} = p_0^{\text{I}} \cdot \left| \frac{-i\pi(\nu_0^{\text{I}} - \nu_0^{\text{II}})}{\Lambda_{12} - i\pi(\nu_0^{\text{I}} - \nu_0^{\text{II}})} \right| \quad (53)$$

and one obtains for the  $\text{Mu}^{\text{II}}$  amplitude:

$$a^{\text{II}} = \left| \frac{(p_0^{\text{I}} + p_0^{\text{II}})\Lambda_{12} - ip_0^{\text{II}}\pi(\nu_0^{\text{I}} - \nu_0^{\text{II}})}{\Lambda_{12} - i\pi(\nu_0^{\text{I}} - \nu_0^{\text{II}})} \right| \quad (54)$$

Here  $\Lambda_{12}$  is the transition rate, and  $p_0^{\text{I}}$  and  $p_0^{\text{II}}$  are the formation probabilities at early times, equal to the amplitudes in the absence of a transition. Below room temperature, results of a simultaneous fit of expressions of equations (53) and (54) to the available data are plotted in Fig. 14, assuming an Arrhenius law (equation (46)) for  $\Lambda_{12}$ . The fitted parameter values are summarized in Table 5. The formation probabilities are in good agreement with the averaged values found for low temperatures. The dashed curve in Fig. 14 is the predicted disappearance rate of  $\text{Mu}^{\text{I}}$  based on the rise of the  $\text{Mu}^{\text{II}}$  signal amplitude. Note that the low temperature values of  $\text{Mu}^{\text{I}}$  lie above the predicted curve and that their temperature-dependence is substantially different from a simple exponential behavior.

The  $\text{Mu}^{\text{II}}$  depolarization rate increases monotonically from approximately zero at 5 K to a room temperature value of 11.5(5)  $\mu\text{s}^{-1}$ . A fit of an Arrhenius-law to the data set up to room temperature leads to the parameter values:

$$\begin{aligned} \Psi &= 66.5(8.3)10^6 \text{ s}^{-1} \\ U &= 46.3(2.6) \text{ meV} \end{aligned} \quad (55)$$

2. *The transition from  $\text{Mu}^{\text{II}}$  to the bare  $\mu^+$  state.* Interesting effects may be expected for CuCl in the high-temperature region. The I–VII cuprous halides are

at the extreme ionic limit of the zincblende materials; all of them undergo a phase transition to the wurtzite structure at approximately the same temperature (680 K in CuCl). This phase change decreases the bonding coordination from four to three. The melting point of CuCl is at 695 K. To study the influence of these phase transitions on the muon states, we have extended our measurements of CuCl up to 733 K.

The free muon precession amplitude together with the  $\text{Mu}^{\text{II}}$  amplitude above 240 K is shown in Fig. 15. A monotonic increase in the  $\mu^+$  signal strength occurs directly above the temperature at which  $\text{Mu}^{\text{II}}$  disappears. The structural phase transition and the melting produce no significant change in the amplitude or depolarization rate of the  $\mu^+$  signal.

For a  $\text{Mu}^{\text{II}} \rightarrow \mu^+$  transformation, the transition model predicts a time-dependent muon polarization in a high transverse field given by:

$$p_{\mu}(t) = p_0 \cos^2 \alpha \cdot \cos(\omega_{\mu} t) \quad (56)$$

with

$$\tan \alpha = -\frac{\pi v_0^{\text{II}}}{\Lambda_{23}} \quad (57)$$

Here  $\Lambda_{23}$  is the transition rate, which is assumed to follow an Arrhenius law. No temperature-independent 'prompt'  $\mu^+$  fraction is included. A temperature-independent  $hf$  parameter  $v_0^{\text{II}} = 1300$  MHz has been assumed. The high-temperature  $\mu^+$  amplitude  $p_0$  is constrained to be equal to the sum of the low-temperature Mu amplitudes  $p_0^{\text{I}} + p_0^{\text{II}}$ . The fitted parameters are given in Table 5. The fitted amplitudes (solid curve) and the predicted depolarization rate for  $\text{Mu}^{\text{II}}$  (dashed curve) are shown in Fig. 15.

