TRI-PP-95-38
June 1995

Inhomogeneous Quantum Diffusion

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Abstract

Quantum diffusion of the muonium (Mu) atom has been studied in solid nitrogen crystals using the technique of Mu spin relaxation. At low temperatures the results are inconsistent with diffusion models using a single correlation time τ_c; instead, the muon polarization exhibits two-component relaxation, which is taken as evidence for the intrinsic inhomogeneity of Mu dynamics in a spatially inhomogeneous crystal. Conventional trapping mechanisms are shown to be ineffective at low temperatures in insulators.

(Submitted to Physical Review Letters)

PACS Nos. 66.30.Jt, 67.80.Mg and 76.75.+i.

The tunneling kinetics of light particles in crystals presents an intriguing problem in condensed matter physics [1–3]. A crucial feature of such tunneling is the smallness of the tunneling bandwidth Δ compared to all other energy parameters of the crystal, in particular the typical phonon energy Θ. As a result, particle tunneling at finite temperatures is strongly influenced by coupling to excitations of the crystal lattice (phonons) in insulators or to conduction electrons in metals [4], which causes dynamical destruction of the bandlike state [5].

Since Δ is small with respect to all other energy parameters in a solid, quantum diffusion (QD) is extremely sensitive to crystal imperfections. Therefore, *localization* of the particle often takes place at a relatively low defect concentration, in which case the interaction with excitations *enables* QD of the particle, measurement of which can thus provide information on crystal disorder.

The importance of muon spin relaxation (μSR) techniques to experimental studies of QD is illustrated by the wide variety of crystals, from metals [6] to insulators [7–10], in which both the positive muon (μ^+) and its neutral hydrogen-like atom muonium (Mu = μ^+e^-) show tunneling effects. This is due primarily to the small mass of the muon (about one ninth that of the proton) and the high sensitivity of the μSR technique to the muon's dynamics [11].

Until very recently, however, studies of Mu diffusion have focussed on nearly perfect crystals, in which bandlike motion of Mu persists at low temperatures. Crystalline defects have been treated mainly as local traps [12] with trapping radii on the order of the lattice constant a. The justification for such an approach was that the characteristic energy of the crystalline distortion, $U(a)$, is usually much less than the characteristic energy of lattice vibrations, Θ. Unfortunately, since it does not take the particle bandwidth Δ into consideration, this comparison turns out to be irrelevant to the problem of particle dynamics, for which the crucial consideration is that Δ is usually several orders of magnitude less than $U(a)$. For example, a typical Mu bandwidth in insulators is on the order of $\Delta \sim 0.01$-0.1 K [9,13], whereas in insulators $U(a)$ could be as large as 10 K. In metals the mismatch is even more drastic: typical values [$U(a) \sim 10^3$ K *vs.* $\Delta \sim 10^{-4}$ K] differ by about seven orders of magnitude. Under these circumstances, the influence of crystalline defects extends over distances much larger than a. If the "disturbed" regions around defects overlap sufficiently, complete particle localization can result.

Most previous experiments on muon diffusion have focussed on normal metals, where coupling of the μ^+ to conduction electrons causes very strong damping, or on very pure insulators, where any effects of crystal imperfections are difficult to observe. Experimental evidence for Mu localization in an imperfect crystal due to suppression of band motion by static disorder was first observed in a solid nitrogen (s-N_2) crystal [9]; however, in that experiment Mu diffusion measurements were restricted to the comparatively high temperature regime governed by pure homogeneous QD. At temperatures well below T_0 [where T_0 is determined by the interplay between the particle's energy level broadening $\Omega(T)$, due to coupling with phonons, 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 should characterize mainly

quasi-localized Mu atoms in the vicinity of defects. Another fraction of Mu atoms initially located far from impurities or defects should move more rapidly and therefore its muon spin polarization should relax more slowly in transverse field due to motional narrowing. At low temperatures, inelastic scattering by phonons is strongly suppressed [14] and these two Mu fractions remain distinct.

