Local Tunneling and Metastability of Muonium in CuCl

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Measurements of the muon spin relaxation of muonium show that the Mu^{I} center in CuCl is an example of metastability in which isolated muonium tunnels locally around the tetrahedral interstitial site with four Cu nearest neighbors, with the stable form ($\mathrm{Mu}^{\mathrm{II}}$) quasistationary at the same interstitial. For $T < 30$ K the inverse correlation time associated with the damped tunneling motion increases with decreasing temperature according to a power law $T^{-2.7(1)}$, which is close to that observed previously for long-range quantum diffusion of muonium in insulators.

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When positive muons are implanted into semiconductors they often form isolated muonium (μ^+e^-) centers whose properties are closely related to those of atomic hydrogen but which are much easier to detect than hydrogen itself. The dynamics of light atoms such as hydrogen or muonium are of special interest because they provide a test for theories on the quantum motion of interstitial atoms or other simple crystalline defects [1-8]. As a result of the smaller mass of the muon compared to the proton ($m_\mu \sim \frac{1}{9} m_p$) an interstitial muonium atom is expected to have considerably larger tunneling matrix elements to neighboring equivalent sites. This greatly enhances the quantum mechanical aspects of muonium motion compared to that of hydrogen. Also, since the muons are studied in the extreme dilute limit (i.e., one at a time) using methods based on the asymmetric decay of muons, there can be no interaction between muonium atoms as there can be for hydrogen atoms.

In this Letter we report the first evidence for local tunneling of muonium in a crystal. Previous work has resulted in a puzzling picture of muonium in CuCl. High-transverse-field muon spin relaxation (μSR) experiments [9] have shown that there are two distinct muonium centers, Mu^{I} and $\mathrm{Mu}^{\mathrm{II}}$, with unusually small and comparable isotropic muon hyperfine (hf) couplings. Although the two centers coexist at low temperatures, one of them, Mu^{I}, was found to be metastable and to convert thermally into the stable form, $\mathrm{Mu}^{\mathrm{II}}$, above 100 K. Measurements of the muonium linewidth as a function of magnetic field led us to conclude that both centers were close to being static. Subsequent muon level-crossing-resonance (μLCR) experiments [10] established unambiguously that both Mu^{I} and $\mathrm{Mu}^{\mathrm{II}}$ were centered at a tetrahedral (T) interstice with four Cu nearest neighbors (T_{Cu}) and that the two centers had nuclear hyperfine (nhf) interactions which differed very little as well. This meant that two different interstitial impurity centers had the same location and virtually the same electronic structure, at least on average. In an effort to understand this seeming paradox, we have investigated the longitudinal relaxation of Mu^{I} and $\mathrm{Mu}^{\mathrm{II}}$ in CuCl. We find that (A) the metastable Mu^{I} is highly mobile, while the stable $\mathrm{Mu}^{\mathrm{II}}$ is quasistationary on the time scale of the muon lifetime ($\tau_\mu = 2.2$ μs), and (B) neither of the two centers is undergoing long-range diffusion. (A) is established by the $1/T_1$ spin relaxation due to the fluctuating nhf interaction as the muonium moves from site to site. (B) follows from the μLCR spectra for both centers whose observation implies there is a static part to the nhf interaction which is not motionally averaged. If the muonium were undergoing rapid long-range diffusion there would be no such component and therefore no coherent transfer of polarization from the muon to the neighboring nuclei at a μLCR. (B) is also confirmed by the present set of measurements of the muon spin polarization in a weak magnetic field applied along the initial muon spin polarization direction. (A) and (B) together imply that the motion of Mu^{I} must be local.

The spin Hamiltonian for stationary muonium surrounded by nuclear spins $\mathbf{J}_i$ in an external field $\mathbf{B}$ is of the form

$$\mathcal{H} = g_e \mu_B \mathbf{S}\cdot\mathbf{B} - g_\mu \mu_\mu \mathbf{I}\cdot\mathbf{B} + A^\mu \mathbf{I}\cdot\mathbf{S} + \sum_i [-g_i \mu_i \mathbf{J}_i\cdot\mathbf{B} + A^n_{\parallel,i} J_i^{z'} S^{z'} + A^n_{\perp,i}(J_i^{x'} S^{x'} + J_i^{y'} S^{y'})] , \tag{1}$$