Note that the observed  $\text{Mu}^{\text{II}}$  depolarization rates are *below* the predicted curve, in contrast to what is expected if channels other than the transformation exist for the depolarization of the precursor state. In nitrogen-rich diamond, for example, Mu trapping at impurities makes the observation of Mu impossible above 150 K, whereas the present measurements on the type-IIb stone show Mu signals up to 400 K. Note, however that since the transferred  $\mu^+$  amplitude in CuCl depends on the temperature-dependent  $\text{Mu}^{\text{II}}$   $hf$  frequency  $A(T)$  (see equation (57)), an extrapolation of this parameter to temperatures above the highest temperature observation of  $\text{Mu}^{\text{II}}$  is necessary. By assuming that  $A$  *decreases* with increasing temperature above 445 K the rise in the  $\mu^+$  amplitude can be explained with a *lower* transition rate  $\Lambda_{23}$ . A fit was performed under the assumption that the transition rate  $\Lambda_{23}$  is equal to the observed temperature-dependent  $\text{Mu}^{\text{II}}$  depolarization rate. The  $\text{Mu}^{\text{II}}$   $hf$  frequency, taken to be temperature-independent, and the fraction  $p(0)$  were allowed to vary. The fitted  $\text{Mu}^{\text{II}}$   $hf$  frequency temperatures was 186(11) MHz, approximately  $\frac{1}{6}$  of the 0 K value of 1213 MHz. The transferred muon fraction  $p(0)$  was again 82(2)%, in good agreement with the values listed in Table 5.

## (c) Discussion

With the high field, high timing resolution apparatus, we have observed two distinct isotropic muonium centers  $\text{Mu}^{\text{I}}$  and  $\text{Mu}^{\text{II}}$  in CuCl and CuBr, with  $hf$  frequencies approximately  $\frac{1}{3}$  of the vacuum value. The  $hf$  parameters for both Mu centers in CuCl and CuBr generally increase with increasing temperature – in contrast to the behavior for the Mu centers observed in other semiconductors. In CuI, only one Mu center is observed, with a  $hf$  parameter which decreases with increasing temperature. An isotropic  $hf$  interaction implies that state occupies a site with high symmetry or that the center is rapidly diffusing between lower-symmetry sites, averaging out the anisotropy. The latter possibility is ruled out by the observation of Kiefl et al. [15] that, with the possible exception of  $\text{Mu}^{\text{I}}$  in CuCl below 10.5 K, no motional averaging of the Mu nuclear hyperfine interaction occurs in any Cu halide (all the host nuclei in these materials have spin). These authors proposed instead that  $\text{Mu}^{\text{I}}$  and  $\text{Mu}^{\text{II}}$  occupy the two inequivalent tetrahedral interstitial sites.

All the Mu centers in CuCl become unstable at the temperature at which the  $hf$  coupling constant reaches a broad maximum. With increasing temperature, first the  $\text{Mu}^{\text{I}}$  centers become unstable, undergoing a thermally-activated transition to  $\text{Mu}^{\text{II}}$ . At still higher temperatures, the  $\text{Mu}^{\text{II}}$  center in CuCl also becomes unstable and makes a transition to the diamagnetic state  $\mu^+$ .

Since the  $\text{Mu}^{\text{II}}$  state is affected directly by both transition processes, an appropriate model to describe its temperature-dependent amplitude is one which includes *both* transition rates  $\Lambda_{12}$  and  $\Lambda_{23}$ . A fit to such a model fails for several reasons: i) the highest-temperature signals observed from the  $\text{Mu}^{\text{I}}$  state are at 100 K, whereas the increase in the free muon signal strength occurs at temperatures above 450 K, and an extrapolation of the temperature-dependent  $\text{Mu}^{\text{I}}$   $hf$  parameter to this temperature is questionable. ii) extrapolation of the  $hf$  parameters to temperatures above 450 K could lead to a crossover of the  $\text{Mu}^{\text{I}}$  and  $\text{Mu}^{\text{II}}$   $hf$  frequencies, resulting in a resonance effect for the  $\text{Mu}^{\text{II}}$  amplitude. The available data show no evidence for such behavior.

Neither Mu depolarization rate can be explained by a simple exponential. The assumption of a second depopulation process for  $\text{Mu}^{\text{I}}$ , for example a transition  $\text{Mu}^{\text{I}} \rightarrow \mu^+$  with a rate  $\Lambda_{13}$ , leads to a  $\text{Mu}^{\text{I}}$  depolarization rate which is equal to the sum  $\Lambda_{12} + \Lambda_{13}$ . The test of such a model will require more data. The

Table 6

Parameters describing the temperature dependence of the depolarization rate of the  $\text{Mu}^{\text{I}}$  and  $\text{Mu}^{\text{II}}$  center in CuCl as a sum of two Arrhenius laws. This behavior is predicted if an additional depolarization process is assumed. The corresponding curves (dot-dashed) are shown in Fig. 14 and Fig. 15.

