PHYSICAL REVIEW B VOLUME 18, NUMBER 7 1 OCTOBER 1978

Positive-muon spin depolarization in solids

T. McMullen and E. Zaremba
Department of Physics, Queen's University, Kingston, Ontario K7L 3N6, Canada
(Received 10 March 1978)

A theory of positive-muon spin depolarization in solids is presented. Treating the interaction of the muon spin with the solid perturbatively, the depolarization rate is related to the temporal correlations of the local magnetic fields at the position of the muon. This general result encompasses both transverse and longitudinal spin depolarization. For some situations it is shown that the local-field correlations can be expressed in terms of two quantities, a muon self-diffusion function which contains the information regarding muon motion, and a function describing the spin dynamics of the solid. When applicable, this separation precisely identifies the aspects of muon motion that are studied by muon-spin-rotation experiments. The consequences of some simple models for muon motion are examined. The effect of the finite spread of the muon wave function when centered on a particular interstitial site is also included. The possible importance of this effect is suggested by calculations which account for the applied-magnetic-field dependence of the depolarization rate in copper.

I. INTRODUCTION

The recent availability of highly polarized muon beams at a number of facilities,[1] has provided a novel probe of the solid state. The majority of the experiments on solids have used positive muons (μ^+) which decay via the parity-violating weak interaction in the process

$$\mu^+ \rightarrow e^+ + \overline{\nu}_\mu + \nu_e .$$

The lifetime against this decay is $\tau_\mu \simeq 2.2$ μsec, and the direction of positron emission is correlated with the μ^+ spin orientation at the instant of decay.[2] It is this asymmetry in the emission of the positron which is the key to the usefulness of muons in studying the properties of condensed matter.

On entering a solid target, the muon thermalizes from energies in the range 5-50 MeV in a distance of a few millimeters and a time ($\sim 10^{-10} - 10^{-9}$ sec) much shorter than τ_μ.[3] In this short time interval, the muon essentially retains its initial spin polarization. The subsequent behavior of the μ^+ spin depends on the relative orientation of the initial μ^+ polarization and the direction of any static magnetic field present, either externally applied or due to the magnetization of the sample. Two cases are of particular interest. In the transverse geometry, the initial polarization is perpendicular to the field and the muon precesses as indicated in Fig. 1. Because of this, the probability of positron detection in, say, the initial polarization direction is modulated as a function of time at the μ^+ precession frequency. For ferromagnetic materials, measurement of this precession frequency has been used to determine the local magnetic field at the interstitial site at which the μ^+ resides.[4-7] In the longitudinal geometry, the initial polarization is parallel to the static field and the polarization simply relaxes to its equilibrium value. The absence of a static field can be considered as the limiting case of either of the above situations. Experiments designed to detect the asymmetry in the positron distribution are collectively referred to as μSR (muon-spin rotation).

In addition to the uniform precession in the transverse geometry, fluctuations in the local magnetic field at the position of the muon lead to a decrease in the polarization of the precessing μ^+ spins.[3] In such an experiment, the number $N(t)$ of positrons detected is measured as a function of the time elapsed since the muon entered the target, and is fitted to

$$\frac{dN(t)}{dt} = N_0 e^{-t/\tau_\mu}[1 + A(t)\cos(\omega_0 t + \phi)] . \tag{1}$$

The constant N_0 is determined by details of the experimental arrangement and the factor $\exp(-t/\tau_\mu)$ accounts for the muon decay. The experimentally interesting information is contained in the quantities $A(t)$, which is related to the polarization of the muons at time t, ϕ, a phase angle containing information about transient effects,[8] and ω_0, the observed μ^+ Larmor frequency.

The oscillatory term in (1) arises from the asymmetry of positron emission associated with a nonzero μ^+ polarization. It is proportional[3] to the expectation value $\langle \hat{d}\cdot \vec{s}(t)\rangle$, where $\hat{d}$ is a vector specifying the direction of the detector relative to the target and $\vec{s}$ is the μ^+ spin operator. Thus, the evaluation of the expectation value $\langle \vec{s}(t)\rangle$ is needed for an understanding of the observed depolarization. The time dependence of this quantity describes the relaxation to equilibrium of the muon polarization and is conveniently formulated in terms of an initial nonequilibrium density matrix

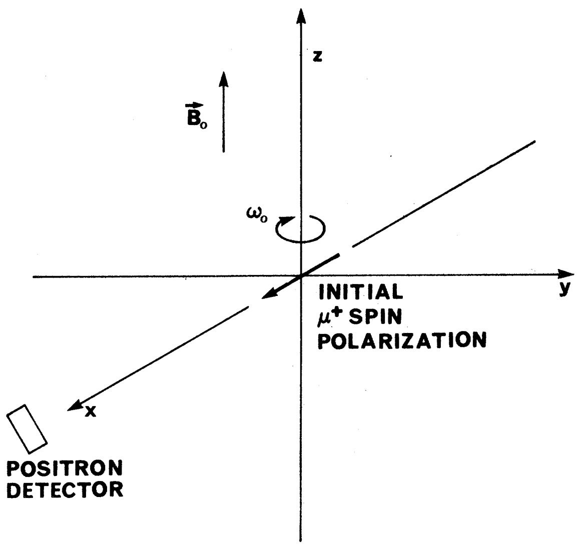


FIG. 1. The transverse depolarization geometry. The μ^+ enters the solid along the x direction and precesses in the x-y plane. The decay positrons are collected at the detector.

(cf. Sec. II).

As mentioned earlier, the depolarization is due to the fluctuating magnetic fields at the position of the muon. These fields arise from the magnetic moments of the spins of the solid, either electronic or nuclear, and the fluctuations occur both as a result of the dynamics of the spins and the motion of the muon. In general, one must simultaneously account for the combined effect of these two factors if useful information regarding microscopic processes is to be extracted from the observations. If the muon is stationary, the depolarization is simply due to the dynamics of the spins in its vicinity, which, however, may be modified by the presence of the muon.[9,10] In this latter situation, information related to the physical environment around the muon can be obtained.

By measuring the temperature dependence of the depolarization rate,[11] additional information concerning the motion of the muon through the solid can be extracted. The nature of this motion, whether it be a thermally activated process or one of quantum tunneling, is of considerable interest as an example of the motion of light interstitials in solids. However, if the dynamics of the spins in the solid exhibits a significant temperature dependence, as in a ferromagnet near T_c,[4] then again the depolarization rate will reflect the combined effects of muon motion and the spin dynamics in the solid. In this situation, it may not be possible to unambiguously relate the observed temperature dependence to the temperature dependence of muon motion.

In Sec. II we present a general theory of muon spin depolarization in solids. Although the formulation is similar to that used in the theory of nuclear magnetic resonance,[12] the experimental details of μSR require a somewhat different approach. For this reason, the derivation of general expressions for $\langle \vec{s}(t)\rangle$ in terms of correlation functions of the fluctuating magnetic fields sampled by the μ^+ is given in some detail. In applying the theory, we shall be concerned primarily with the case in which depolarization is due to the fields of nuclear magnetic moments. To the extent that the presence of the muon does not effect the dynamics of the nuclear spins, it is shown in Sec. III that the correlation functions can be factored into a part describing the muon motion and a part referring to the correlations of the nuclear spins. Some aspects of the muon motion are then discussed with a view to realistically incorporating the nature of the intersititial state. The nuclear spin correlations and the resulting depolarization rate are calculated in Sec. IV and simplified expressions applicable to the stationary and motionally narrowed limits are obtained. The influence of quadrupolar interactions is also considered, but only in the stationary limit. We conclude with a discussion of our results in Sec. V.

II. FORMALISM

In the transverse geometry with the detector in the beam direction, the oscillatory term in (1) is to be identified as

$$A(t)\cos(\omega_0 t+\phi)\propto\langle s_x(t)\rangle=\mathrm{Re}\langle s_+(t)\rangle\,, \tag{2}$$

where

$$s_\pm = s_x \pm i s_y\,. \tag{3}$$

One expects, for times longer than a few ω_0^{-1}, that the expectation value of the spin will behave as

$$\langle s_x(t)\rangle=\langle s_x(0)\rangle\,\mathrm{Re}\,(e^{-i\omega_0 t-i\phi-\Gamma(t)t})\,, \tag{4}$$

where the decaying amplitude $A(t)$ has been written in the form $\exp[-\Gamma(t)t]$, thereby defining the depolarization rate $\Gamma(t)$, which in general is time dependent.

If the coupling of the muon spin to the solid is weak, $\langle s_x(t)\rangle$ can be determined by perturbation theory. Specifically, the result of such a calculation will have the form

$$\langle s_x(t)\rangle=\langle s_x(0)\rangle\,\mathrm{Re}\{e^{-i\omega_A t}[1-i(\Delta\omega_{(1)}+\Delta\omega_{(2)})t -\tfrac{1}{2}(\Delta\omega_{(1)}t)^2-\Gamma_{(2)}(t)t -i\phi_{(2)}+\cdots]\}. \tag{5}$$

Here the subscripts refer to the order in the interaction to which the various quantities are calculated, with only those terms to second order being explicitly shown. (The zero- and first-order contributions to ϕ and Γ will be shown to vanish.) The observed precession frequency ω_0 will be a sum of two terms, the frequency ω_A in the externally applied field and a frequency shift $\Delta\omega = \Delta\omega_{(1)} + \Delta\omega_{(2)} + \cdots$ due to the interactions with the solid. A comparison of (5) and (4) thus provides the perturbation theory estimates of the various quantities ω_0, ϕ, and $\Gamma(t)$. To the extent that the coupling is indeed weak, the second-order calculation is adequate. For the longitudinal geometry, similar arguments apply to $\langle s_z(t)\rangle$ which will also be calculated. However, in this case, no oscillatory behavior is observed.