The formation of two independent ensembles of particles is determined by the initial conditions, *i.e.* the locations of Mu atoms with respect to defects just after thermalization. Thus the form of the muon polarization function $P(t)$ at low temperatures will be critically dependent [14] upon the particle bandwidth Δ and the defect concentration n. A distinctive two-component composition of $P(t)$ is a direct manifestation of the crystal's *spatial inhomogeneity* and must be a universal feature of particle diffusion in imperfect (real) crystals whenever static level shifts ξ exceed $\Omega(T)$.

Measurements of T_2^{-1} reveal particle diffusion only through "motional narrowing" (the reduction of T_2^{-1} by stochastic averaging), which is effective only for hop rates $\tau_c^{-1} > T_2^{-1}(\max)$, where $T_2^{-1}(\max)$ is the static relaxation rate [15,9]. By contrast, the relaxation rate T_1^{-1} of the Mu spin in *longitudinal* magnetic field (LF) is an *increasing* function of τ_c^{-1} up to the so-called "T_1 minimum" and can thus be used to measure both the very slow hop rates of localized particles (using weak LF) and the very fast hop rates of particles in the undisturbed host crystal far from impurities or defects (using strong LF). In a highly disordered crystal (where defects are present in the vicinity of all sites visited by the diffusing particle) it is possible to observe fractional particle localization *via* the two-component (or, in general, multi-component) composition of $P(t)$ in T_1^{-1} measurements. In this Letter we present evidence for the dramatic effect of such crystal disorder on Mu QD in s-N_2.

Because of the long-ranged character of the defect potential, at low temperatures even weak interactions with defects may be stronger than the inelastic interaction with the environment, leading to effective traps for diffusing particles. As a result, for many years μ^+ and Mu QD in crystals was discussed [12] in terms of trapping effects regardless of the temperature range or the nature of the crystal. In this Letter we present experimental evidence that such trapping effects, which may be dominant in metals [16], can be rather ineffective in insulators at low temperatures.

The experiment was performed on the M13 and M20B beam lines at TRIUMF. Ultra high purity $^{14}N_2$ (impurity content $\sim 10^{-5}$) was condensed into a silver sample cell. Experimental details can be found in [17]. Conventional time differential μ^+SR spectra were taken with an external magnetic field applied either parallel or perpendicular to the initial muon polarization. The longitudinal field (LF) and weak transverse field (TF) μSR techniques, details of which can be found elsewhere [11], produce direct measurements of the muon decay asymmetry time spectrum $A(t)$, which is proportional to the polarization function $P(t)$.

The effective spin Hamiltonian for static Mu in (s-N_2) in an external magnetic field consists of electron, muon and nuclear Zeeman interactions, the Mu hyperfine (HF) interaction and nuclear hyperfine (NHF) interactions [9]. Qualitatively, the NHF interaction results in relaxation of the Mu electron spin, which in turn leads to depolar-

ization of the μ^+ *via* the HF interaction. When Mu diffuses in a LF, fluctuations of the NHF interaction induce transitions between Mu HF levels and thus depolarize the μ^+. The resulting muon spin polarization function includes several transitions between Mu HF levels [18]. In s-N_2, an unusually weak NHF parameter δ allows LF experiments in very weak fields [9] where the muon longitudinal polarization function $P_{LF}(t)$ has an exponential form with a characteristic relaxation rate T_1^{-1} given by

$$P_{LF}(t) = e^{-t/T_1} \qquad \text{with} \qquad T_1^{-1} \simeq \frac{2\delta^2\tau_c}{1+\omega_0^2\tau_c^2}\,, \tag{1}$$

where $\omega_0 = \gamma_{Mu}H$ is the Mu intra-triplet transition frequency in the (weak) magnetic field H ($\gamma_{Mu}/2\pi = 1.4012$ MHz/G) and τ_c^{-1} is the Mu hop rate (*cf.* [15]).

