Two-Phonon Quantum Diffusion of Muonium in Solid Nitrogen

V. Storchak,* J.H. Brewer, W.N. Hardy, S.R. Kreitzman, and G.D. Morris
Canadian Institute for Advanced Research and Department of Physics, University of British Columbia, Vancouver, British Columbia, Canada V6T 2A3
(Received 30 September 1993)

The spin dynamics of the muonium (μ^+e^- or Mu) atom diffusing in solid nitrogen ($^{14}N_2$) has been studied using the techniques of muonium spin rotation and relaxation. The temperature dependence of the Mu hop rate τ_c^{-1} reveals that Mu diffusion in solid nitrogen is a quantum tunneling process governed by the two-phonon interaction. At low temperatures the Mu atom is strongly localized by suppression of band motion due to interaction with defects.

PACS numbers: 66.30.Jt, 67.80.Mg, 76.75.+i

When positive muons are implanted into insulators they often form muonium (μ^+e^- or Mu) atoms, analogous to hydrogen atoms but nearly an order of magnitude lighter [1]. The dynamics of such light atoms, being intrinsically quantum mechanical in nature, is of special interest because it provides critical tests of quantum diffusion theories [2–6].

Studies of the diffusion of hydrogen atoms [7] and μ^+ [8] in metals, as well as Mu diffusion in insulators [9–11], have convincingly shown the quantum mechanical character of the phenomenon, most clearly seen at low temperatures where the particle hop rate τ_c^{-1} *increases* with *decreasing* temperature T according to the power law $\tau_c^{-1} \propto T^{-\alpha}$, thus manifesting the onset of the coherent process. In metals, coupling to conduction electrons is the dominant scattering mechanism [12] and causes $\alpha < 1$. In insulators, where phonon scattering processes prevail, α is predicted [2,6] to be 7 or 9 at low temperatures where the absorption of single phonons shifts the energy of the diffusing particle too much for tunneling to occur and so two-phonon diagrams (which can leave the energy almost unchanged) are expected to dominate. Surprisingly, the experimental results on Mu diffusion in *ionic* insulators [9,10] indicate that α is generally close to 3; this "universal" power-law behavior with $\alpha \approx 3$ prompted the authors of Ref. [5] to conclude that muonium diffusion is governed by *one*-phonon scattering. On the other hand, in Ref. [13] it was shown that $\alpha \approx 3$ can also be obtained from *two*-phonon scattering processes if the actual phonon spectrum of the ionic crystal is taken into account; unfortunately, that procedure requires introduction of adjustable parameters. The phonon spectrum of solid nitrogen is consistent with the Debye approximation assumed in more *ab initio* theories, which may thus be tested more directly by experiment. In this Letter we present the first unambiguous evidence for *two*-phonon quantum diffusion of muonium.

In addition, we present here the first observation of gradual muonium localization as $T \to 0$ in an imperfect crystal due to suppression of Mu band motion by static disorder. Previous studies of Mu diffusion have focused on nearly perfect crystals, in which bandlike propagation of Mu persists as $T \to 0$. At temperatures $T < T_0$ [where T_0 is determined by the interplay between the phonon width $\Omega(T)$ and the typical difference ξ between energy levels at adjacent tunneling sites due to static disorder] the observed average *transverse* field relaxation rate T_2^{-1} of muonium characterizes mainly *quasistatic* Mu atoms in the vicinity of defects or impurities [14]. Another fraction of Mu atoms located far from impurities or defects moves more rapidly and relaxes slowly in transverse field due to motional narrowing. This *inhomogeneous diffusion* is a universal feature of Mu diffusion in imperfect (real) crystals whenever static level shifts ξ exceed $\Omega(T)$. In contrast to T_2^{-1}, the relaxation rate T_1^{-1} of the muonium spin in *longitudinal* field is determined mainly by the *moving* Mu atoms far from impurities or defects, and thus provides information about the undisturbed host crystal. In the experiment described here, both T_2^{-1} and T_1^{-1} were measured as functions of temperature in order to clearly identify and distinguish the effects of localization by defects and diffusion in the intrinsic host lattice.