	$\Psi_1$ ( $10^6 \text{ s}^{-1}$ )	$U_1$ (meV)	$\Psi_2$ ( $10^6 \text{ s}^{-1}$ )	$U_2$ (meV)
$\text{Mu}^{\text{I}}$ depolarization rate:	70	1.35	180	20
$\text{Mu}^{\text{II}}$ depolarization rate:	53	42.7	$1.4 \times 10^6$	355



dot-dashed curves plotted in Figs. 14 and 15 were obtained from the sum of two Arrhenius curves with the parameters given in Table 6, and are only intended to guide the eye.

## VI. Thermally-activated transitions in high-purity silicon

### (a) The $\text{Mu} \leftrightarrow \mu^+$ transition above 240 K

As in diamond [2], three different muon states,  $\text{Mu}$ ,  $\text{Mu}^*$  and  $\mu^+$ , are seen in high-purity silicon at temperatures below 100 K. Data on the temperature-dependent muonium dynamics obtained from measurements on various samples [5, 27, 52–55] are presented in Fig. 16. At the lowest temperatures only a small  $\mu^+$  fraction is seen, together with the  $\text{Mu}^*$  and  $\text{Mu}$  fractions indicated by the arrows in the third section of the figure. As the temperature is increased, first the  $\text{Mu}^*$  state becomes unstable, as indicated by its increasing depolarization rate  $\lambda_{\text{Mu}^*}$ . The subsequent rise in the  $\mu^+$  amplitude  $a_{\mu^+}$  indicates that a  $\text{Mu}^* \rightarrow \mu^+$  transition occurs. Next the  $\text{Mu}$  state becomes unstable, also ending up as  $\mu^+$ . At the highest temperatures yet studied, even the  $\mu^+$  appears to become unstable. Since not only the  $\mu^+$  amplitude, but also its depolarization rate increases for temperatures over 400 K, a simple transition model  $\text{Mu} \rightarrow \mu^+$  fails to describe the data.

The normalized precession amplitudes and depolarization rates of the  $\text{Mu}$  and  $\mu^+$  states at high-temperatures in a transverse field of 106 G are shown in Fig. 17. The plotted total  $\text{Mu}$  amplitude has been corrected for the finite time-resolution of the  $\mu\text{SR}$  apparatus. For temperatures above 240 K, the  $\text{Mu}^* \rightarrow \mu^+$  transition is already complete, leading to an enhanced  $\mu^+$  amplitude of 45.86(55)%. The  $\text{Mu}$  amplitude was found to be 61.5(2.6)% and was held fixed during the analysis of the muonium depolarization rates. The small  $\mu^+$  background signal from the cryostat and oven were taken into account.

In order to consistently describe the  $\mu^+$  and  $\text{Mu}$  data, we propose that a reversible transition,  $\text{Mu} \leftrightarrow \mu^+$ , between the  $\text{Mu}$  and the  $\mu^+$  states occurs. The spin dynamics for such a process is described by equations (19, 20) with  $\Lambda_{12}$  and  $\Lambda_{21}$  representing the rates for the processes  $\text{Mu} \rightarrow \mu^+$  and  $\mu^+ \rightarrow \text{Mu}$ , respectively. Use of the reduced differential equation set given in the Appendix (equations (A3, A4)) simplifies the problem. We then obtain 5 coupled differential equations which cannot be solved analytically. Although information on the temperature-dependence of the  $hf$  parameter  $A(T)$  for  $\text{Mu}$  in  $\text{Si}$  is available from [5], it is not needed for a description of the total  $\text{Mu}$  amplitude, given by  $2(a_{12} + a_{23})$ , since this sum is independent of  $A$ .

A combined fit of the precession amplitudes and depolarization rates of  $\text{Mu}$  and  $\mu^+$  state to the transition model  $\text{Mu} \leftrightarrow \mu^+$  is plotted in Fig. 17. The fitted Arrhenius parameters for the transition rates are summarized in Table 7. Below room-temperature, the  $\text{Mu} \rightarrow \mu^+$  transition at the rate  $\Lambda_{12}$  is dominant, with an almost negligible effect from  $\Lambda_{21}$ . Above 600 K the  $\mu^+$  depolarization rate is