The Hamiltonian H describing a single μ^+ in a solid consists of a number of terms, representing (i) the solid in the externally applied magnetic field; (ii) the μ^+ kinetic energy; (iii) the electrostatic interaction of the μ^+ with the electrons and ions; (iv) the interaction of the μ^+ spin with the electronic and nuclear spins; and (v) the interaction of the μ^+ spin with the applied field $\vec{B}_0$. The terms (i)–(iii) will be referred to collectively as H^0, while (iv) and (v) are, respectively,

$$H' = -\vec{\mu}_m \cdot \vec{B}(\vec{r}_m) \tag{6}$$

and

$$H_A = -\vec{\mu}_m \cdot \vec{B}_0 . \tag{7}$$

In these expressions, the μ^+ magnetic moment is

$$\vec{\mu}_m = \gamma_m \vec{S} = \tfrac{1}{2}\hbar\gamma_m\vec{\sigma} , \tag{8}$$

where $\gamma_m = 8.517\times 10^4$ G sec^{-1} is the gyromagnetic ratio and $\vec{s} = \frac{1}{2}\hbar\vec{\sigma}$ is the spin angular momentum. The operator $\vec{B}(\vec{r}_m)$ represents the microscopic magnetic field at the position of the muon due to the surrounding electrons and nuclei. The nuclear contribution is simply the magnetic dipolar field, while the electronic contribution (in metals) includes the Fermi contact interaction.

Due to the rapid thermalization,[3] the initial state of the system will be taken to be a μ^+ in a spin state with polarization $\vec{P}$ but otherwise in thermal equilibrium with the solid (i.e., with respect to H^0). The corresponding density matrix is

$$\rho = \frac{e^{-\beta H^0}}{\mathrm{Tr}\,e^{-\beta H^0}}\,\frac{(1+\vec{P}\cdot\vec{\sigma})}{2} \equiv \frac{\rho_0(1+\vec{P}\cdot\vec{\sigma})}{2} . \tag{9}$$

It is convenient to introduce

$$P_\pm = P_x \pm iP_y , \tag{10}$$

although with the applied magnetic field in the z direction, P_y can be chosen to be zero without loss of generality. The transverse geometry corresponds to $P_x = 1$ and $P_y = P_z = 0$ while longitudinal geometry is specified by $P_x = P_y = 0$ and $P_z = 1$.

Using this density matrix, the time development of the Pauli operators is given by

$$\langle\vec{\sigma}(t)\rangle = \mathrm{Tr}\,\rho U^\dagger(t)\vec{\sigma}(t)U(t) \equiv \mathrm{Tr}\,\rho(t)\vec{\sigma}(t) , \tag{11}$$

where $\rho(t) = U(t)\rho U^\dagger(t)$ with

$$U(t) = \exp\left(-\frac{i}{\hbar}\int_0^t d\tau\, H'(\tau)\right)_+ . \tag{12}$$

Here the subscript "+" indicates a positive time ordering, and all operators $O(t)$ develop in time according to

$$\exp[i(H^0 + H_A)t/\hbar]\, O \exp[-i(H^0 + H_A)t/\hbar] .$$

Since $\vec{\sigma}$ commutes with H^0 and H_A commutes with all operators not containing $\vec{\sigma}$, the time dependence of $\vec{\sigma}$ can be extracted explicitly, giving

$$\begin{aligned} \sigma_\pm(t) &= \sigma_\pm e^{\mp i\omega_A t} , \\ \sigma_z(t) &= \sigma_z , \end{aligned} \tag{13}$$

where $\omega_A = \gamma_m B_0$ is the μ^+ precession frequency in the applied field.

Expanding the operators U in (11) in powers of H', we obtain the perturbation series

$$\begin{aligned} \langle\vec{\sigma}(t)\rangle &= \langle\vec{\sigma}(t)\rangle_0 + \frac{i}{\hbar}\int_0^t dt'\,\langle[H'(t'),\vec{\sigma}(t)]\rangle_0 \\ &\quad + \frac{1}{\hbar^2}\int_0^t dt'\int_0^{t'} dt''\langle\{H'(t''),[\vec{\sigma}(t),H'(t')]\}\rangle_0 \\ &\quad + \cdots \\ &\equiv \langle\vec{\sigma}(t)\rangle_{(0)} + \langle\vec{\sigma}(t)\rangle_{(1)} + \langle\vec{\sigma}(t)\rangle_{(2)} + \cdots , \end{aligned} \tag{14}$$

where $\langle\ \rangle_0$ indicates a trace with respect to the initial density matrix ρ, and $[\ ,\ ]$ is the commutator. The lowest-order term gives

$$\langle\sigma_+(t)\rangle_{(0)} = P_+ e^{-i\omega_A t} \tag{15}$$

and

$$\langle\sigma_z(t)\rangle_{(0)} = P_z . \tag{16}$$

The term linear in H' contains the expectation value $\langle\vec{B}(\vec{r}_m)\rangle_0$, i.e., the average magnetic field at the position of the muon. Assuming that only the z component of this field $\langle B_z(\vec{r}_m)\rangle_0$ is nonvanishing, we find

$$\langle\sigma_+(t)\rangle_{(1)} = P_+ e^{-i\omega_A t}[-i\gamma_m\langle B_z(\vec{r}_m)\rangle_0 t] \tag{17}$$

and $\langle\sigma_z(t)\rangle_{(1)} = 0$. The contribution (17) is clearly the first term in the expansion (5) involving the frequency shift $\Delta\omega_{(1)} = \gamma_m\langle B_z(\vec{r}_m)\rangle_0$. The average field $\langle B_z(\vec{r}_m)\rangle_0$ may be comparable to B_0 when electron spin contributions are important, as in ferromagnets, although the nuclear contributions are negligible. We suppose that the summation of this and similar terms [the second-order contribution is given explicitly in (32b)] can be absorbed in $\langle\sigma_+(t)\rangle_{(0)}$ by replacing ω_A in (15) by the observed

Larmor precission frequency ω_0. By this replacement, we have effectively absorbed the average internal field $\langle\vec{B}(\vec{r}_m)\rangle_0$ into the term H_A of (7), leaving the fluctuations from the average value to define the perturbation H'. This replacement is to be understood in the following.

In a similar fashion, the spin traces for the second order term can be carried out with the result

$$\langle\sigma_+(t)\rangle_{(2)} = -\frac{\gamma_m^2}{2} e^{-i\omega_0 t}\int_0^t dt' \int_0^{t'} dt'' \big(P_+\langle\{B_z(t'),B_z(t'')\}\rangle_0 + \tfrac{1}{2}P_+\langle\{\tilde{B}_+(t'),\tilde{B}_-(t'')\}\rangle_0 - \tfrac{1}{2}P_-\langle\{\tilde{B}_+(t'),\tilde{B}_+(t'')\}\rangle_0 - P_z\langle\{B_z(t'),\tilde{B}_+(t'')\}\rangle_0 + \langle[\tilde{B}_+(t'),B_z(t'')]\rangle_0 - \langle[B_z(t'),\tilde{B}_+(t'')]\rangle_0\big) \tag{18}$$

and

$$\langle\sigma_z(t)\rangle_{(2)} = -\frac{\gamma_m^2}{4}\int_0^t dt' \int_0^{t'} dt'' \big(P_z\langle\{\tilde{B}_+(t'),\tilde{B}_-(t'')\}\rangle_0 + P_z\langle\{\tilde{B}_-(t'),\tilde{B}_+(t'')\}\rangle_0 - P_-\langle\{\tilde{B}_+(t'),B_z(t'')\}\rangle_0 - P_+\langle\{\tilde{B}_-(t'),B_z(t'')\}\rangle_0 + \langle[\tilde{B}_-(t'),\tilde{B}_+(t'')]\rangle_0 - \langle[\tilde{B}_+(t'),\tilde{B}_-(t'')]\rangle_0\big), \tag{19}$$

where we have defined

$$\tilde{B}_\pm(t) = e^{\pm i\omega_0 t}B_\pm(t), \tag{20}$$

$$B_\pm(t) = B_x(t) \pm iB_y(t). \tag{21}$$

It is to be noted that $\vec{B}(t)$ represents the time-dependent operator $e^{iH^0t/\hbar}\vec{B}(\vec{r}_m)e^{-iH^0t/\hbar}$. The anticommutator is denoted by $\{\ ,\ \}$. Again, ω_A has been replaced by the precession frequency ω_0. The terms involving commutators in (18) and (19) are inherently quantum mechanical, for they would be identically zero if $\vec{B}$ were a classical field. Furthermore, the commutator terms arise even when $\vec{P}=0$ and therefore correspond to the equilibration of the system in which the initial density matrix $e^{-\beta H^0}$ eventually evolves into the equilibrium density matrix $e^{-\beta H}$ as a result of the interactions H'. Since the equilibrium polarization in the external field is negligible, the contribution of the commutator terms is small compared to the remaining terms when $\vec{P}\neq 0$ and therefore will be ignored.