The effective spin Hamiltonian for static Mu in solid nitrogen in an external field $\mathbf{H}$, assuming an isotropic nuclear hyperfine interaction, has the form [15]

$$\mathcal{H} = hA\mathbf{S}_e \cdot \mathbf{S}_\mu - g_e\mu_b\mathbf{S}_e \cdot \mathbf{H} - g_\mu\mu_\mu\mathbf{S}_\mu \cdot \mathbf{H} + h\sum_n \delta\,\mathbf{S}_e \cdot \mathbf{S}_n - \sum_n g_n\mu_n\mathbf{S}_n \cdot \mathbf{H}\,, \quad (1)$$

where A is the muonium hyperfine parameter, δ is the nuclear hyperfine parameter, and $\mathbf{S}$, g, and μ are the spins, g factors, and magnetic moments of the respective particles. The summations are over all participating nuclei. Nuclear quadrupole interactions are known to be small and have been neglected [16]. Qualitatively, the nuclear hyperfine interaction results in relaxation of the Mu electron spin, which in turn leads to depolarization of the μ^+ *via* the hyperfine interaction. The muonium hyperfine frequency in solid nitrogen A =4494(5) MHz has been found [17] to be very close to the vacuum value $A_{\rm vac}$ = 4463 MHz. Thus the muonium spin relaxation rate is determined by the nuclear hyperfine interaction $\delta \ll A$. In transverse field the muonium relaxation rate

0031-9007/94/72(19)/3056(4)$06.00

due to nuclear hyperfine interactions "motionally narrowed" by Mu diffusion is given (in the limit of fast diffusion, $\tau_c^{-1} \gg \delta$) by (fast-hopping limit)

$$T_2^{-1} \approx 2\delta^2\tau_c. \quad (2)$$

For slowly diffusing muonium ($\tau_c^{-1} \lesssim \delta$), depolarization takes place on a time scale shorter than the residence time, giving (static limit)

$$T_2^{-1} = \delta. \quad (3)$$

Thus, transverse field measurements of Mu diffusion are effective only for $\tau_c^{-1} > \delta$ and one cannot determine $\tau_c^{-1} < \delta$ from transverse field experiments; but in weak longitudinal field, as we shall show, it is sometimes possible to determine much slower hop rates, $\tau_c^{-1} \ll \delta$.

The basic idea of T_1^{-1} measurements [18,19] is that the nuclear hyperfine interaction is treated as an effective magnetic field acting on the muonium electron, which is a good approximation in the high field limit $\gamma_e H \gg \delta$, where γ_e is the electron gyromagnetic ratio. When Mu diffuses, the fluctuations of this effective field induce transitions between Mu hyperfine levels and thus depolarize the μ^+. The resulting muon spin polarization function $P_\parallel(t)$ was calculated in Ref. [19]. The general expression, which includes several transitions between Mu hyperfine levels, allows one to extract values of τ_c^{-1} and δ from T_1^{-1}; in solid nitrogen, δ has a rather low value (see below) which allows longitudinal field experiments in very weak fields where these equations simplify to a familiar form:

$$P_\parallel(t) = P_0\, e^{-tT_1^{-1}} \quad \text{with} \quad T_1^{-1} = \frac{2\delta^2\tau_c}{1+\omega_0^2\tau_c^2}, \quad (4)$$

where $\omega_0 = \gamma_{\mathrm{Mu}} H$ is the Mu intratriplet transition frequency in the (weak) magnetic field H. ($\gamma_{\mathrm{Mu}}/2\pi = 1.4012$ MHz/G.)