It should be emphasized that a description of the relaxation function in terms of Eq. (1) [a "single τ_c" approximation] is not possible when crystal inhomogeneity causes a spatial distribution of τ_c which we will characterize as $\tau_c(R)$ [where R is the distance to the nearest defect].

Typical LF-μSR time spectra in s-N_2 at $H = 8$ G are shown in Fig. 1. The observed relaxation is attributed entirely to the muonium fraction, since the diamagnetic complex in s-N_2 is known to be a static, virtually nonrelaxing $N_2\mu^+$ ion [19]. Other possibilities for muon relaxation in s-N_2 were also ruled out [9].

At temperatures above about 10 K, excellent fits to the data were obtained using expression (1), which assumes that *all* Mu atoms diffuse at the same rate for their entire lifetimes. However, below 10 K it was impossible to fit experimental spectra using a single exponential relaxation function (1). Figure 1 clearly shows that at low temperatures the polarization function consists of at least two exponential terms. At temperatures below about 8 K a large, almost non-relaxing component (on the μSR time scale) was observed. This component corresponds to an almost static part of the Mu ensemble. A multi-component $P(t)$ is clear evidence for the spatial inhomogeneity of the crystal; muon diffusion experiments in superconducting Al with impurities also show a multi-component $P(t)$, probably due to inhomogeneous diffusion [20].

Experimental time spectra were compared with the simplest possible two-component expression

$$A(t) = A_F \exp(-T_{1_F}^{-1}t) + A_S \exp(-T_{1_S}^{-1}t), \tag{2}$$

where A_F and A_S are the asymmetries (amplitudes) of the fast- and slow-relaxing components and $T_{1_F}^{-1}$ and $T_{1_S}^{-1}$ are their respective relaxation rates. Figure 2 shows the temperature dependences of these asymmetries and relaxation rates obtained by fitting expression (2) to the data. Above 10 K there is no measurable fast-relaxing component; the entire Mu polarization can be attributed to the slow-relaxing part of the Mu ensemble. As the temperature is reduced below 10 K, A_S decreases and the fast-relaxing component correspondingly increases, clearly indicating the onset of inhomogeneous Mu diffusion. At lower temperatures both A_S and A_F level off, accounting for about 70% and 30% of the Mu polarization, respectively.

The well-known T_1 minimum (T_1^{-1} maximum) effect [15] is clearly seen around 11 K, indicating that at this temperature the Mu hop rate matches the transition frequencies

between triplet Mu Zeeman levels in $H = 8$ Oe. The temperature dependence of $T_{1_S}^{-1}$ at low temperatures indicates that the slow component undergoes gradual localization as the temperature is reduced, while the fast-relaxing component has a temperature-independent relaxation rate. At $T = 6$ K, $T_{1_F}^{-1}$ exceeds $T_{1_S}^{-1}$ by more than two orders of magnitude.

Figure 2(c) displays the temperature dependence of the Mu hop rates for the fast and slow components derived from expression (1) with a fixed value of $\delta = 14.9(0.8)$ MHz obtained from T_1^{-1}-maximum conditions [9]. Above about 9 K, Mu exhibits quantum tunneling with a characteristic $\tau_c^{-1} \propto T^7$ temperature dependence [9]. Below this temperature the slow component displays strong localization while the fast component shows temperature-independent Mu motion with about two jumps per muon lifetime.

The muonium hop rate is predicted [3] to have the form

$$\tau_c^{-1} \propto \tilde{\Delta}_0^2 \frac{\Omega(T)}{\xi^2(R) + \Omega^2(T)}, \tag{3}$$

where $\tilde{\Delta}_0$ is the renormalized tunneling amplitude. At low temperatures the phonon width is reduced [$\xi > \Omega(T)$] and $\tau_c^{-1} \propto \tilde{\Delta}_0^2[\Omega(T)/\xi^2(R)]$. In this case inhomogeneity of the crystal results in static level shifts $\xi(R)$ causing a spatial distribution of $\tau_c^{-1}(R)$ and thus, through Eq. (1), a distribution of $T_1^{-1}(R)$.