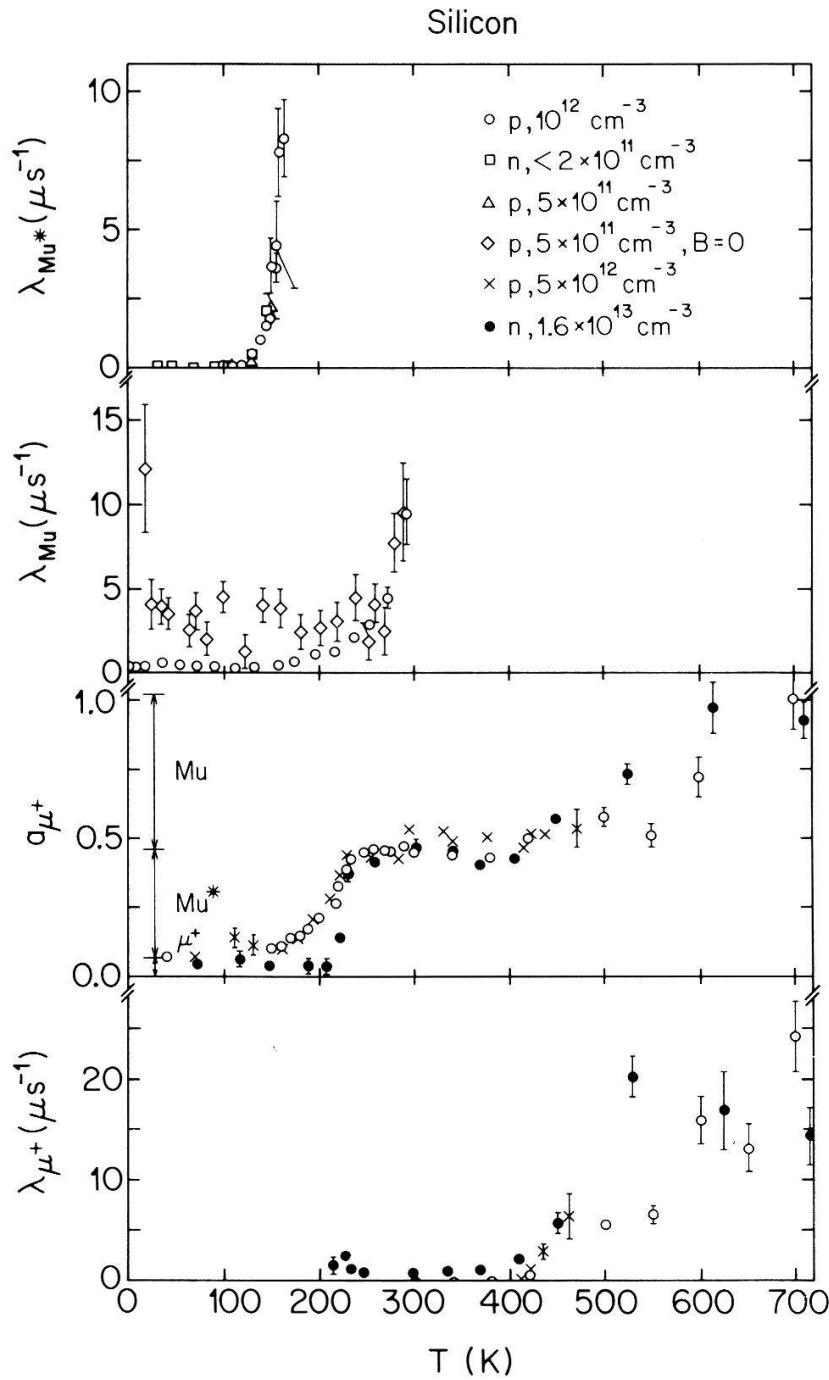


Figure 16

Collected data on muonium dynamics in various high-purity silicon samples:  $p, 10^{12} \text{ cm}^{-3}$  [52];  $n, < 2 \times 10^{11} \text{ cm}^{-3}$  [53];  $p, 5 \times 10^{11} \text{ cm}^{-3}$  [27];  $p, 5 \times 10^{11} \text{ cm}^{-3}, B=0$  [5];  $p, 5 \times 10^{12} \text{ cm}^{-3}$  [54];  $n, 1.6 \times 10^{13} \text{ cm}^{-3}$  [55].

approximately half the  $\Lambda_{21}$  transition rate. A basic property of a reversible process is the appearance of a shift in the precession frequencies for high transition rates. We compare the predicted  $\mu^+$  frequency shift based on the fitted Arrhenius parameters with the observed frequency shift in Fig. 17. The consistent explanation of the amplitudes, relaxation rates and  $\mu^+$  frequency shift are strong evidence for the reversible  $\text{Mu} \leftrightarrow \mu^+$  transition model.