Although the expressions in (18) and (19) are rather complicated, their content can be clarified by considering a particular example. If we take $P_x=1$ and $P_y=P_z=0$, the magnetic fields parallel and perpendicular to the spin directions in a rotating frame are, respectively,

$$B_\parallel(t) = B_x(t)\cos\omega_0 t - B_y(t)\sin\omega_0 t,$$

$$B_\perp(t) = B_x(t)\sin\omega_0 t + B_y(t)\cos\omega_0 t.$$

In terms of these fields, $\langle\sigma_x(t)\rangle_{(2)}$ can be expressed as

$$\langle\sigma_x(t)\rangle_{(2)} = -\frac{\gamma_m^2}{2}\int_0^t dt' \times\int_0^{t'} dt'' \big([\langle\{B_z(t'),B_z(t'')\}\rangle_0 + \langle\{B_\perp(t'),B_\perp(t'')\}\rangle_0]\cos\omega_0 t - \langle\{B_\parallel(t'),B_\perp(t'')\}\rangle_0\sin\omega_0 t\big). \tag{22}$$

The term proportional to $\cos\omega_0 t$ is in phase with the muon precession and B_z and $B_\perp$ appear symmetrically. Thus field fluctuations in these two directions behave equivalently with regard to destroying the in-phase component of the spin. In addition, it is seen that an out-of-phase component proportional to $\sin\omega_0 t$ develops in time and is due to the cross correlation between $B_\parallel$ and $B_\perp$. In general, the observed polarization consists of a decaying in-phase component and this growing out-of-phase component.

It is apparent from (18) and (19) that the time dependence of the nonequilibrium polarization is governed by the symmetrized correlation functions

$$\Phi_{ij}(t'-t'') = \langle B_i(t')B_j(t'') + B_j(t'')B_i(t')\rangle_0. \tag{23}$$

The equilibrium average implies that Φ_{ij} depends only on the time difference $\tau = t'-t''$.[13] As a result, one of the time integrals in (18) and (19) can be carried out to give our final general result for the second-order contributions to $\langle\vec{\sigma}(t)\rangle$:

$$\langle\sigma_+(t)\rangle_{(2)} = -\frac{\gamma_m^2}{2}e^{-i\omega_0 t}\int_0^t d\tau\left(P_+(t-\tau)\Phi_{zz}(\tau) + \tfrac{1}{2}P_+(t-\tau)e^{i\omega_0\tau}\Phi_{+-}(\tau) + \frac{iP_-}{4\omega_0}(e^{i\omega_0(2t-\tau)} - e^{i\omega_0\tau})\Phi_{++}(\tau) + \frac{iP_z}{\omega_0}(e^{+i\omega_0(t-\tau)}-1)\Phi_{z+}(\tau)\right) \tag{24}$$

and

$$\langle\sigma_z(t)\rangle_{(2)} = -\frac{\gamma_m^2}{4}\int_0^t d\tau\left(P_z(t-\tau)[e^{i\omega_0\tau}\Phi_{+-}(\tau)+e^{-i\omega_0\tau}\Phi_{-+}(\tau)]\right.$$
$$\left.-\frac{iP_+}{\omega_0}(e^{-i\omega_0 t}-e^{-i\omega_0\tau})\Phi_{-z}(\tau)+\frac{iP_-}{\omega_0}(e^{i\omega_0 t}-e^{i\omega_0\tau})\Phi_{+z}(\tau)\right). \tag{25}$$

The expression for $\langle\sigma_-(t)\rangle_{(2)}$ is just the complex conjugate of (24).

Since our main interest here is the depolarization rate in the transverse geometry, we restrict ourselves in the remainder of this paper to the particular case of $P_x=1$ and $P_y=P_z=0$ with a detector in the x direction so that only $\langle\sigma_x(t)\rangle$ need be considered. To further simplify (24) it is convenient to introduce the Fourier transform

$$\Phi_{ij}(\omega)=\int_{-\infty}^{\infty}d\tau\, e^{i\omega\tau}\Phi_{ij}(\tau). \tag{26}$$

We then obtain

$$\langle\sigma_x(t)\rangle_{(2)} = -\frac{\gamma_m^2}{4}e^{-i\omega_0 t}\int\frac{d\omega}{2\pi}\left(tf_t(\omega)[\Phi_{zz}(\omega)+\tfrac{1}{2}\Phi_{+-}(\omega+\omega_0)]-\frac{g_t(\omega)}{2\omega_0}[\Phi_{xx}(\omega+\omega_0)-\Phi_{yy}(\omega+\omega_0)]\right)+\text{c.c.}, \tag{27}$$

where we have defined the functions

$$f_t(\omega)=\frac{1-i\omega t-e^{-i\omega t}}{\omega^2 t}, \tag{28}$$

$$g_t(\omega)=\frac{1-e^{-i\omega t}}{\omega}, \tag{29}$$

which have δ-function and principal-value parts at large times:

$$\lim_{t\to\infty}f_t(\omega)=\pi\delta(\omega)-iP/\omega, \tag{30}$$

$$\lim_{t\to\infty}g_t(\omega)=P/\omega+i\pi\delta(\omega). \tag{31}$$

These functions are shown in Fig. 2. It is clear from the above that for times much longer than the Larmor period $2\pi/\omega_0$, the term in (27) containing $f_t(\omega)$ is dominant, growing linearly in t, and gives the asymptotic time dependence of the second-order contribution.

Comparing (27) with (5), we can make the following identification:

$$\left.\begin{matrix}\Gamma(t)t\\ \Delta\omega_{(2)}t+\phi\end{matrix}\right\}=\gamma_m^2\times\left\{\begin{matrix}\text{Re}\\ \text{Im}\end{matrix}\right.\int\frac{d\omega}{4\pi}\left(tf_t(\omega)[\Phi_{zz}(\omega)+\tfrac{1}{2}\Phi_{+-}(\omega+\omega_0)]-\frac{g_t(\omega)}{2\omega_0}[\Phi_{xx}(\omega+\omega_0)-\Phi_{yy}(\omega+\omega_0)]\right). \qquad \begin{matrix}(32\text{a})\\(32\text{b})\end{matrix}$$

As indicated in (32b), the frequency shift $\Delta\omega_{(2)}$ and phase ϕ cannot be unambiguously defined for all times. At small times, transient effects are important and it is not meaningful to think in terms of a frequency shift and phase. However, asymptotically in time, the right-hand side of (32b) contains a term growing linearly in time and a constant correction. These terms can be associated with the frequency shift and phase, respectively. It is useful, however, to consider the depolarization rate $\Gamma(t)$ as being defined by (32a) for all times.

The interpretation given to the two terms multiplying $f_t(\omega)$ in (32) is similar to that in the case of NMR. $\Phi_{zz}(\omega)$ describes fluctuations of the local field along the applied field direction. This term, therefore, corresponds to a distribution of precession frequencies which leads to a dephasing of an ensemble of spins initially polarized in a given direction. This contribution is sometimes referred to as secular broadening.[14] The second term $\Phi_{+-}(\omega+\omega_0)$ involves spin-flip processes; the requirement of energy conservation results in the argument of Φ_{+-} being displaced by ω_0. This term is referred to as either nonsecular or lifetime broadening.[14] It should be emphasized, however, that both dephasing and spin flipping have the same observable effect in that they decrease the polarization of the ensemble of spins.

When the x and y directions are equivalent, the term in (32) containing $g_t(\omega)$ drops out. In any event, this term is small when $\omega_0 t\gg 1$ and will be ignored in the following. Furthermore, we shall deal only with the depolarization rate defined in (32a). Its general behavior can easily be understood by considering Fig. 3. If the local fields are constant in time, $\Phi_{ij}(\omega)=4\pi\langle B_i^2\rangle_0\delta_{ij}\delta(\omega)$. From (32), this gives

$$\Gamma(t)t=\frac{(\gamma_m t)^2}{2}\langle B_z^2\rangle_0+\frac{\gamma_m^2}{2}\frac{1-\cos\omega_0 t}{\omega_0^2}\times(\langle B_x^2\rangle_0+\langle B_y^2\rangle_0). \tag{33}$$

Thus, for a range of times satisfying $\omega_0 t\gg 1$ but during which the local fields remain constant, the decay of the polarization has the Gaussian form

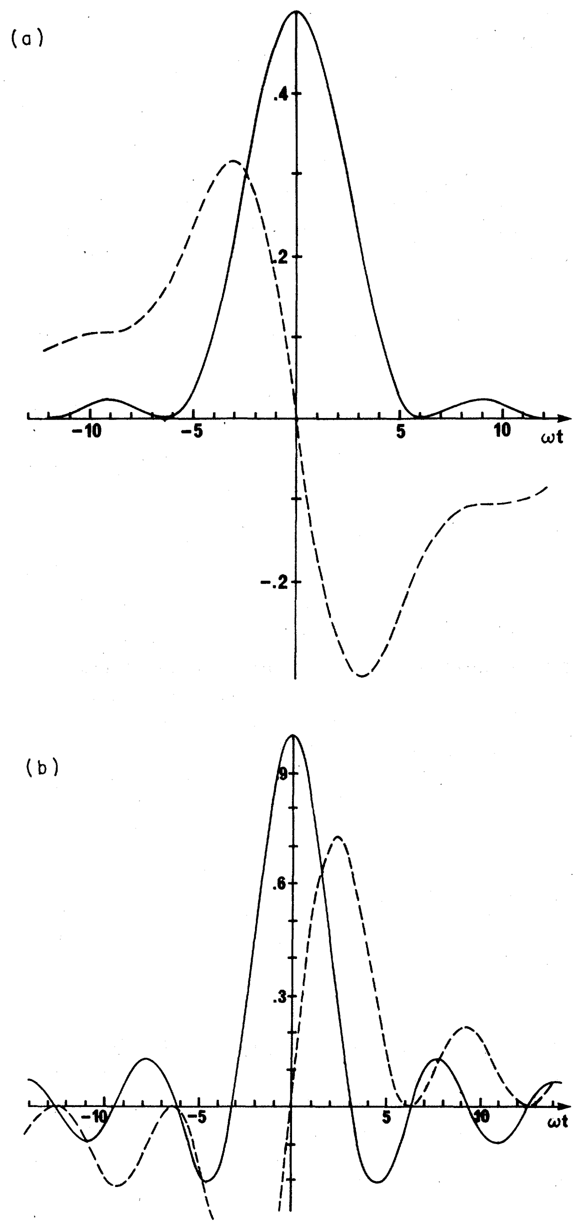


FIG. 2. The functions (a) $\mathrm{Re}[f_t(\omega)/t]$ and $\mathrm{Im}[f_t(\omega)/t]$ and (b) $\mathrm{Re}[g_t(\omega)/t]$ and $\mathrm{Im}[g_t(\omega)/t]$ vs ωt. Real and imaginary parts are shown as solid and broken curves, respectively.