Reduction of the Mu diffusion rate in s-N_2 at low temperatures has been explained [9] in terms of orientational ordering of N_2 molecules in s-N_2 below $T_{\alpha\beta} \approx 36$ K. Heat capacity, thermal expansion and NMR data in s-N_2 all show peculiarities at low temperatures which are attributed to "orientational defects" caused by an anisotropic interaction between N_2 molecules [21]. This is a peculiar intrinsic property of crystalline nitrogen, which can be considered as homogeneous at high temperature but has the properties of a translationally disordered lattice below $T_{\alpha\beta}$. Thus different interstitial lattice sites for the Mu atom which are energetically degenerate at high temperatures become separated by static level shifts $\xi(R)$ at low temperatures due to defects in the molecular orientational ordering; this produces "crystal disorder" for Mu diffusion so that Mu has to overcome energy shifts $\xi(R)$ and the hop rate is decreased according to Eq. (3). This picture is consistent with the behaviour of the slow-relaxing component, while the fast-relaxing component probably represents those Mu atoms (about 30%) undergoing coherent tunneling which scatter elastically off distorted regions near defects.

Figure 3 shows the temperature dependence of the transverse relaxation rate T_2^{-1} of muonium in pure s-N_2 (a) and in s-N_2 with 10^{-3} CO impurities (b). When Mu hops rapidly in s-N_2 (causing low values of T_2^{-1} due to dynamical "narrowing"), the Mu atom finds a CO impurity in the N_2+CO crystal and reacts chemically (probably to form the MuCO· radical [22]), which explains the fact that the maximum T_2^{-1} value for Mu in s-N_2+CO significantly exceeds that for static Mu in pure nitrogen where it is determined by the interaction of localized Mu with the nuclear magnetic moments of neighboring N_2 molecules. This chemical reaction is manifest in an exponential relaxation of the Mu polarization, the rate of which is determined by the time required for Mu to approach

the CO impurity within a distance a, after which the reaction occurs immediately. This description in terms of chemical reaction controlled by Mu diffusion is almost perfectly analogous to the phenomenology of trapping.

At high temperatures the clear maximum in T_2^{-1} for Mu in s-N_2+CO marks the crossover from fast to slow Mu diffusion near CO impurities, which in turn reflects the interplay between $\Omega(T)$ and ξ in the denominator of Eq. (3). In this temperature range the strong coupling to phonons allows Mu to overcome the defect potential and move to react with CO. However, the energy shift ξ which the particle has to overcome is much larger close to the defect than far from it, making the Mu hop rate strongly dependent on the distance from the defect.

At low temperatures the suppression of inelastic interactions with the lattice changes Mu diffusion drastically. There is no longer an energy bath from which Mu can gain the energy needed to overcome site energy differences close to CO impurities. Therefore, Mu atoms are stuck (or "frozen") far from impurities, causing a strong reduction of the reaction rate (Mu relaxation rate). Muonium atoms are then effectively excluded from the volumes around the impurities and T_2^{-1} is the same for pure N_2 and N_2+CO crystals, as clearly seen in the experiment (Fig. 3).

The trapping rate K in an imperfect crystal is usually expressed as

$$K = 4\pi c n R_T D(R_T), \tag{4}$$

where c is a numerical coefficient on the order of unity, n is the impurity concentration, R_T is trapping radius defined by the condition $U(R_T) = T$ and $D(R_T)$ is the diffusion coefficient [24]. In "dirty" insulators (and superconductors [23]) at low temperatures the temperature dependence of $D(R_T)$ is opposite to that in a perfect crystal [see Eq. (3)]. Thus the trapping rate decreases rapidly with temperature, making the trapping mechanism essentially ineffective, as demonstrated by our experiment in N_2+CO. It should be noted, however, that in normal metals strong coupling to conduction electrons produces $\Omega(T) \propto T$ [4]. Thus for $\xi < T$ the diffusion process in normal metals is rather *homogeneous* (for $\xi > T$ the particle might be considered as already trapped).