The main feature of Eq. (4) is the well-known T_1^{-1}-maximum effect [20] at $\omega_0\tau_c = 1$ with

$$T_1^{-1}(\max) = \delta^2/\omega_0\,. \quad (5)$$

In this paper we present the first observations of T_1^{-1} maxima for muonium relaxation in solid nitrogen and the first use of combined T_1^{-1} and T_2^{-1} measurements to determine the Mu hop rate over a range from $\tau_c^{-1} \ll \delta$ to $\tau_c^{-1} \gg \delta$.

The experiment was performed on the M13 and M20B beam lines at TRIUMF. Transverse field measurements [17] revealed a strong nonmonotonic temperature dependence of T_2^{-1}. Typical μSR time spectra in longitudinal field in solid nitrogen are shown in Fig. 1. The observed relaxation is attributed entirely to the muonium fraction, as the diamagnetic complex in solid nitrogen is known [21] to be the static $N_2\mu^+$ ion, whose relaxation rate is about 0.1×10^6 s^{-1} [22] — far slower than that evident in Fig. 1. Moreover, the amplitude of the relaxing component in zero field is equal to the amplitude of the muonium precession signal in transverse field. Complete quenching of the low-temperature relaxation in longitudinal field ≈ 1 kG allows us to rule out spin-exchange reactions with possible paramagnetic impurities (e.g., O_2) as the cause of muonium spin relaxation. We are therefore confident that the relaxation presented in Fig. 1 is due entirely to Mu motion in the nuclear hyperfine fields of solid nitrogen.

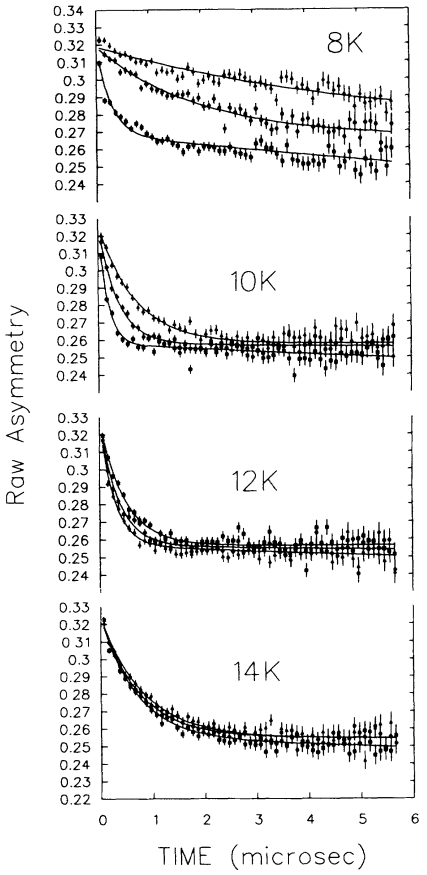

FIG. 1. μSR spectra in longitudinal field in solid nitrogen for $H_\parallel = 4$ G (triangles), 8 G (circles), and 12 G (squares) at different temperatures.

Figure 2 shows the temperature dependence of T_2^{-1} in transverse field and T_1^{-1} for several values of longitudinal field for Mu in solid nitrogen. At temperatures above 15 K, where $\omega_0\tau_c \ll 1$, T_1^{-1} becomes independent of field and equal to T_2^{-1}. From Eq. (4) we get the well-known [20] relation for fast diffusion ($\delta\tau_c \ll 1$) and low field ($\omega_0\tau_c \ll 1$):

$$T_1^{-1} = 2\delta^2\tau_c = T_2^{-1}. \quad (6)$$

The T_1^{-1}-maximum effect is clearly seen around 10–11 K for all longitudinal fields. For lower longitudinal field the T_1^{-1} maximum is shifted to lower temperature where τ_c is correspondingly shorter. The T_1^{-1}-maximum con-