$\exp(-\frac{1}{2}t^2\gamma_m^2\langle B_z^2\rangle_0)$. For a rapidly moving muon the local fields fluctuate in time and the δ-function peaks in $\Phi_{ij}(\omega)$ are broadened, the width being related to the inverse of the characteristic time of motion τ_c. Since the function $\mathrm{Re}[f_t(\omega)]$ provides a window of width $\sim t^{-1}$, only the spectral density within this window contributes significantly. Thus, if the inverse width satisfies $\tau_c \ll t$, $\mathrm{Re}[f_t(\omega)]$ acts

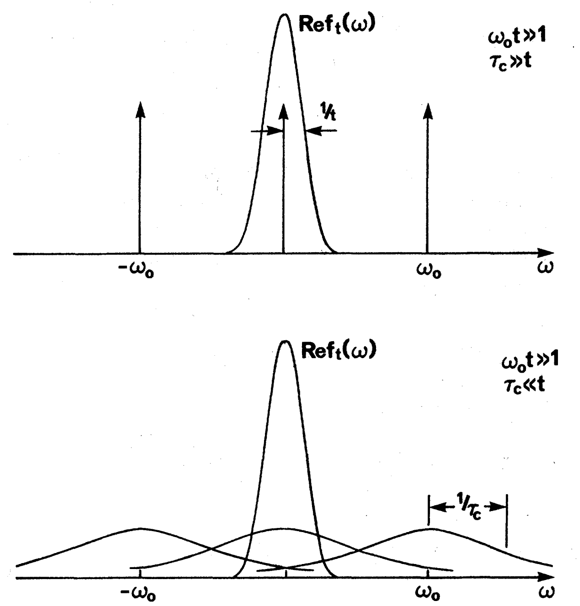


FIG. 3. Schematic illustration of the situation in the stationary ($\tau_c \gg t$) and motional narrowing ($\tau_c \ll t$) limits. The contributions to $\Gamma(t)$, Eq. (32a), are shown in terms of the spectral densities $\Phi_{zz}(\omega)$, centered at $\omega = 0$, and $\Phi_{+-}(\omega)$, centered at $\omega = \pm\,\omega_0$.

as a δ function (see Fig. 3) and we find

$$\Gamma(t)t = \tfrac{1}{4}\gamma_m^2 t[\Phi_{zz}(0) + \tfrac{1}{2}\Phi_{+-}(\omega_0)]\,. \tag{34}$$

Thus at long times $\Gamma(t)$ is a constant and the depolarization is exponential. Since $\Phi_{zz}(0)$ decreases with decreasing τ_c, the depolarization rate decreases and we observe, in the NMR terminology, the effect of "motional narrowing." It should be noted that in the extreme motional-narrowing limit, the spectral density $\Phi_{+-}(\omega)$ also becomes important in determining the depolarization rate. These points are discussed further in Sec. IV.

III. MUON SELF-DIFFUSION FUNCTION

The depolarization rate (32) is determined by the correlation functions $\Phi_{ij}(\tau)$ of the local fields at the position of the μ^+. These correlations are influenced both by the behavior of the surrounding electronic and nuclear moments causing the fields and by the motion of the μ^+ itself. Since one of the goals of μSR is to learn about the behavior of light interstitials in solids, it is of interest to identify those aspects of μ^+ motion that influence the depolarization rate. As we shall see, this can be done with the aid of one idealization.

The anticommutator (23) can be rewritten as

$$\Phi_{ij}(t'-t'')=\int d^3r'\int d^3r''\,\langle\delta(\vec{r}\,'-\vec{r}_m(t'))B_i(\vec{r}\,',t')\delta(\vec{r}\,''-\vec{r}_m(t''))B_j(\vec{r}\,'',t'')$$
$$+\delta(\vec{r}\,''-\vec{r}_m(t''))B_j(\vec{r}\,'',t'')\delta(\vec{r}\,'-\vec{r}_m(t'))B_i(\vec{r}\,',t')\rangle_0\,, \tag{35}$$

where $\vec{r}_m(t)$ is the μ^+ position operator and $B_i(\vec{r}\,',t')$ is the operator obtained by formally replacing $\vec{r}_m(t')$ by $\vec{r}\,'$ in $B_i(t')$. In general, the time evolution of the magnetic field $B_i(\vec{r},t)$ is coupled to that of the muon and the average to be performed in (35) is extremely difficult. However, if the spin degrees of freedom of the solid are only weakly influenced by the presence of the muon, the time dependence of the fields can be taken, to a first approximation, as that occuring in the absence of the muon. With this assumption, the average in (35) factors into two statistically independent parts giving

$$\Phi_{ij}(t'-t'')=\int d^3r'\int d^3r''\,[G_s(\vec{r}\,'t'\,|\,\vec{r}\,''t'')F_{ij}(\vec{r}\,'t'\,|\,\vec{r}\,''t'')+G_s(\vec{r}\,''t''\,|\,\vec{r}\,'t')F_{ji}(\vec{r}\,''t''\,|\,\vec{r}\,'t')]\,, \tag{36}$$

where

$$G_s(\vec{r}\,'t'\,|\,\vec{r}\,''t'')\equiv\langle\delta(\vec{r}\,'-\vec{r}_m(t'))\delta(\vec{r}\,''-\vec{r}_m(t''))\rangle_0 \tag{37}$$

will be called the μ^+ self-diffusion function,[15] and

$$F_{ij}(\vec{r}\,'t'\,|\,\vec{r}\,''t'')=\langle B_i(\vec{r}\,'t')B_j(\vec{r}\,''t'')\rangle_0 \tag{38}$$

is the field correlation function for the unperturbed solid. The above approximation neglects the effects of any lattice distortion induced by the muon on the spin degrees of freedom of the solid. More importantly, it fails to account for the coupling of the nuclear quadrupolar moments to the electric field gradients set up by the μ^+ which, as recently shown,[9,10] can play an important role. Of course, if the nuclear quadrupole moment is zero, or the magnetic field is sufficiently strong, this interaction has little effect, and it is to these situations that the above approximation is applicable. We shall return to the question of quadrupolar effects within our formulation in Sec. IV.

Within the approximation leading to (36), the effects of μ^+ motion have been isolated in the self-diffusion function G_s. In calculating the depolarization rate, the correlation of the field fluctuations between the space-time points $(\vec{r}\,',t')$ and $(\vec{r}\,'',t'')$ is weighted by the probability that the muon migrates from one point to the other. If the field-field correlations decrease with increasing separation, the motion of the μ^+ inevitably leads to a decreasing depolarization rate. An understanding of motional narrowing can thus be obtained by studying the properties of G_s. The behavior of F_{ij} will be discussed in detail in Sec. IV for the fields due to nuclear magnetic moments.

The strong Coulomb repulsion between the muon and the nuclei of the solid provides energetically favorable positions at interstitial sites. Because of its large mass, one would expect the muon wave function to be reasonably well localized at these positions, and polaronic effects will increase this tendency to localization. With this picture in mind, we imagine a reference system defined by some effective static potential in which the muon would propagate as a particle in a narrow band. This reference provides a basis of localized tight-binding states which can be used to describe the interstitial state of the muon. To make use of this physical picture it is convenient to express the self-diffusion function in second quantized notation,

$$G_s(\vec{r}t\,|\,\vec{r}\,'t')=\langle\psi^\dagger(\vec{r}t)\psi(\vec{r}t)\;\psi^\dagger(\vec{r}\,'t')\psi(\vec{r}\,'t')\rangle_0\,. \tag{39}$$

Introducing a complete set of orthonormal localized states $\{\phi_l(\vec{r})\}$ of the reference system, such as Wannier states centered on the interstitial sites l, (39) can be written as

$$G_s(\vec{r}t\,|\,\vec{r}\,'t')=\sum_{\substack{ll'\\mm'}}\phi_l^*(\vec{r})\phi_{l'}(\vec{r})\phi_m^*(\vec{r}\,')$$
$$\times\,\phi_{m'}(\vec{r}\,')G_s(ll't\,|\,mm't')\,, \tag{40}$$

with

$$G_s(ll't\,|\,mm't')=\langle c_l^\dagger(t)c_{l'}(t)c_m^\dagger(t')c_{m'}(t')\rangle_0\,. \tag{41}$$

The summation over l in general includes all states on the lth site. For the purposes of the following qualitative discussion we suppose that it is adequate to consider only a single state on each site. If these states are indeed well-localized, the products $\phi_l^*(\vec{r})\phi_{l'}(\vec{r})$ are small unless $l=l'$, and only the diagonal elements

$$G_s(lt\,|\,l't')\equiv\langle n_l(t)n_{l'}(t')\rangle_0 \tag{42}$$

are important. This quantity is just the correlation function for particle number $n_l=c_l^\dagger c_l$ on the lth and l'th sites. We shall assume that these terms do provide the main contribution to $G_s(\vec{r}t\,|\,\vec{r}\,'t')$. Their explicit evaluation of course requires a specific model for the muon-solid interaction.