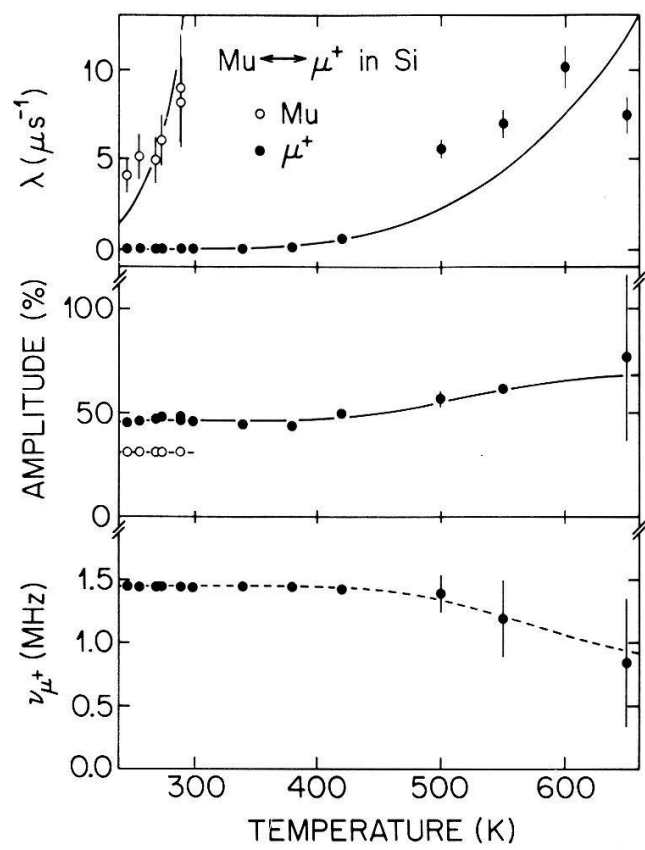


Figure 17  
Temperature dependence of the Mu and  $\mu^+$  amplitudes and depolarization rates measured for a  $10^{12}\text{ cm}^{-3}$  (*p*-type) silicon sample in a field of 1.1 mT. The solid curves are fits to the  $\text{Mu} \leftrightarrow \mu^+$  transition model. Also shown is the predicted  $\mu^+$  frequency shift  $\nu_{\mu^+}$  (dashed curve) together with the corresponding experimental data.

(b) The  $\text{Mu}^* \rightarrow \mu^+$  transition

As mentioned above, the  $\text{Mu}^*$  state in Si is unstable above 150 K and is no longer observable above 165 K. The rise in the  $\mu^+$  amplitude above 150 K indicates that a  $\text{Mu}^* \rightarrow \mu^+$  transition occurs. Since no related increase of the  $\mu^+$  relaxation rate is observed, the transition is believed to be irreversible.

In the absence of additional depolarization, such as from the scattering of

Table 7  
Model parameters describing the thermally-activated transitions  $\text{Mu} \leftrightarrow \mu^+$  and  $\text{Mu}^* \rightarrow \mu^+$  observed in high-purity silicon. The fitted Mu and  $\mu^+$  Arrhenius parameters (equation (46)) are based on a  $\text{Mu} \leftrightarrow \mu^+$  transition, and the  $\text{Mu}^*$  parameters are from fits of the  $\text{Mu}^*$  depolarization rates to an Arrhenius law. The fraction and Arrhenius parameters specified for a particular state refer to the amount of muon polarization transferred from the state indicated and the rate at which this state is depleted.

	Mu*	Mu	$\mu^+$
fraction $p(0)$ (%)	39.0(1.4)	61.5(2.6)	6.75(23)
$\Psi$ ( $10^9\text{ s}^{-1}$ )	948(71)	197(52)	21(5)
$U$ (meV)	167(9)	246(8)	386(9)



free carriers by  $\text{Mu}^*$ , the  $\text{Mu}^*$  damping rate of the precursor  $\text{Mu}^*$  state is equal to the  $\text{Mu} \rightarrow \mu^+$  transition rate  $\Lambda$ . The temperature dependence of the  $\text{Mu}^*$  relaxation rate was studied in the range of 100 K to 200 K in an applied field of 29 mT [56]. A fit of the  $\text{Mu}^*$  relaxation rate to an Arrhenius law (equation (46)) leads to the parameter values listed in Table 7.

The sample was oriented with the  $\langle 110 \rangle$  axis perpendicular to the external field, and an analysis of the  $\text{Mu}^*$  frequencies at 40 K yielded the following angles between the field and the  $\text{Mu}^*$  symmetry axes:  $103.7^\circ$  (two states),  $120.5^\circ$  and  $11^\circ$ . Since analytical solutions for isolated  $\text{Mu}^*$  are only available for  $\vec{n} \perp \vec{B}$  or  $\vec{n} \parallel \vec{B}$ , the transition problem must be solved numerically. With the polarization simultaneously transferred from all four  $\text{Mu}^*$  centers at the same rate  $\Lambda(T)$ , and including the  $\text{Mu} \leftrightarrow \mu^+$  process, the dimension of the matrix to be diagonalized is 78 (see equation (23–25)). The large computing effort made fitting impractical.