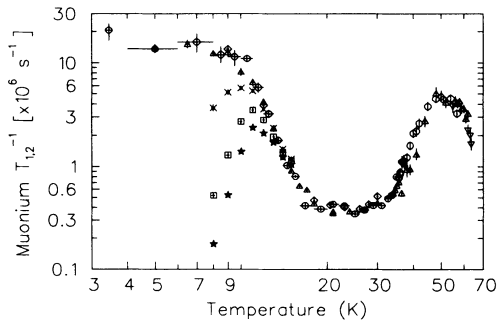

FIG. 2. Muonium relaxation rates in ultrahigh purity solid N_2 in weak transverse field (circles, triangles, diamonds, and inverted triangles correspond to different samples) and several longitudinal fields (stars: 12 G; squares: 8 G; crosses: 4 G).

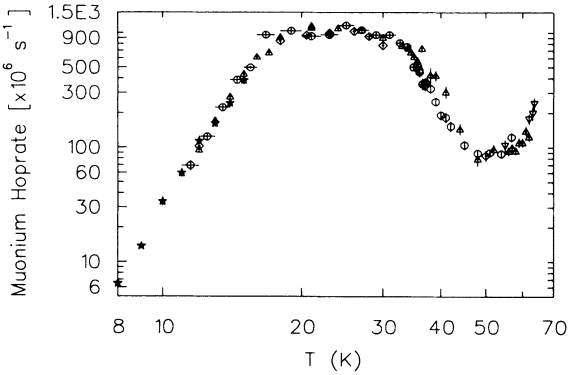

FIG. 3. Temperature dependence of the muonium hop rate in ultrahigh purity solid N_2. Stars correspond to the combined longitudinal field measurements; circles, triangles, diamonds, and inverted triangles correspond to transverse field measurements in different samples.

dition thus produces an absolute calibration of the hop rate. Equation (5) allowed us to determine the parameter δ independently for each longitudinal field; all three values are consistent with the combined result, δ=14.9(0.8) MHz, which in turn is within 7% of the value obtained from transverse field measurements [17] at low T [see Eq. (3) and Fig. 2].

Figure 3 presents the temperature dependence of the muonium hop rate τ_c^{-1} in solid nitrogen derived from Eq. (4) and complemented by the transverse field data for $T > 12$ K, where motional narrowing leads to Eq. (6).

For temperatures $T \ll \Theta$ (the Debye temperature) quantum diffusion is believed [6] to be governed by two-phonon processes, for which τ_c^{-1} is given by

$$\tau_c^{-1} = \frac{4Z}{3} \frac{\tilde{\Delta}_0^2 \Omega(T)}{\Omega^2(T) + \xi^2}, \tag{7}$$

where Z is the number of the equivalent wells in the nearest coordination sphere and $\tilde{\Delta}_0$ is the renormalized bandwidth for Mu diffusion. The main feature of Eq. (7) is the minimum of $\tau_c(T)$ at $\xi \sim \Omega(T)$. When $\xi < \Omega$,

$$\tau_c^{-1} \propto \tilde{\Delta}_0^2 / \Omega(T), \tag{8}$$

but if $\xi \gg \Omega$, then

$$\tau_c^{-1} \propto \tilde{\Delta}_0^2 \Omega(T) / \xi^2, \tag{9}$$

giving the opposite temperature dependence so that Mu atoms are localized as $T \to 0$.

The only effect of the one-phonon interaction is an exponential renormalization of the tunneling amplitude. The two-phonon width $\Omega(T)$ is determined by the phonon spectrum of the lattice. In the $T \to 0$ limit only acoustic phonons are important and

$$\Omega(T) \propto T^{7(+2)}. \tag{10}$$

The two additional powers of T appear only in the case of muonium tunneling between absolutely equivalent sites.

