

Destruction of Bandlike Propagation in Orientationally Ordered Crystals

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The quantum diffusion of interstitial muonium atoms in solid methanes (CH_4 and CD_4) has been studied in the temperature range from 10 to 90 K using the technique of muonium spin relaxation in transverse magnetic field. In the high temperature crystalline phase, which is characterized by rotating molecules, muonium dynamics becomes bandlike with decreasing T . At low temperatures, slowing down of molecular rotation and molecular freezing in the orientationally ordered phase render adjacent tunneling sites inequivalent, resulting in strong particle localization. [S0031-9007(99)08729-3]

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Condensed matter physicists have a long-standing interest in the tunneling dynamics of light particles, e.g., electrons, muons, impurity atoms, isotopic defects, etc. The basic issue in nonclassical transport is whether a wave-like or particlelike description is appropriate, i.e., whether the tunneling is coherent or incoherent. This depends on whether the interaction with the environment is such as to lead to spatial localization of the wave function or to bandlike (Bloch wave) motion. One of the possible channels for localization of a particle is through its interaction with lattice excitations (phonons, librations, magnons, etc.). In a dissipative environment [1,2] the lattice excitations can be represented as a bath of harmonic oscillators; interaction with this environment causes a crossover from coherent quantum tunneling to incoherent hopping dynamics when the particle "dressed" with the lattice excitations can be effectively thought of as a *polaron*.

At low temperatures, the environmental excitations are frozen out. In this case, conventional understanding suggests that the only possible channel for particle localization is the introduction of crystal disorder, which thus may dramatically change the transport properties of a solid. A well-known example is the spatial localization of electron states near the Fermi level in a disordered metallic system, which leads to a transition into a dielectric state (the Anderson transition) [3]: coherent tunneling of a particle is possible only between levels with the same energy (e.g., between equivalent sites in a crystalline lattice); in the case of strong randomness, states with the same energy may be too spatially separated for tunneling to be effective. In this Letter we present experimental studies of a novel and somewhat counterintuitive case, namely,

the situation in molecular crystals where *ordering* causes localization of interstitial particles.

Although the concept of localization by disorder has been introduced primarily in order to describe the electronic transport properties of solids, it may also be applied to the quantum dynamics of heavier particles, whether charged or neutral [4–6]. Recent experimental results for positive muons (μ^+) in dilute metallic alloys [7], as well as for muonium atoms ($\text{Mu} = \mu^+ + e^-$) in "dirty" insulators [8,9], clearly indicated that crystal disorder introduced by impurities dramatically changes the nature of quantum diffusion for particles ~ 200 times heavier than the electron. In these experiments the environmental coupling could be varied or switched on and off by changing the temperature: for interstitial muons in aluminum metal [7] the low energy couplings to conduction electrons are suppressed below the superconducting transition, as a BCS energy gap opens at the Fermi surface, while for muonium in insulators [8,9] inelastic interactions with phonons are frozen out at low temperatures. Similar arguments apply for the well-known system of a dilute solution of heavy ^3He atoms in a ^4He crystal [10,11].

A common and crucial feature of all the above-mentioned experiments is that the particle tunneling bandwidth Δ is small compared with all other relevant energy parameters, especially U , the characteristic energy level *shift* due to crystalline disorder. For example, for elastic strains $U(r) \sim (a/r)^{-3}$, where r is the distance from a defect and a is the lattice constant, typical values of $U(a) \sim 10^3$ K exceed muon bandwidths in metals by 6–7 orders of magnitude; in insulators the difference is not so extreme but still $U(a) \gg \Delta$ [4,12]. Under these

circumstances, the influence of crystalline defects extends over distances $R \sim a[U(a)/\Delta]^{1/3} \gg a$. The quantum diffusion of the interstitial particle is therefore dominated in these cases by *strong, long-range* crystal disorder. An essential characteristic of particle transport under these conditions is its *inhomogeneity* at low temperatures [4,12] where the particle dynamics cannot be described in terms of a single correlation time τ_c . At temperatures low enough that the particle's energy level broadening due to coupling with lattice excitations, $\Omega(T)$, is much less than the *difference* (due to disorder) between energy levels at two *adjacent* tunneling sites, $\xi(R) = a[dU/dr]_{r=R}$, the particle hop rate is predicted [4] to follow

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

where $\tilde{\Delta}_0$ is the tunneling amplitude. Equation (1) describes the dynamics of particles in the vicinity of defects. Another fraction of particles initially located so far from impurities or defects that $\tilde{\Delta}_0$ exceeds $\xi(R)$ [as well as $\Omega(T)$] undergoes bandlike propagation. This picture of spatially inhomogeneous dynamics manifests itself in the appearance of two distinct components in the muon polarization function $P(t)$ [7–9].