With this simplification, (36) becomes

$$\Phi_{ij}(\tau)=\sum_{lm}[G_s(l\tau\,|\,m)F_{ij}(l\tau\,|\,m)$$
$$+G_s(l,-\tau\,|\,m)F_{ji}(l,-\tau\,|\,m)]\,, \tag{43}$$

where

$$F_{ij}(l\tau|m)=\int d^3r\int d^3r'\,|\phi_l(\vec r)|^2\,F_{ij}(\vec r\tau|\vec r'0)\,|\phi_m(\vec r')|^2. \tag{44}$$

In terms of these quantities, the depolarization rate is

$$\Gamma(t)=\mathrm{Re}\int\frac{d\omega}{4\pi}f_t(\omega)\int\frac{d\omega'}{2\pi}\sum_{lm}G_s(l,\omega'|m)\,[F_{zz}(l,\omega-\omega'|m)+e^{-\beta\hbar(\omega+\omega')}F_{zz}(l,\omega+\omega'|m)$$
$$+\tfrac{1}{2}F_{+-}(l,\omega_0+\omega-\omega'|m)+\tfrac{1}{2}e^{-\beta\hbar(\omega+\omega'+\omega_0)}F_{+-}(m,\omega_0+\omega+\omega'|l)]. \tag{45}$$

Here we have made use of the symmetry property

$$F_{ji}(l,-\omega|m)=e^{-\beta\hbar\omega}F_{ij}(m,\omega|l) \tag{46}$$

which applies to the canonical ensemble average.

In order to obtain a qualitative understanding of μ^+ motion, we consider the evaluation of $G_s(l\tau|m)$ for various simple models. For a tight-binding model with Hamiltonian $H_{\mathrm{TB}}=\sum_{lm}t_{lm}c_l^\dagger c_m$ and energy dispersion $\epsilon_{\vec k}=\sum_l t_{lm}e^{i\vec k\cdot(\vec R_l-\vec R_m)}$ we obtain[16]

$$G_s(l\tau|m)=\frac{1}{N^2}\sum_{\vec q}^{\mathrm{BZ}}e^{-i\vec q\cdot(\vec R_l-\vec R_m)}\times\sum_{\vec k}^{\mathrm{BZ}}\frac{e^{-\beta\epsilon_{\vec k}}}{Z}e^{i(\epsilon_{\vec k}-\epsilon_{\vec k+\vec q})\tau/\hbar}, \tag{47}$$

where $Z=\sum_{\vec q}^{\mathrm{BZ}}e^{-\beta\epsilon_{\vec q}}$ is the muon partition function and $\vec R_l$ denote the various μ^+ interstitial sites. At $\tau=0$, this expression reduces to $G_s(l0|m)=N^{-1}\delta_{lm}$. For temperatures much less than the bandwidth, the large-time behavior is determined by the low-energy states. We can then expand $\epsilon_{\vec k}$ and about $\vec k=0$ as $\epsilon_{\vec k}=\hbar^2k^2/2m^*$ and extend the summations to all values of $\vec k$, obtaining

$$G_s(l\tau|m)\xrightarrow[\tau\to\infty]{}\frac{\Omega_0}{N}\left(\frac{m^*}{2\pi\tau(kT\tau+i\hbar)}\right)^{3/2}\times\exp[-m^*|\vec R_l-\vec R_m|^2/2\tau(kT\tau+i\hbar)], \tag{48}$$

where Ω_0 is the volume per site. This is the usual expression for a free quantum particle.[15] For times larger than $\hbar/kT\simeq7.7\times10^{-12}/T$ sec, quantum effects are not important and the motion is that of a free classical particle. The amplitude at the original site $G_s(l\tau|l)$ behaves as τ^{-3} for long times.

An alternative semiclassical description of μ^+ motion is based on the assumption that the site occupation number satisfies the rate equation

$$\dot n_l(\tau)=\sum_m[W_{lm}n_m(\tau)-W_{ml}n_l(\tau)], \tag{49}$$

where W_{lm} is the transition rate from the mth to the lth site. The self-diffusion function $G_s(l\tau|m)$ is then the solution to (49) with the initial condition $N^{-1}\delta_{lm}$. If the sites form a Bravais lattice, the solution can be expressed as

$$G_s(l\tau|m)=\frac{1}{N^2}\sum_{\vec q}^{\mathrm{BZ}}e^{-i\vec q\cdot(\vec R_l-\vec R_m)}\times\exp\left(-\sum_n W_{n0}(1-\cos\vec q\cdot\vec R_{n0})\tau\right). \tag{50}$$

This expression is similar to (47), with thermal averaging giving a temperature-dependent transition rate W. The explicit evaluation of (50) is difficult although the long-time behavior can be extracted easily. Expanding $\cos\vec q\cdot\vec R_{n0}$ in powers of q and assuming the occupied sites to have cubic symmetry, we find

$$G_s(l\tau|m)\xrightarrow[\tau\to\infty]{}\frac{\Omega_0}{N}\left(\frac{1}{4\pi D\tau}\right)^{3/2}\exp(-|\vec R_l-\vec R_m|^2/4D\tau), \tag{51}$$

where the diffusion constant is defined as

$$D=\frac{1}{6}\sum_n W_{n0}R_{n0}^2. \tag{52}$$

(51) is the usual result for a diffusing classical particle. In this case the single site amplitude decays as $\tau^{-3/2}$, that is, more slowly than for the free particle. This is simply a consequence of the particle returning to the origin as a result of "collisions."

If the particle were forever lost after leaving a particular site, the on-site correlation would behave as

$$G_s(l\tau|l)\sim(1/N)\exp(-\tau/\tau_c), \tag{53}$$

which follows from (49) by neglecting the scattering-in term. In neither the free nor diffusing particle limits is an exponentially decreasing time dependence observed, although for practical purposes it may be convenient to use a function of the form (53). In order to identify the parameter τ_c it is useful to consider the regime in which the muon is rapidly moving. In this case, $G_s(l,\tau|l)$

has a short correlation time compared to other times in the problem and therefore $G_s(l,\omega|l)$ in (45) can be replaced by $G_s(l,\omega=0|l)$. Furthermore, if $NG_s(l,\tau|l)$ is given the interpretation, strictly correct in the classical limit, of being the probability of residing on a site l for a time τ, one can define the mean time of stay as

$$\begin{aligned}\tau_s &\equiv \mathrm{Re}\int_0^\infty d\tau\,\tau\left(-\frac{d}{d\tau}NG_s(l,\tau|l)\right)\\ &= \mathrm{Re}\int_0^\infty d\tau\, NG_s(l,\tau|l)\\ &= \tfrac{1}{2}NG_s(l,\omega=0|l)\,.\end{aligned} \tag{54}$$

Thus in the rapidly moving limit, the depolarization rate is proportional to the mean time of stay. In addition, a consistent choice for the parameter τ_c in (53) is clearly τ_s. The usefulness of this choice is demonstrated in Fig. 4 where a comparison of the exponential approximation and the rate equation solution for a simple cubic lattice is made. The similarity of the curves suggests that data analysis based on the exponential approximation directly gives an estimate of the mean time of stay.

IV. FIELD-CORRELATION FUNCTIONS

In this section we return to the evaluation of the field-correlation functions $F_{ij}(\vec{r}t|\vec{r}'t')$ for the specific example of the local fields being due to nuclear magnetic moments.

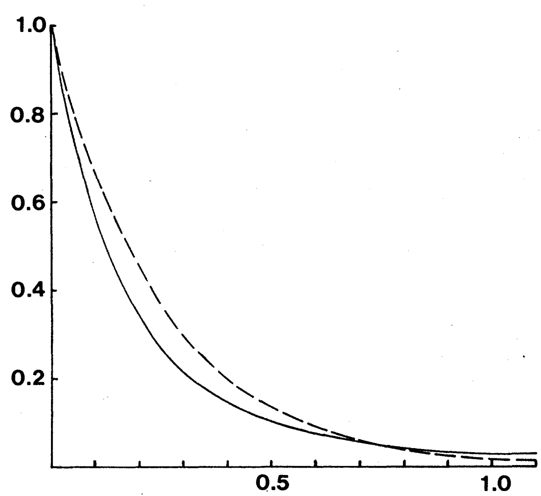


FIG. 4. The solid curve gives $G_s(l,\tau|l)$ from Eq. (50) as a function of $W\tau$ for nearest-neighbor hopping on a simple cubic lattice. For comparison, the exponential approximation (53) is shown by the broken curve with τ_c equal to the mean time of stay ($\tau_s = 0.246/W$).

A. Free nuclear moments

Following the discussion of Sec. III, we begin by evaluating F_{ij} for the unperturbed solid. The nuclear moments $\vec{\mu}_i$ are located at the positions $\vec{R}_i$, the possibility of different isotopes being allowed for by the site index i. The magnetic moment is related to the nuclear spin $\vec{S}_i$ by

$$\vec{\mu}_i = \gamma_i\vec{S}_i \equiv \hbar\gamma_i\vec{I}_i\,, \tag{55}$$

where γ_i is the gyromagnetic ratio.

The dipolar field at the position $\vec{r}$ is

$$\vec{B}(\vec{r}) = \sum_i \gamma_i \frac{3\hat{n}_i(\hat{n}_i\cdot\vec{S}_i) - \vec{S}_i}{|\vec{r}-\vec{R}_i|^3}\,, \tag{56}$$

where the unit vector $\hat{n}_i$ is $(\vec{r}-\vec{R}_i)/|\vec{r}-\vec{R}_i|$. In the following, we shall assume the nuclei to be fixed at their equilibrium positions and neglect the effect of their vibrational motion. Since these vibrations occur on a time scale of 10^{-12} sec, their effects are averaged out in a Larmor period (10^{-6}–10^{-8} sec). Furthermore, our assumption neglects the effect on the dipolar field of the local distortion around the muon.