In the temperature range $30 < T < 50$ K, the measured Mu hop rate exhibits an empirical temperature dependence $\tau_c^{-1} \propto T^{-\alpha}$ with $\alpha = 7.3(2)$; since, from Eq. (8), $\tau_c^{-1} \propto \Omega^{-1}(T)$, we have $\Omega(T) \propto T^7$ as expected [Eq. (10)]. This is the first experimental confirmation of the T^{-7} dependence of τ_c^{-1} predicted by the two-phonon theory of quantum diffusion [6].

Below about 30 K the Mu hop rate levels off, presumably due to band motion with an estimated [13] renormalized bandwidth of $\tilde{\Delta}_0 \sim 10^{-2}$ K, in agreement with the value deduced from the high-temperature data where one-phonon interactions lead to an enhanced fluctuational preparation of the barrier (FPB) effect [17]. Alternative explanations of the T independence of τ_c^{-1} between 18 and 30 K might include interaction of Mu with residual impurities [17] or the effect of delocalization on Mu relaxation [23].

Muonium motion slows down again below about 18 K, probably due to the orientational ordering of N_2 molecules. Heat capacity, [24] thermal expansion [25], and NMR [26] data in solid nitrogen all show peculiarities at about 20 K which are attributed to "orientational defects" caused by an anisotropic interaction between N_2 molecules. Above about 20 K, large-angle librations of the host molecules average the Mu-N_2 interaction energy to a well-defined, site-independent value; below this temperature, Mu energy levels at neighboring sites differ by a typical static shift ξ which impedes Mu diffusion according to Eq. (7). For H atoms in solid nitrogen these energy shifts are ~ 1 K [27]; ξ for Mu in solid nitrogen appears to be of comparable magnitude. Since $\tau_c^{-1}(T)$ below 18 K is unaffected by doping with up to 0.01% impurities [17], this retarding of Mu diffusion at low temperature is believed to be an intrinsic property of solid nitrogen.

For $T < 18$ K the data in Fig. 3 obey

$$\tau_c^{-1} = \tau_0^{-1} \left(\frac{T}{\Theta} \right)^{\alpha}, \tag{11}$$

with $\Theta = 83$ K (the Debye temperature of nitrogen) [16], $\tau_0^{-1} = 3.6(8) \times 10^{13}$ s^{-1} and $\alpha = 6.7(1)$.

The change in the temperature dependence of the Mu hop rate from a T^7 to a T^{-7} law reflects a crossover from Eq. (8) to Eq. (9). According to theory [6], $\tau_0^{-1} \sim 10^4 \Theta \tilde{\Delta}_0^2 / \xi^2$. Using the experimental value of τ_0^{-1} and $\xi \sim 1$ K [27], we get $\tilde{\Delta}_0 \sim 10^{-2}$ K, in agreement with the values obtained from the bandlike motion regime and the high-temperature one-phonon regime. This value for the Mu bandwidth in solid nitrogen should be compared with the bandwidth scale $\Delta \sim 10^{-4}$ K obtained for the quantum diffusion of ^{3}He atoms in ^{4}He crystals [28]. Although the former is much larger, the qualitative similarity of these results suggests a common dynamical behavior for light particles in insulators, as opposed to metals, where different scattering mechanisms lead to quite different impurity dynamics.

To summarize, we have used a combination of longitudinal and transverse muonium relaxation rate measurements in solid nitrogen to obtain the first observation of the $T^{\pm 7}$ temperature dependence of the Mu hop rate predicted by the theory of two-phonon scattering processes [6]. We have also presented the first observation of low temperature localization of quantum mechanically diffusing Mu due to interaction with lattice defects.

This work was supported by the Canadian Institute for Advanced Research, the Natural Sciences and Engineering Research Council, and (through TRIUMF) the National Research Council of Canada. One of us (V.S.) is grateful to NSERC of Canada for providing an International Scientific Exchange Award. We would like to thank K. Hoyle and C. Ballard for technical support. We are grateful to N.V. Prokof'ev for helpful discussions.

* Permanent address: Kurchatov Institute, Kurchatov sq. 46, Moscow 123182, Russia.