The observed  $\mu^+$  amplitude at 10.6 and 287.1 mT as function of temperature in the range 100 K to 300 K are shown in Fig. 18 together with the model calculations based on the transition rate  $\Lambda(T)$ . The prompt formation probability for  $\mu^+$ , taken from measurements at 150 K and 287.1 mT, is 6.83(23)%, and that of the  $\text{Mu}^*$  state was taken to be the difference 39.0(1.4)% between the  $\mu^+$  amplitude in the range 275–400 K and this value.

The agreement between experiment and theory is encouraging. The fact that the predicted rise in  $a_{\mu^+}$  occurs at a higher temperature than that observed is

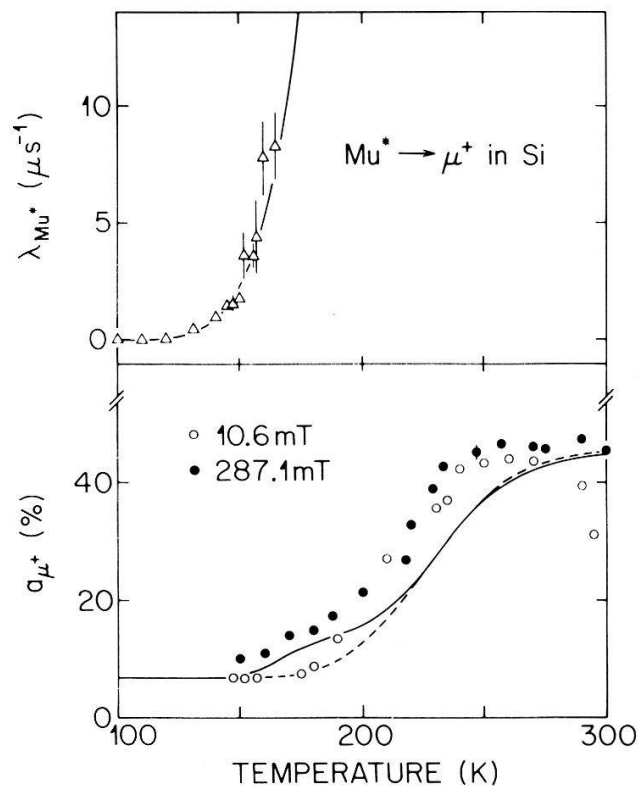


Figure 18

The thermally-activated  $\text{Mu}^* \rightarrow \mu^+$  transition observed in Si. The dot-dashed curve is a fit of an Arrhenius law to the  $\text{Mu}^*$  depolarization rate. The solid line is a theoretical calculation based on the transition model described in the text.

reminiscent of the case  $\text{Mu}^{\text{II}} \rightarrow \mu^+$  in CuCl, and, as discussed there, may indicate a sharp decrease in the  $\text{Mu}^*$   $hf$  frequency above 160 K. The different behavior of the  $\mu^+$  amplitude for the two fields appears to be well-represented. Not understood at the moment are the low values of the  $\mu^+$  amplitude for 287.1 mT above 270 K. A possible explanation is an interference effect between the two processes  $\text{Mu}^* \rightarrow \mu^+$  and  $\text{Mu} \leftrightarrow \mu^+$ .

### (c) *Discussion*

As discussed in Section IV, the thermally-activated transition from Mu to  $\text{Mu}^*$  in diamond allows an experimental determination of the sign of the  $\text{Mu}^*$   $hf$  coupling constants  $A_s$  and  $A_p$ , relative to the Mu  $hf$  coupling constant  $A(\text{Mu})$ . In *electron-irradiated* silicon no Mu signal is observed [57], implying that Mu is diffusing and becoming trapped at radiation defect centers. At the applied field where the Mu and  $\text{Mu}^*$  frequencies coincide, a resonant transfer of the muon polarization from Mu to  $\text{Mu}^*$  is observed, but the resonance is too broad to permit a determination of the sign of the  $\text{Mu}^*$  hyperfine coupling constants.

In high-purity silicon, two transitions occur. In the temperature range 120–250 K,  $\text{Mu}^*$  makes a transition to the  $\mu^+$  state. Above 200 K, one finds that the Mu state undergoes a reversible  $\text{Mu} \leftrightarrow \mu^+$  transition. The increase in the  $\text{Mu}^*$  and Mu depolarization rates and the subsequent rises in the  $\mu^+$  amplitude and relaxation rate with increasing temperature can be accounted for using the transition model. A sign determination of the  $\text{Mu}^*$   $hf$  parameters is not possible using the  $\text{Mu}^* \rightarrow \mu^+$  because the bound electron is lost during the reaction and therefore, in contrast to the case of diamond, no selection rules for the polarization transfer.