Since the dipole interaction between the nuclear spins is not important during the time of a depolarization experiment, the spins can be treated as independent. Thus, the only time dependence of the nuclear fields, in the absence of quadrupole interactions, arises from the precessional motion of the spins in the external field and is given by

$$I_{iz}(t) = I_{iz}\,, \tag{57a}$$

$$I_{i\pm}(t) = I_{i\pm}e^{\mp i\omega_i t}, \quad \omega_i = \gamma_i B_0\,. \tag{57b}$$

The evaluation of (38) involves a spin trace over nuclear spin configurations. Since the nuclear polarization due to the external field is negligible, the density matrix for each spin is proportional to a unit matrix and we have

$$F_{ij}(\vec{r}t|\vec{r}'t') = F_{ji}(\vec{r}'t'|\vec{r}t) \tag{58}$$

by the cyclic property of the trace. In this situation, the Boltzmann factors appearing in (45) and (46) can be replaced by unity. Since the spins do not interact, there are no correlations between different sites and the quantities to be evaluated are of the form

$$\begin{aligned}\langle\vec{u}\cdot\vec{I}_i(t)\vec{v}\cdot\vec{I}_j(t')\rangle &= \tfrac{1}{6}\,\delta_{ij}I_i(I_i+1)\\ &\quad\times(u_+v_-e^{i\omega_i\tau} + u_-v_+e^{-i\omega_i\tau} + 2u_zv_z)\,.\end{aligned} \tag{59}$$

Using this result we find

$$F_{zz}(\vec{r}t|\vec{r}'t') = \sum_i \frac{1}{6} \frac{(\hbar\gamma_i)^2 I_i(I_i+1)}{|\vec{r}-\vec{R}_i|^3 |\vec{r}'-\vec{R}_i|^3} \times [9n_{iz}n'_{iz}(n_{i+}n'_{i-}e^{i\omega_i\tau} + n_{i-}n'_{i+}e^{-i\omega_i\tau}) + 2(3n_{iz}^2-1)(3n_{iz}'^2-1)] \tag{60a}$$

and

$$F_{+-}(\vec{r}t|\vec{r}'t') = \sum_i \frac{1}{6} \frac{(\hbar\gamma_i)^2 I_i(I_i+1)}{|\vec{r}-\vec{R}_i|^3 |\vec{r}'-\vec{R}_i|^3} \times [(3n_{i+}n_{i-}-2)(3n'_{i+}n'_{i-}-2)e^{-i\omega_i\tau} + 9n_{i+}^2 n_{i-}'^2 e^{i\omega_i\tau} + 18 n_{i+}n_{iz}n'_{i-}n'_{iz}] . \tag{60b}$$

$\hat{n}'_i$ is defined as $(\vec{r}'-\vec{R}_i)/|\vec{r}'-\vec{R}_i|$.

Since the muon self-diffusion function is invariant with respect to translations by a lattice vector, the field-correlation functions can be averaged over the random positions of the various isotopic spins. If the αth species occurs with probability p_α, the average of Eqs. (60a) and (60b) allows the replacement

$$(\hbar\gamma_i)^2 I_i(I_i+1)e^{\pm i\omega_i\tau} \to \sum_\alpha p_\alpha(\hbar\gamma_\alpha)^2 \times I_\alpha(I_\alpha+1)e^{\pm i\omega_\alpha\tau}. \tag{61}$$

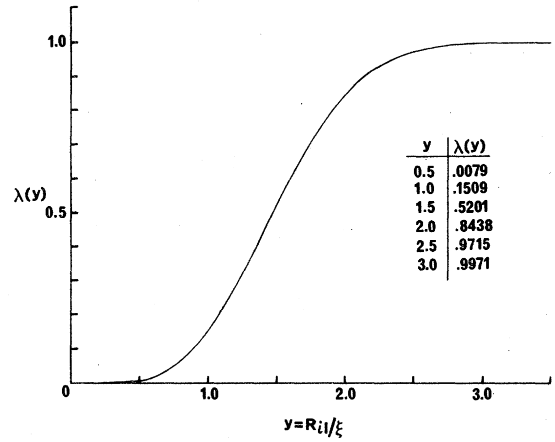
Thus the field-correlation functions involve geometrical sums multiplied by factors having oscillatory time dependences at the various nuclear Larmor frequencies.

The quantity of most interest is the field correlation function in the site representation defined in (44). We note that each of the terms in $F_{ij}(\vec{r}t|\vec{r}'t')$ contains an angular function which is simply proportional to a product of spherical harmonics of order 2: $Y_2^\mu(\theta_i,\phi_i)Y_2^{\mu*}(\theta'_i,\phi'_i)$. The polar angles (θ_i,ϕ_i) define the orientation of the vector $\vec{r}-\vec{R}_i$ within a coordinate system which has its z-axis aligned with the external magnetic field. Thus, in evaluating $F_{ij}(lt|mt')$ we require integrals of the type

$$J_{il}^{(\mu)} \equiv \int d^3r \frac{|\phi_l(\vec{r})|^2 Y_2^\mu(\theta_i,\phi_i)}{|\vec{r}-\vec{R}_i|^3} , \tag{62}$$

which is related to the dipolar field of the ith nucleus averaged over the position of the muon centerd on the lth site. The weight function $|\phi_l(\vec{r})|^2$ has the spatial symmetry of the particular site being considered. Since the essential aspect is its degree of localization about the lth site rather than its symmetry, it is useful to parametrize it by a spherically symmetric function. In particular, if $|\phi_l(\vec{r})|^2$ is chosen to be a Gaussian

$$|\phi_l(\vec{r})|^2 = (\pi\xi^2)^{-3/2}\exp(-|\vec{r}-\vec{R}_l|^2/\xi^2) . \tag{63}$$



y	λ(y)
0.5	.0079
1.0	.1509
1.5	.5201
2.0	.8438
2.5	.9715
3.0	.9971

FIG. 5. The function $\lambda(R_{il}/\xi)$ for a Gaussian μ^+ wave function.

Equation (62) reduces to the general form

$$J_{il}^{(\mu)} = [Y_2^\mu(\theta_{il},\phi_{il})/R_{il}^3]\lambda(R_{il}/\xi) , \tag{64}$$

where (θ_{il},ϕ_{il}) define the orientation of $\vec{R}_l-\vec{R}_i \equiv \vec{R}_{il}$. The scale factor $\lambda(R_{il}/\xi)$ is given explicitly by

$$\lambda(y) = y^3\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{dx}{x}\left[e^{-(x-y)^2}\left(\frac{1}{\alpha}-\frac{3}{\alpha^2}+\frac{3}{\alpha^3}\right) - e^{-(x+y)^2}\left(\frac{1}{\alpha}+\frac{3}{\alpha^2}+\frac{3}{\alpha^3}\right)\right] , \tag{65}$$

with $\alpha = 2xy$. $\lambda(y)$ is plotted in Fig. 5 which shows that $\lambda(y)$ rapidly approaches unity for y greater than one. Thus, for nuclear sites beyond a distance ξ from the muon, $J_i^{(\mu)}$ has a value corresponding to the μ^+ being fixed at the position $\vec{R}_l$. However, the values for nearest-neighbor sites can be reduced significantly by the smearing of the μ^+ position. This effect is opposite to that previously assumed.[9] If the spread is sufficiently large, its effect on the magnitude of the depolarization rate must be taken into account.

With the above results we finally obtain

$$F_{zz}(lt|mt') = \frac{16\pi}{15}\sum_\alpha p_\alpha(\hbar\gamma_\alpha)^2 I_\alpha(I_\alpha+1) \times \sum_i J_{il}^{(0)}J_{im}^{(0)*} + \frac{4\pi}{5}\sum_\alpha p_\alpha(\hbar\gamma_\alpha)^2 I_\alpha(I_\alpha+1)e^{i\omega_\alpha\tau} \times \sum_i J_{il}^{(1)}J_{im}^{(1)*} + \text{c.c.} \tag{66}$$

and

$$F_{+-}(lt|mt') = \sum_\alpha p_\alpha(\hbar\gamma_\alpha)^2 I_\alpha(I_\alpha+1) \times\left(\frac{8\pi}{15}\, e^{-i\omega_\alpha\tau} \sum_i J_{il}^{(0)} J_{im}^{(0)*} + \frac{8\pi}{5} \sum_i J_{il}^{(1)} J_{im}^{(1)*} + \frac{16\pi}{5}\, e^{i\omega_\alpha\tau} \sum_i J_{il}^{(2)} J_{im}^{(2)*}\right). \tag{67}$$

Since the functions $F_{ij}(lt|mt')$ decrease with increasing site separation $\vec{R}_l - \vec{R}_m$, the largest contribution to the depolarization rate in (45) is expected to come from the $l=m$ terms in the site summations, even when the muon is diffusing. For a stationary muon, only these terms contribute since $G_s(l\tau|m) = N^{-1}\delta_{lm}$. We shall make the approximation of retaining only these terms in obtaining the estimates of the depolarization rate which follow.

In order to evaluate (45), we shall make use of the approximate form for the self-diffusion function given in (53), which is chosen for its mathematical simplicity. As discussed previously, τ_c is to be interpreted as the mean time τ_s that a muon resides on a particular site before hopping to an adjacent site. The details of the hopping process will not be specified further since only the qualitative dependence of the polarization rate on the magnitude of τ_c will be discussed.