In contrast to the above picture, the evidence presented in this Letter illustrates the dramatic effect of *weak, short-range* disorder on muonium dynamics in the *homogeneous* regime. In the harmonic approximation, the transport properties of a neutral particle in a simple crystalline insulator (e.g., a monatomic or ionic crystal) depend only on the phonon modes of the lattice. For crystals composed of molecules, two additional contributions enter from the internal vibrational and rotational degrees of freedom of the molecules. Internal vibrations of molecules scarcely change the particle dynamics because of their extremely high frequencies. Molecular rotation, however, is a different matter. Two extremes are possible: the molecules may rotate almost freely in the crystal, or the rotational motion may be severely restricted and hence transformed into torsional excitations (*librons*). Since typical rotational frequencies are still much higher than the particle bandwidth, in the first extreme the energy levels in different unit cells are degenerate and therefore particle dynamics remain unperturbed. In the second extreme the anisotropic interaction between molecules (which causes orientational ordering in the first place) changes the crystalline potential so that this degeneracy is lifted. As far as the particle dynamics are concerned, this splitting of the energy levels of adjacent sites acts as an effective disorder, creating the bias ξ . To demonstrate this, a suitable molecular lattice must be found where (a) this disorder is essentially weak and *short range* and (b) both extremes can be reached in the accessible temperature range. The simplest molecular solids are the cryocrystals formed by the small light-weight molecules, namely, solid H₂, D₂, CH₄, CD₄, N₂, N₂O, CO₂, etc. In solid N₂O and CO₂ the anisotropic part of intermolecular interaction is so strong that the lat-

tice keeps its orientational order in the entire solid phase. In solid para-H₂ and ortho-D₂, by contrast, this interaction is so weak that orientational order cannot be reached even at the lowest temperatures. Here we report our study of muonium dynamics in solid methanes (CH₄ and CD₄) which undergo orientational ordering in the solid phase. In solid CH₄ this transition takes place at $T = 20.4$ K while in solid CD₄ partial orientational ordering occurs at $T = 27$ K with a further transition to complete molecular ordering at $T = 22.1$ K [13,14].

The experiments were performed on the M13 beam line at TRIUMF and on the EMu beam line of the ISIS Pulsed Muon Facility at the Rutherford Appleton Laboratory. At ISIS, ultrahigh purity methanes (less than 10^{-5} impurity content) were condensed from the gas phase into a liquid and then frozen into a disk-shaped cell (20 mm in diameter and 5 mm deep). At TRIUMF, methane crystals (18 mm in diameter and 4 mm thick) were carefully grown from the liquid phase at typical speeds of about 5 mm/h by applying a vertical temperature gradient of about 5 K across the cell. At both laboratories, positive muons of 28 MeV/c momentum and 100% spin polarization were stopped in the samples and μ^+ SR time spectra were recorded at various different temperatures and applied magnetic fields. Positrons from the muon decay are emitted preferentially along the direction of the muon polarization so that the time differential μ^+ SR technique, details of which can be found elsewhere [15], produces direct measurements of the time dependence of the muon decay asymmetry $A(t)$, which is proportional to the muon polarization function $P(t)$.

Formation of atomic muonium (Mu) in solid methanes was detected by observing the precession signal at the characteristic muonium frequency $\omega_{\text{Mu}} = \gamma_{\text{Mu}}H$, where $\gamma_{\text{Mu}}/2\pi = 1.4012$ MHz/G, in a weak transverse magnetic field H . The effective spin Hamiltonian of static isotropic muonium in a crystal has the form [12]

$$\mathcal{H} = hA\vec{S}_e \cdot \vec{S}_\mu - g_e\mu_b\vec{S}_e \cdot \vec{H} - g_\mu\mu_\mu\vec{S}_\mu \cdot \vec{H} + h \sum_n \delta_n\vec{S}_e \cdot \vec{S}_n - \sum_n g_n\mu_n\vec{S}_n \cdot \vec{H}, \quad (2)$$

where A is the muonium hyperfine (HF) parameter [measured to be 4474(220) MHz in solid CH₄, consistent with the vacuum-state value $A_{\text{vac}} = 4463$ MHz for isotropic Mu], δ_n is nuclear hyperfine (NHF) coupling with the n th neighbor nucleus, and \vec{S} , g , and μ are the spins, g factors, and magnetic moments of the respective particles. The NHF parameter δ , which sets the time scale for muonium spin relaxation, is a measure of the combined effect of all the δ_n . Qualitatively, modulation of the NHF interactions results in relaxation of the muonium electron spin, which in turn leads to the observed muon depolarization *via* the muonium HF interaction. In a transverse magnetic field H high enough to make the condition $\gamma_{\text{Mu}}H \gg \delta$ valid, the muonium polarization function, which represents the envelope of the precession signal,