## VII. Conclusions

Thermally-activated transitions among the various muon states were investigated in the elemental semiconductors silicon and diamond and in the compound semiconductors CuCl, CuBr and CuI. In this Paper, a general theory was developed which describes the spin dynamics of irreversible and reversible transitions among an arbitrary number of different muon states and which can treat the conservation or loss of the electron polarization. The results obtained can be quantitatively described using the theory.

Our study of the Mu to  $\text{Mu}^*$  transition in type-IIb diamond establishes that the isotropic part of the  $\text{Mu}^*$  hyperfine interaction is *negative*. This implies that  $\text{Mu}^*$  is not simply a distorted version of isotropic Mu, since this would require a positive hyperfine interaction. Instead, it is a paramagnetic complex similar to a molecular radical with the unpaired electron removed from the muon. The weak negative spin density at the muon is then the result of an exchange polarization mechanism. Among the models for the  $\text{Mu}^*$  state, the relaxed bond-center model

is at present the leading contender. It is supported both by the 'Level-Crossing-Resonance' measurements of the  $\text{Mu}^*$  nuclear hyperfine interaction in silicon [49] and GaAs [50], and by cluster calculations [46, 48]. The large Arrhenius prefactor  $\Psi$  for the transition rate excludes a model where Mu hops around in the lattice and finds an existing lattice-ion vacancy, where it becomes trapped as  $\text{Mu}^*$ . Isotropic Mu is believed to be located at or near an interstitial site in the diamond lattice [31–38].

For all the investigated transitions, the assumption of an Arrhenius law for the temperature-dependent reaction rate  $\Lambda(T)$  is supported by the data. In diamond, a single Arrhenius-law describes the  $\text{Mu} \rightarrow \text{Mu}^*$  reaction over more than 5 orders of magnitude in  $\Lambda$ . The prediction of the theory is verified that, in the absence of additional depolarization mechanisms, the depolarization rate for an irreversible process is equal to the transition rate. Measurements on a nitrogen-rich diamond [2] show that rapid Mu relaxation, presumably due to impurity trapping, reduces the maximum possible temperature of Mu observation from 400 K to 150 K. The observation of a  $\text{Mu} \leftrightarrow \mu^+$  process in Si establishes that a rapid, reversible transition among muon states leads to a shift in the precession frequencies. A further conclusion drawn from our investigations on diamond and CuCl is that the electron spin is conserved during the transition from one paramagnetic muonium state to another.

The measurements performed on CuCl above 500 K show no appreciable effect of the structural phase transition or the sample melting on the  $\mu\text{SR}$  signals. At low temperatures, the *hf* coupling constants for both muonium centers in CuCl and CuBr generally increase with increasing temperature – opposite to what is observed for isotropic muonium centers in other semiconductors [3]. This may be related to the marginal stability of these materials [26, 58].

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## Appendix

In this appendix reduced set of differential equations treating the time dependent muon polarization in the  $\text{Mu}^*$  state are listed.

Following Ivanter and Smilga [17] and Brewer et al. [22], we introduce new vectors  $\vec{P}$  and new matrices  $M$  (see equations (13) and (14)) to obtain reduced set of coupled differential equations. In the following section, the expressions for  $\vec{P}$  and  $M$  are summarized for  $\vec{n} \perp \vec{B}$  and  $\vec{n} \parallel \vec{B}$  with respect to the longitudinal and transversal subsystem.

(1)  $\text{Mu}^*$  with  $\vec{n} \parallel \vec{B} \parallel z$ -axis

(1.1) Longitudinal subsystem

$$\vec{P} = \begin{pmatrix} p_\mu^3 \\ p_e^3 \\ p^{11} + p^{22} \\ p^{12} - p^{21} \end{pmatrix} \quad (\text{A1})$$

$$M = \begin{pmatrix} 0 & 0 & 0 & -\frac{1}{2}\omega_0 \\ 0 & -2\nu_{\text{ex}} & 0 & \frac{1}{2}\omega_0 \\ 0 & 0 & -2\nu_{\text{ex}} & -(\omega_e + \omega_\mu) \\ \omega_0 & -\omega_0 & (\omega_e + \omega_\mu) & -2\nu_{\text{ex}} \end{pmatrix} \quad (\text{A2})$$