The Fourier transform of (53) is the Lorentzian

$$G_s(l\omega|l) = (1/N) 2\tau_c / [(\omega\tau_c)^2 + 1]\,. \tag{68}$$

The transforms of the field-correlation functions given by (66) and (67) contain δ-function contributions at $\omega = 0$ and at the nuclear Larmor frequencies $\omega = \pm\omega_\alpha$. The relative importance of the various terms depends on the degree to which the Lorentzian (68) overlaps these δ-function contributions and, as explained in Sec. II, leads to behavior ranging between the stationary and motional-narrowing limits. Within the single-site approximation, this entire range of behavior is described by the depolarization rate

$$\Gamma(t) = \mathrm{Re} \sum_\alpha p_\alpha(\hbar\gamma_m\gamma_\alpha)^2 I_\alpha(I_\alpha+1)\left\{\frac{16\pi}{15} f_t\!\left(\frac{-i}{\tau_c}\right)\sum_i |J_{il}^{(0)}|^2 + \frac{4\pi}{5}\left[f_t\!\left(\omega_\alpha - \frac{i}{\tau_c}\right) + f_t\!\left(-\omega_\alpha - \frac{i}{\tau_c}\right)\right]\sum_i |J_{il}^{(1)}|^2 + \frac{4\pi}{15} f_t\!\left(\omega_\alpha - \omega_0 - \frac{i}{\tau_c}\right)\sum_i |J_{il}^{(0)}|^2 + \frac{4\pi}{5} f_t\!\left(-\omega_0 - \frac{i}{\tau_c}\right)\sum_i |J_{il}^{(1)}|^2 + \frac{8\pi}{5} f_t\!\left(-\omega_\alpha - \omega_0 - \frac{i}{\tau_c}\right)\sum_i |J_{il}^{(2)}|^2\right\} \tag{69}$$

This expression simplifies in two important limits.

1. Stationary limit

For a stationary muon, τ_c is much longer than any other time in the problem. Considering the limit $\tau_c \gg t \gg T$, where T is a typical Larmor period, the first term in (69) dominates and we find

$$\Gamma_s(t) = \frac{1}{6}\, t \sum_\alpha p_\alpha(\hbar\gamma_m\gamma_\alpha)^2 I_\alpha(I_\alpha+1) \times \sum_i (3\cos^2\theta_{il} - 1)^2 \frac{\lambda^2(R_{il}/\xi)}{R_{il}^6} \equiv \sigma_s^2 t\,. \tag{70}$$

Except for the scale factor $\lambda(R_{il}/\xi)$ which accounts for the spatial spread of the muon wave function, this is the usual dipolar-broadening result familiar in NMR[17] and used in the interpretation of μSR experiments. Since the nearest-neighbor terms usually contribute most to the summation, $\Gamma_s(t)$ is sensitive to the spread of the muon wave function and therefore can provide some information concerning its localization.

2. Motional narrowing

Here we consider the extreme limit $t \gg T \gg \tau_c$ corresponding to the muon sitting on a site for a time much shorter than the Larmor period. The factors f_t in (69) can then be replaced by τ_c and

$$\Gamma_{\mathrm{MN}}(t) = \frac{1}{6}\, \tau_c \sum_\alpha p_\alpha(\hbar\gamma_m\gamma_\alpha)^2 I_\alpha(I_\alpha+1) \times \sum_i (3\cos^2\theta_{il} + 7) \frac{\lambda^2(R_{il}/\xi)}{R_{il}^6}\,. \tag{71}$$

For rapid motion through the lattice, the polarization decreases exponentially with a time constant determined by field fluctuations both parallel and perpendicular to the external field. This should be contrasted with the dependence of Γ_s on only

F_{zz} for the stationary case. It should be noted in particular that $\Gamma_{\rm MN}$ is not simply $2\sigma_s^2\tau_c$, as suggested previously,[18] and consequently does not exhibit the same anisotropy with respect to the field direction as does Γ_s. However, as a practical matter, the first term in (69) dominates for $\omega_0\tau_c > 1$ and the depolarization rate then behaves as

$$\Gamma(t)t \simeq 2\sigma_s^2\tau_c^2(e^{-t/\tau_c}+t/\tau_c-1). \qquad (72)$$

The remaining terms do not become significant until $\omega_0\tau_c \simeq 1$, at which point $\Gamma(t)$ has decreased by roughly a factor $(\omega_0 t)^{-2}$, which is typically between 10^{-2} and 10^{-4}. Thus the effect of the other terms in (69) can be observed only if depolarization rates of this magnitude can be measured.

B. Quadrupole effects

We shall now consider the more general situation in which the nuclei also have quadrupole moments which can couple to electric field gradients. Since a muon is positively charged, the dynamics of the nuclear spins in its vicinity are modified as a result of the quadrupole interaction. In a metal the fields produced by the muon are rapidly screened within a distance of the order of an interatomic spacing and only those spins within this distance will experience appreciable field gradients. Nevertheless, the quadrupole coupling can have a profound effect on the depolarization rate since the near-neighbor spins contribute most to the rate. Recent experiments[9] on Cu have demonstrated the importance of quadrupole effects for sufficiently weak applied magnetic fields, and the dependence of the depolarization rate as a function of field strength could be well accounted for in terms of the quadrupole interaction.[10]

The experiments for Cu were performed at temperatures sufficiently low that the muon was stationary. In this situation, the arguments of Sec. III can be generalized by evaluating $F_{ij}(r't'|r''t'')$ in the presence of the field gradients set up by the muon. Specifically, one must calculate $F_{ij}(l\tau|l)$ in (44) corresponding to the muon occupying site l. Since the vibrational motion of the muon occurs on a time scale of 10^{-12} sec, a time much shorter than the Larmor period, the neighboring nuclei experience an electric field obtained by averaging over the instantaneous positions of the muon within the site. Assuming axially symmetric fields, the dynamics of neighboring nuclei is determined by the Hamiltonian[19]

$$\mathcal{H}^i = -\gamma_i\hbar B_0 I_{iz} + \frac{e^2(qQ)_i}{4I_i(2I_i-1)}(3I_{iz'}^2 - I_i^2), \qquad (73)$$

where $(eqQ)_i$ is the product of the electric field gradient in the direction z' and the nuclear quadrupole moment. The time dependence of the nuclear spins is accordingly modified from that given in (57).

If the muon is moving, the situation is complicated considerably since the factorization in (36) is not valid. However, since the single-site contribution to the depolarization rate given in (45) is the most important, a reasonable estimate of $\Gamma(t)$ can be obtained by using (68) for the self-diffusion function and evaluating $F_{ij}(l\tau|l)$ as described above for the stationary muon. For simplicity, we consider only the stationary limit $G_s(l\tau|m)=(1/N)\delta_{lm}$.

The field correlation functions can be evaluated using the eigenstates of the Hamiltonian $\mathcal{H}^i$,

$$\mathcal{H}^i|m\rangle_i = E_m^i|m\rangle_i \qquad (74)$$

where the subscript i denotes the ith nucleus. Using this basis we obtain the result

$$\Gamma(t) = \sum_i (\hbar\gamma_m\gamma_i)^2\lambda^2(R_{il}/\xi)R_{il}^{-6}(2I_i+1)^{-1}\sum_{mn}\Big[\mathrm{Re}f_t(\omega_{nm}^i)\,|\langle m|3n_{iz}(\hat{n}_i\cdot\vec{\mathrm{I}}_i) - I_{iz}|n\rangle_i|^2 + \tfrac{1}{2}\,\mathrm{Re}f_t(\omega_{nm}^i-\omega_0)\,|\langle m|3n_{i+}(\hat{n}_i\cdot\vec{\mathrm{I}}_i) - I_{i+}|n\rangle_i|^2\Big]. \qquad (75)$$

Since $\mathrm{Re}f_t(\omega)$ behaves as a δ function at large times, the only terms contributing to the summation are those for which $(E_n^i - E_m^i)/\hbar \equiv \omega_{nm}^i = 0$ or $\omega_{nm}^i - \omega_0 = 0$. The former situation is always true for the diagonal terms $m=n$. However, the latter situation is a resonance condition corresponding to the excitation frequency of the Zeeman-quadrupole Hamiltonian being equal to the Larmor precession frequency of the muon. Since ω_0 is proportional to B_0 while ω_{nm}^i is independent of field for small fields, such a crossover must always occur and should be accompanied by an increase in the observed depolarization rate.

As an application of the quadrupole result, we have considered the field dependence of the depolarization rate in Cu. With the muon occupying an octahedral site, it was assumed that only nearest-neighbor nuclei experience a field gradient in the radial direction. Retaining only the diagonal terms in the F_{zz} contribution, the depolarization rates $\sigma_{hkl}(B_0) \equiv (\Gamma/t)^{1/2}$ were calculated from (75) for various symmetry directions and the results are plotted in Fig. 6. The value of the wave function width parameter ξ was adjusted to 0.90 Å to obtain a fit to the observed σ_{100} rate in the high-field limit. A good fit to the data could then be obtained