is usually well approximated by a single exponential function $P(t) \sim \exp(-t/T_2)$, where T_2 is the transverse relaxation time of the muonium spin. The muonium relaxation rate T_2^{-1} has a simple form in two limits: if muonium “hops” from site to site at a rate $\tau_c^{-1} \gg \delta$ (*fast hopping* limit), then the transverse relaxation rate is given by $T_2^{-1} \approx \delta^2 \tau_c$. For very *slow* diffusion ($\tau_c^{-1} \lesssim \delta$) muonium spin relaxation takes place on a time scale shorter than τ_c and $T_2^{-1} \approx \delta$. [In this case $P(t)$ is better approximated by a Gaussian relaxation function.]

Figure 1 presents the temperature dependences of the muonium transverse relaxation rate T_2^{-1} in solid CH_4 and CD_4 , extracted from the spectra by fitting single-exponential relaxation functions. Such fits were quite good in the entire measured temperature range, which is taken as evidence that the muonium dynamics in solid methanes can be described in terms of diffusion models using a *single* τ_c approximation. This in turn suggests that muonium dynamics in methanes are *homogeneous* in nature. The strong temperature dependence of T_2^{-1} abruptly levels off between about 45 and 55 K in CH_4 and between about 32 and 40 K in CD_4 . Such behavior in the fast hopping regime indicates that the Mu correlation time τ_c stays constant in the indicated temperature ranges in both crystals. At the lowest measured temperatures (below about 20 K), T_2^{-1} again levels off in both crystals due to Mu localization, giving $\delta_1 \approx 5 \times 10^7 \text{ s}^{-1}$ for CH_4 and $\delta_2 \approx 8 \times 10^6 \text{ s}^{-1}$ for CD_4 . The ratio δ_1/δ_2 is about twice as large as the ratio of proton to deuteron magnetic moments; further scaling by $\sqrt{S_n(S_n + 1)}$ just increases the apparent discrepancy. Evidently the NHF interaction governing muonium relaxation does not scale simply with the gyromagnetic ratio of the nucleus in this case. Other candidates for the muonium spin relaxation mechanism, such as spin-exchange reactions with possible paramagnetic impurities (e.g., O_2) or electrons from the muon track, were ruled out by measurements in longitudinal magnetic and electric fields [16–19].

Figure 2 shows the temperature dependences of the muonium hop rate τ_c^{-1} in the solid methanes, extracted

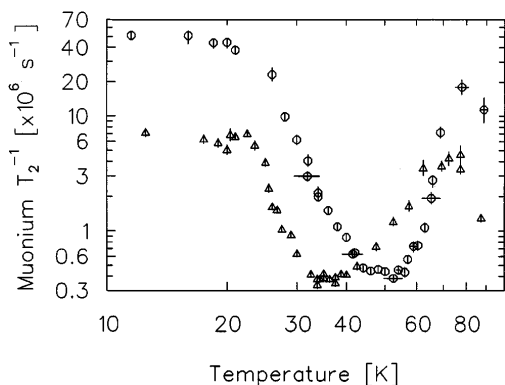


FIG. 1. Temperature dependence of muonium relaxation rate in solid methanes in weak transverse field $H = 5 \text{ G}$ (circles: CH_4 ; triangles: CD_4).

in the regime of dynamical averaging using the values of δ obtained above. At high temperatures—above 55 K for CH_4 and above 40 K for CD_4 —the hop rate in both crystals *increases* with *decreasing* temperature. This is an unambiguous manifestation of quantum diffusion which has also been recognized for muonium in KCl [20] and solid nitrogen [21]. In the appropriate temperature ranges in both KCl and nitrogen, the muonium hop rate exhibits an empirical temperature dependence $\tau_c^{-1} \propto T^{-\alpha}$ with $\alpha \approx 3$ in KCl and $\alpha \approx 7$ in nitrogen. In solid CD_4 similar fits yield α between 5 and 6, while in CH_4 α is between 7 and 11 depending on the temperature range.