In conclusion, we have presented the first clear evidence of spatially inhomogeneous quantum diffusion of Mu atoms in a translationally disordered crystal. The trapping mechanism is shown to be ineffective at low temperatures in insulators.

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. Support of the International Science Foundation (through Grant N9D000) and Prof. S.T. Belyaev is acknowledged by one of us (VS). We would like to thank K. Hoyle and C. Ballard for technical support and N.V. Prokof'ev for helpful discussions.

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FIGURE CAPTIONS

Fig. 1. Muon spin relaxation spectra for muonium in solid nitrogen in a longitudinal field of $H = 8$ Oe at $T = 10$ K (diamonds), 8 K (triangles) and 6 K (circles). Note the presence of two components in the relaxation function at low temperatures.

Fig. 2. Temperature dependence of slow-relaxing (circles) and fast-relaxing (stars) muonium signals in solid nitrogen: (a) slow (A_S) and fast (A_F) muonium asymmetries (amplitudes); (b) slow ($T_{1_S}^{-1}$) and fast ($T_{1_F}^{-1}$) longitudinal relaxation rates; (c) slow ($\tau_{c_S}^{-1}$) and fast ($\tau_{c_F}^{-1}$) muonium hop rates.

Fig. 3. Temperature dependence of the transverse relaxation rate (T_2^{-1}) of muonium (a) in pure nitrogen crystals (triangles, two different samples) and (b) in a crystal of $N_2 + 10^{-3}$ CO.

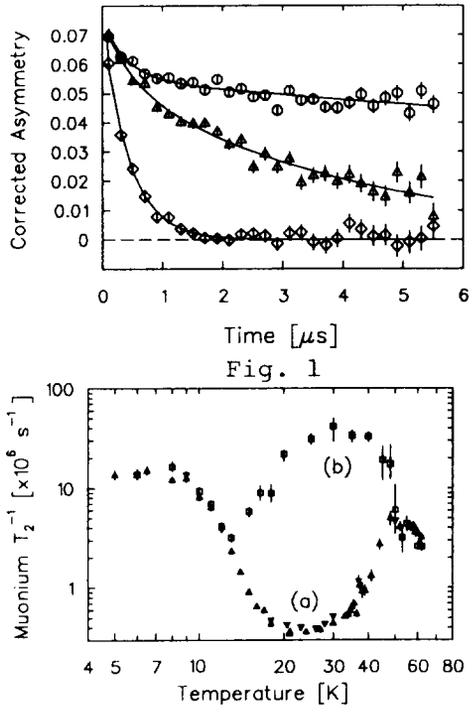

Fig. 1

Fig. 2

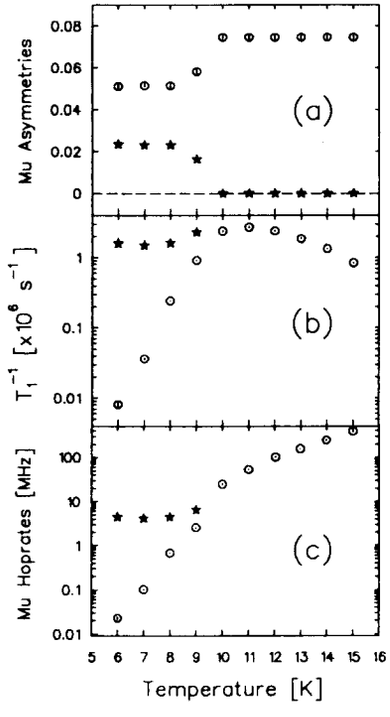

Fig. 3