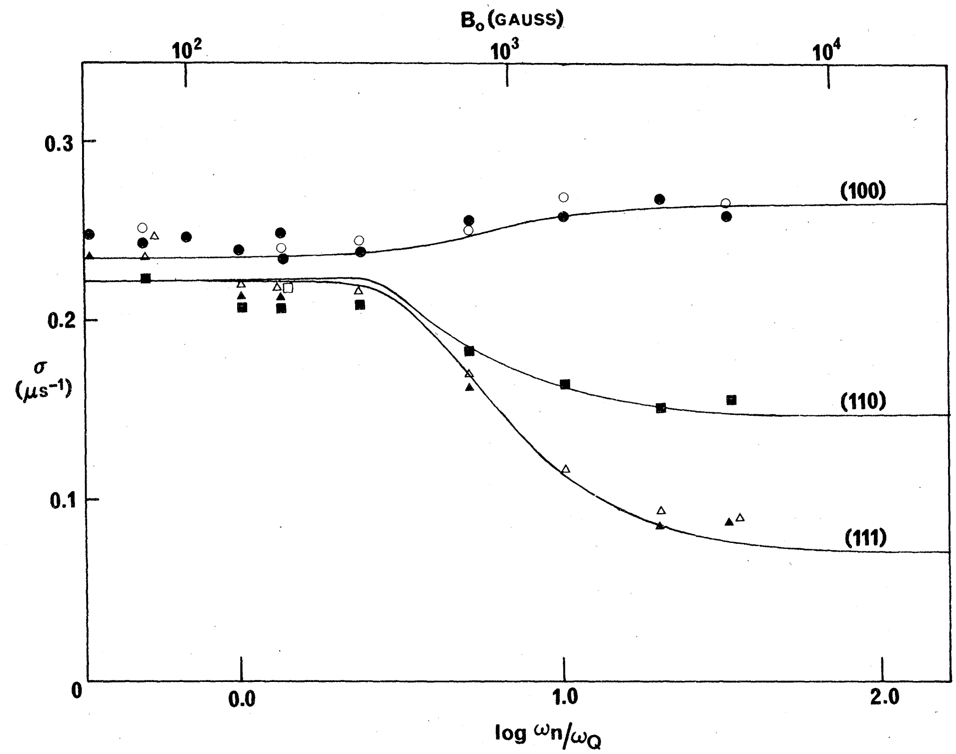


FIG. 6. Field dependence of the depolarization rate in copper for various symmetry directions. The experimental points are taken from Ref. 9.

using $\omega_E/2\pi \equiv e^2qQ/4I(2I-1)h = 0.17$ MHz, which is close to the value of 0.16 MHz based on the assumption of a point muon and nearest-neighbor nuclei being displaced away from the muon site.[9] The two models are essentially equivalent in that both decrease the nearest-neighbor contribution to the rate by the appropriate amount. The existing calculation[20] of the potential seen by a point positive charge in Cu suggests that the assumed value for the wave function width is unrealistically large. On the other hand, this width allows an explanation of the data even if the nearest neighbors are displaced inward, toward the muon, as electron gas calculations[21] indicate. Since the effects of lattice displacement and wave function spread are, in principle, both present, it would be of considerable interest to obtain reliable interstitial potentials for the positive muon in a crystal.

V. DISCUSSION

In the preceding sections we have presented a general theory of positive-muon spin depolarization in solids. Our emphasis has been on the transverse geometry, although expressions for arbitrary polarization are given in Sec. II. The central result (32) gives an expression for the depolarization rate $\Gamma(t)$ (as well as for the frequency shift and phase) in terms of the correlations of the local field at the position of the muon. The relevant correlation functions $\Phi_{ij}(\omega)$ were studied in detail for the case in which the depolarization is caused by the nuclear spins. Provided that quadrupole effects could be neglected, the muon self-diffusion function G_s emerged as the natural way of including the μ^+ motion. In this description, correlation functions $F_{ij}(l, \omega \mid m)$ accompanying G_s were defined which describe the correlations of the nuclear dipolar fields at the various sites sampled by the muon in its motion through the lattice. By introducing these functions, one can systematically examine the implications of various models of μ^+ motion on the depolarization rate.

In the stationary μ^+ limit, our expression reduces to the usual dipolar broadening result familiar from NMR, with the one modification of allowing for the spread of the μ^+ wave function about the interstitial site. For a Gaussian wave function, the effect of this modification is to reduce Γ_s, although the reduction is only significant if the parameter ξ is larger than about one half the distance from the muon to the nearest neighbor nuclei. In considering the field dependence of the rate in Cu, it was found that the experimental observations could be explained by taking $\xi = 0.9$ Å. The scarcity of information about interstitial potentials makes it difficult to decide whether or not a width of this magnitude is a viable alternative to the explanation based on the assumption of nuclear displacements.

Once motion on the time scale of $\tau_\mu = 2.2$ μsec becomes significant, the depolarization rate decreases, which is the analogue of motional narrowing in NMR. In contrast to the stationary limit, multisite correlations $F_{ij}(l, \omega|m)$ contribute to Γ, weighted appropriately by the self-diffusion function [cf. Eq. (45)]. The results of Sec. IV were obtained within the single-site approximation; calculations for the simple cubic lattice have shown, however, that correlations between nearest-neighbor interstitial sites can contribute to the rate in certain situations. Neglecting such contributions can lead to erroneous estimates of the μ^+ hopping rate.

In the extreme motional-narrowing limit, $\Gamma(t)$ is time independent and proportional to τ_s, the mean time of stay on a particular site (again using the single-site approximation). In addition, in a cubic environment it exhibits an isotropic external field dependence. It would be interesting to study the transition from anisotropic to isotropic field dependence by performing experiments at high fields and spanning temperatures from the stationary to the motional-narrowing limits. However, a severe limitation on such experiments is that Γ must be measured within a time $\sim\tau_\mu$, thus placing a lower limit of about 10^{-9}–10^{-8} Sec on τ_s.

We have not considered the longitudinal geometry in any detail here. It is, however, clear from (24) and (25) that the spin-flip contribution Φ_{+-} is common to both the longitudinal and transverse cases. In particular, the longitudinal depolarization will be relatively small, even for a stationary μ^+, unless the external field is such that $\omega_0 t \lesssim 1$. This observation suggests the possibility of studying Φ_{+-} in some detail by performing longitudinal depolarization experiments as a function of magnetic field. Unfortunately, the interpretation of such field-dependent measurements would in general be complicated by the nuclear quadrupole interaction.

Finally, we should mention the depolarization due to the conduction electrons of a metal. Using the Fermi contact electron-muon interaction one obtains from (32) an expression identical to the Korringa relaxation rate[22] for nuclei in simple metals (i.e., noninteracting electrons). However, the numerical value of the rate is much smaller[23] than the nuclear dipole contribution. In strongly interacting electron systems, such as metallic ferromagnets, the situation may be different. The anomalous temperature dependence of the depolarization rate observed in ferromagnets near T_c (Ref. 4) indicates that electron-muon interactions are playing a dominant role. It would therefore be of interest to extend our treatment to the problem of spin depolarization in ferromagnets.

ACKNOWLEDGMENT

This work was supported in part by a grant from the National Research Council of Canada.

---

[1]Laboratories at which muon studies of solids are carried on include: Schweizerisches Institut für Nuklearforschung (SIN), 5234 Villigen, Switzerland; CERN, Geneva, Switzerland; TRIUMF (Tri-University Meson Facility), Vancouver, British Columbia, Canada; SREL (Space Radiation Effects Laboratory) Newport News, Virginia; Clinton P. Anderson Meson Physics Facility (LAMPF), Los Alamos, New Mexico; JINR Laboratory of Nuclear Problems, Dubna, USSR.

[2]See, for example, E. D. Commins, *Weak Interactions* (McGraw-Hill, New York, 1973).

[3]J. H. Brewer, K. M. Crowe, F. N. Gygax, and A. Schenck, in *Muon Physics*, edited by V. W. Hughes and C. S. Wu (Academic, New York, 1975), Vol. III, Chap. 7.

[4]M. L. G. Foy, N. Heiman, W. J. Kossler, and C. E. Stronach, Phys. Rev. Lett. 30, 1064 (1973).

[5]B. D. Patterson, K. M. Crowe, F. N. Gygax, R. F. Johnson, A. M. Portis, and J. H. Brewer; Phys. Lett. A 46, 453 (1974).

[6]I. I. Gurevich, A. I. Klimov, V. N. Maiorov, E. A. Meleshko, I. A. Muratova, B. A. Nikolskii, V. S. Roganov, V. I. Selivanov, and V. A. Suetin, Sov. Phys.-JETP 39, 178 (1974).

[7]H. Graf, W. Hofmann, W. Kündig, P. F. Meier, B. D. Patterson, and W. Reichart, Solid State Commun. 23, 653 (1977).

[8]The phase angle used in this context is not be confused with the geometry-dependent phase ϕ_0 associated with the experimental arrangement. The observed phase is a sum of both ϕ_0 and ϕ.

[9]M. Camani, F. N. Gygax, W. Ruegg, A. Schenck, and H. Schilling, Phys. Rev. Lett. 39, 836 (1977).

[10]O. Hartmann, Phys. Rev. Lett. 39, 832 (1977).

[11]V. G. Grebinnik, I. I. Gurevich, V. A. Zhukov, A. P. Manych, E. A. Meleshko, I. A. Muratova, B. A. Nikolskii, V. I. Selivanov, and V. A. Suetin, Sov. Phys.-JETP 41, 777 (1976).

[12]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford, London, 1961), Chap. 8.

[13]If trapping of the muon at defects or impurities in the solid is important, the initial density matrix ρ will not represent an equilibrium condition with respect to H^0. In this situation the stationary property does not apply and $\Phi_{ij}(t,t')$ will be a function of both time arguments.

[14]C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963).

[15]L. Van Hove, Phys. Rev. 95, 249 (1954).

[16]The periodic zone scheme has been used.

[17]Reference 14, p. 58.

[18]W. B. Gauster, A. T. Fiory, K. G. Lynn, W. J. Kossler, D. M. Parkin, C. E. Stronach, and W. F. Lankford, in Proceedings of the International Conference on the Properties of Atomic Defects in Metals, Argonne National Laboratory, October, 1976 (unpublished).

[19]Reference 14, Chap. 6.

[20]S. Prakash [Phys. Lett. A 61, 405 (1977)] calculates a potential which would predict $\sigma \sim 0.3$ Å for μ^+.

[21]Z. D. Popović, M. J. Stott, J. P. Carbotte, and G. R. Piercy, Phys. Rev. B 13, 590 (1976).

[22]J. Korringa, Physica (Utr.) 16, 601 (1950).

[23]Data for hydrogen in niobium are given by H. Lütgemeier, R. R. Arons, and H. G. Bohn, J. Mag. Res. 8, 74 (1972).