The *plateaus* in $\tau_c^{-1}(T)$ around 45–55 K in CH_4 and 32–40 K in CD_4 must represent the onset of muonium band motion [4,12], which occurs if the coherence is preserved ($\Omega \ll \tilde{\Delta}_0$ but still $T > \tilde{\Delta}_0$) and the disorder is weak ($\xi \ll \tilde{\Delta}_0$). In this case the “hop rate” is independent of temperature and is given [22] by $\tau_c^{-1} = 2\sqrt{2} \tilde{\Delta}_0$. From this relation the muonium bandwidth is determined to be about $3 \times 10^{-2} \text{ K}$ in CH_4 and about 10^{-3} K in CD_4 . These values may be compared with muonium bandwidths in KCl and solid nitrogen (0.16 K and 10^{-2} K , respectively) [12].

The band motion does not extend, however, to the lowest temperatures: the correlation time begins to increase with decreasing temperature below about 45 K in CH_4 and about 30 K in CD_4 . These data indicate that interstitial muonium atoms undergo gradual localization in methanes at low temperatures where $\Omega \ll \xi$ and that the particle dynamics follow Eq. (1). Here, the temperature dependence of the muonium hop rate obeys the power law $\tau_c^{-1} \sim 10^4 \Theta \tilde{\Delta}_0^2 / \xi^2 (T/\Theta)^\alpha$ [4] with $\alpha = 6.8(4)$ and ξ lying between 10^{-1} and 10^{-2} K in both crystals. In this temperature range the observed power law is believed to be due to two-phonon dissipation in the regime of static destruction of the band [23]. This phenomenon can be explained in terms of the slowing down of molecular rotations in the crystal. At high temperatures, when the characteristic time of molecular reorientation $\tau_r \ll \tau_c$, the anisotropic molecular interactions are averaged out so that $\xi \ll \tilde{\Delta}_0$ and muonium undergoes unperturbed bandlike

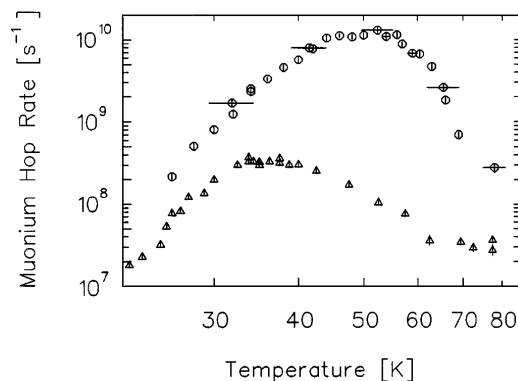


FIG. 2. Temperature dependence of muonium hop rate in solid methanes (circles: CH_4 ; triangles: CD_4).

propagation. Slowing down of the molecular rotations may lead to the opposite condition when $\tau_r \gg \tau_c$ well above the temperature of orientational ordering due to incomplete averaging of the anisotropic interactions: measurements of infrared absorption [24] and neutron scattering [25] as well as thermodynamic experiments [13] clearly show that the molecular rotation in CH₄ and CD₄ is not free even at the highest temperatures in the disordered phases; rather, all these experiments reveal properties of a system of hindered rotators whose dynamics slow down as the temperature drops.

The orientational dynamics of the host molecules may well be the cause of the distinctive isotope effect on the muonium correlation time in solid methanes. It is not really the host molecule *mass* which determines the tunneling matrix element for a diffusing particle but rather the *interaction potential* [4,6]. The anisotropic part amounts to about 25% of the molecular interaction which determines the potential relief for a diffusing particle in the van der Waals cryocrystals [26]. Neutron scattering studies of the rotational excitations show that in a given rotational potential CD₄ molecules exhibit a stronger effective octupole moment than CH₄ and thus increase the molecular field [27]. One might be surprised that the muonium correlation time is more than an order of magnitude shorter in CH₄ than in CD₄. However, the potential barrier for muonium diffusion appears in the exponent of the tunneling matrix element. A well-known example is the ³He-⁴He system, where the correlation time of ³He atoms increases by almost 2 orders of magnitude when the molar volume of the crystal is reduced by only 3% [28]. In the same manner one can explain the fact that the plateau of the muonium τ_c^{-1} shifts to lower temperatures in CD₄ than in CH₄ by noting the higher value of Δ_0 in CH₄: τ_c^{-1} levels off when Δ_0 becomes greater than $\Omega(T)$. Unfortunately, the existing data do not allow us to make any definite statement about the relative values of the energy level broadening in CH₄ and CD₄ nor about the possible muonium sites in these crystals; therefore, other explanations of the observed effects cannot be ruled out.

In conclusion, we have presented an observation of the destruction of bandlike motion of light interstitial particles in molecular crystals at low temperatures in the regime of *homogeneous* diffusion. We suggest that the particle localization is due to slowing down of molecular rotations and subsequent orientational ordering in these crystals. This study complements our knowledge of the nature of neutral particle localization due to *long-range* disorder in the *inhomogeneous* regime.

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