[1] D.C. Walker, *Muon and Muonium Chemistry* (Cambridge Univ. Press, Cambridge, 1983); A. Schenck, *Muon Spin Rotation: Principles and Applications in Solid State Physics* (Adam Hilger, Bristol, 1986); D.G. Fleming *et al.*, Phys. Rev. A **26**, 2527 (1982).
[2] A.F. Andreev and I.M. Lifshitz, Zh. Eksp. Teor. Fiz. **56**, 2057 (1969) [Sov. Phys. JETP **29**, 1107 (1969)].
[3] C.P. Flynn and A.M. Stoneham, Phys. Rev. B **1**, 3966 (1970).
[4] Yu.M. Kagan and L.A. Maksimov, Zh. Eksp. Teor. Fiz. **65**, 622 (1973) [Sov. Phys. JETP **38**, 307 (1974)]; Yu.M. Kagan and M.I. Klinger, J. Phys. C **7**, 2791 (1974).
[5] P.C.E. Stamp and Chao Zhang, Phys. Rev. Lett. **66**, 1902 (1991).
[6] Yu.M. Kagan and N.V. Prokof'ev, in *Quantum Tunneling in Condensed Media*, edited by A.J. Leggett and Yu.M. Kagan (North-Holland, Amsterdam, 1992), p. 37.
[7] D. Steinbinder *et al.*, Europhys. Lett. **6**, 535 (1988).
[8] See, for example, G.M. Luke *et al.*, Phys. Rev. B **43**, 3284 (1991), and references therein.
[9] R. Kadono, Hyperfine Interact. **64**, 615 (1990).
[10] J.W. Schneider *et al.*, Phys. Rev. Lett. **68**, 3196 (1992).
[11] V. Storchak *et al.*, Phys. Lett. **32A**, 77 (1992).
[12] J. Kondo, Physica (Amsterdam) **125B**, 279 (1984); **126B**, 377 (1984); K. Yamada, Prog. Theor. Phys. **72**, 195 (1984).
[13] Yu.M. Kagan and N.V. Prokof'ev, Phys. Lett. A **150**, 320 (1990).
[14] Yu.M. Kagan and N.V. Prokof'ev, Phys. Lett. A **159**, 289 (1991).
[15] V.G. Storchak *et al.*, JETP Lett. **52**, 581 (1990).
[16] *Cryocrystals*, edited by B.I. Verkin and A.F. Prikhotko (Naukova Dumka, Kiev, 1983).
[17] V. Storchak *et al.*, Phys. Lett. A **182**, 449 (1993).
[18] R.F. Kiefl *et al.*, Phys. Rev. Lett. **62**, 792 (1989).
[19] M. Celio, Helv. Phys. Acta **60**, 600 (1987); H.K. Yen, M.Sc. thesis, University of British Columbia, 1988 (unpublished).
[20] C.P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1980).
[21] V. Storchak *et al.*, Chem. Phys. Lett. **200**, 546 (1992).
[22] B.F. Kirillov *et al.*, Hyperfine Interact. **65**, 819 (1990).
[23] G. Gunnarsson and P. Hedegård, Europhys. Lett. **18**, 367 (1992).
[24] M.I. Bagatskii *et al.*, Phys. Status Solidi **26**, 453 (1968).
[25] V.G. Manzhelii *et al.*, Phys. Status Solidi **13**, 351 (1966).
[26] A.S. DeReggi *et al.*, J. Magn. Reson. **1**, 144 (1969).
[27] P. Sieghban and B. Lui, J. Chem. Phys. **68**, 2457 (1978).
[28] M.G. Richards *et al.*, J. Low Temp. Phys. **24**, 1 (1976); V.A. Mikheev *et al.*, Fiz. Nizk. Temp. **3**, 386 (1977) [Sov. J. Low Temp. Phys. **3**, 186 (1977)].