(1.2) Transversal subsystem

$$\vec{P} = \begin{pmatrix} p_\mu^1 + ip_\mu^2 \\ p_e^1 + ip_e^2 \\ p^{13} + ip^{23} \\ p^{31} + ip^{32} \end{pmatrix} \quad (\text{A3})$$

$$M = \begin{pmatrix} -i\omega_\mu & 0 & \frac{i}{2}(\omega_0 + \omega^*) & -\frac{i}{2}\omega_0 \\ 0 & i\omega_e - 2\nu_{\text{ex}} & -\frac{i}{2}\omega_0 & \frac{i}{2}(\omega_0 + \omega^*) \\ \frac{i}{2}(\omega_0 + \omega^*) & -\frac{i}{2}\omega_0 & -i\omega_\mu - 2\nu_{\text{ex}} & 0 \\ -\frac{i}{2}\omega_0 & \frac{i}{2}(\omega_0 + \omega^*) & 0 & i\omega_e - 2\nu_{\text{ex}} \end{pmatrix} \quad (\text{A4})$$

(2)  $\text{Mu}^*$  with  $\vec{n} \perp \vec{B} \parallel z$ -axis

It is convenient to introduce  $\beta$ , the angle between the  $x$ -axis and  $\vec{n}$ . Then we can write  $\vec{n} = (\cos \beta, \sin \beta, 0)$ .

## (2.1) Longitudinal subsystem

$$\vec{P} = \begin{pmatrix} p_\mu^3 \\ p_e^3 \\ p^{11} \\ p^{22} \\ p^{12} \\ p^{21} \end{pmatrix} \quad (\text{A5})$$

$$M = \frac{1}{2} \begin{pmatrix} 0 & 0 & -\omega^* n_1 n_2 \\ 0 & -4v_{\text{ex}} & -\omega^* n_1 n_2 \\ \omega^* n_1 n_2 & \omega^* n_1 n_2 & -4v_{\text{ex}} \\ -\omega^* n_1 n_2 & -\omega^* n_1 n_2 & 0 \\ (\omega_0 + \omega^* n_2^2) & -(\omega_0 + \omega^* n_1^2) & 2\omega_e \\ -(\omega_0 + \omega^* n_1^2) & (\omega_0 + \omega^* n_2^2) & -2\omega_\mu \end{pmatrix}$$

$$\begin{pmatrix} \omega^* n_1 n_2 & -(\omega_0 + \omega^* n_2^2) & (\omega_0 + \omega^* n_1^2) \\ \omega^* n_1 n_2 & (\omega_0 + \omega^* n_1^2) & -(\omega_0 + \omega^* n_2^2) \\ 0 & -2\omega_e & 2\omega_\mu \\ -4v_{\text{ex}} & -2\omega_\mu & 2\omega_e \\ 2\omega_\mu & -4v_{\text{ex}} & 0 \\ -2\omega_e & 0 & -4v_{\text{ex}} \end{pmatrix} \quad (\text{A6})$$

## (2.2) Transversal subsystem

$$\vec{P} = \begin{pmatrix} p_\mu^1 + ip_\mu^2 \\ p_e^1 + ip_e^2 \\ p^{13} + ip^{23} \\ p^{31} + ip^{32} \\ p_\mu^1 - ip_\mu^2 \\ p_e^1 - ip_e^2 \\ p^{13} - ip^{23} \\ p^{31} - ip^{32} \end{pmatrix} \quad (\text{A7})$$

$$A = \begin{pmatrix} -i\omega_\mu & 0 & \frac{i}{2}\omega_0 & -\frac{i}{2}(\omega_0 + \frac{1}{2}\omega^*) \\ 0 & i\omega_e - 2\nu_{\text{ex}} & -\frac{i}{2}(\omega_0 + \frac{1}{2}\omega^*) & \frac{i}{2}\omega_0 \\ \frac{i}{2}\omega_0 & -\frac{i}{2}(\omega_0 + \frac{1}{2}\omega^*) & -i\omega_\mu - 2\nu_{\text{ex}} & 0 \\ -\frac{i}{2}(\omega_0 + \frac{1}{2}\omega^*) & \frac{i}{2}\omega_0 & 0 & i\omega_e - 2\nu_{\text{ex}} \end{pmatrix} \quad (\text{A8})$$

$$C = i \frac{\omega^*}{4} \exp[-2i\beta] \cdot \begin{pmatrix} & & & 1 \\ & & 1 & \\ & -1 & & \\ -1 & & & \end{pmatrix} \quad (\text{A9})$$

$$M = \begin{pmatrix} A & C^* \\ C & A^* \end{pmatrix} \quad (\text{A10})$$

The failure to reduce the problem to four dimensions is due to the fact that in general  $p_\mu^1$  and  $p_\mu^2$  are no longer separated by the phase  $\pi/2$ . If one is only interested in either  $p_\mu^1$  or  $p_\mu^2$ , such a reduction can be achieved.

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