where A^μ is the muon hf parameter, $\mathbf{I}$ is the muon spin, $\mathbf{S}$ is the electron spin, $A^n_{\parallel,i}$ and $A^n_{\perp,i}$ are the parallel and perpendicular nhf parameters for nucleus i, respectively, and $\hat{\mathbf{z}}^i$ is the muon-nuclear unit vector. For simplicity and because the present study does not require more generality, we have assumed that the muon hf interaction and electron g tensors are isotropic, that the nhf interaction is axially symmetric about $\hat{\mathbf{z}}^i$, and that the small nuclear electric quadrupole interactions can be neglected. For stationary muonium, the muon spin polarization $p_\parallel(t,B)$ and the corresponding μLCR spectrum $\bar{p}_\parallel(B)$ can readily be calculated from Eq. (1), as has been shown elsewhere [11]. The two quantities are related by

$$\bar{p}_\parallel(B)=\frac{1}{\tau_\mu}\int_0^\infty p_\parallel(t,B)e^{-t/\tau_\mu}dt\,. \tag{2}$$

If the muonium is hopping between electrostatically equivalent sites the unpaired electron experiences a fluctuating nhf interaction originating from the randomly oriented nuclear spins. These fluctuations induce transitions between the muonium hf levels and thereby cause the muon spin polarization to relax. Celio and Yen [12] have calculated the time evolution of $p_\parallel$ by applying Redfield's theory to a simplified model in which the nhf interaction is replaced by a fluctuating electron Zeeman term:

$$\mathcal{H}_n=\delta_{\mathrm{ex}}\mathbf{S}\cdot\mathbf{T}(t)\,, \tag{3}$$

where δ_{ex} is an effective nhf interaction strength and $\mathbf{T}(t)$ a unit vector randomly fluctuating with a correlation time τ_c. Under these circumstances $p_\parallel(t,B,\delta_{\mathrm{ex}},\tau_c)$ is a sum of four exponentials with prefactors and exponents that can be evaluated numerically by diagonalizing a small matrix. Note that from this model one expects measurable longitudinal relaxation in all cases where there is a fluctuating nhf field with an appreciable amplitude δ_{ex}, i.e., for both local and long-range motion. On the other hand, the μLCR's will vanish if there is no static component of the nhf field, such as is the case for rapid long-range diffusion.

The measurements were performed on the M15 beam line at TRIUMF, which provides a beam of 100% spin-polarized muons with a momentum of 28 MeV/c. Muons were stopped in a single crystal of CuCl measuring about 13 mm in diameter by 2 mm thick and grown by one of us (C.S.). In the temperature range 1-250 K conventional μSR spectra [13] were taken with an external field applied parallel to the initial muon spin polarization and parallel to a $\langle 111\rangle$ crystal axis. After background subtraction and after correcting for instrumental asymmetry, the measured asymmetry spectra $A(t)$ are proportional to $p_\parallel(t)$. Typical spectra are shown in Fig. 1.

Figure 2(a) shows the temperature dependence of the average muon relaxation rate $1/T_1$ for Mu$^{\mathrm{I}}$ and Mu$^{\mathrm{II}}$ in CuCl for three different magnetic fields, obtained by fitting a single exponential to each spectrum separately. Note the T_1 minima (indicated by arrows), which occur when the inverse correlation time, $1/\tau_c$, matches the smallest intratriplet transition, ω_{12}, in the Breit-Rabi diagram for muonium. The presence of such minima is im-

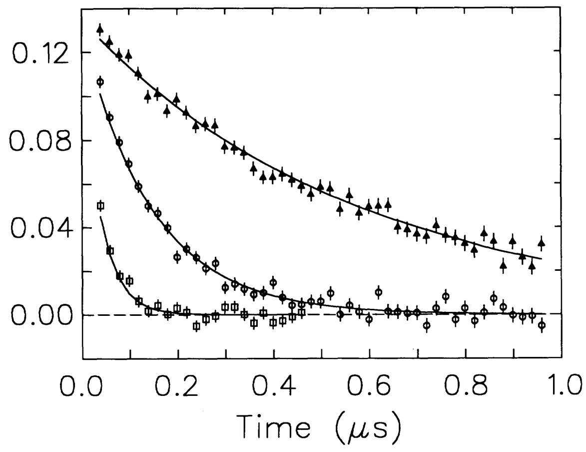

FIG. 1. Typical muon spin relaxation spectra for muonium in CuCl with magnetic fields (from top to bottom) of 0.4, 0.2, and 0.1 T applied along the initial muon spin polarization, shown here for $T=10$ K (predominantly Mu$^{\mathrm{I}}$). The solid lines are fitted curves from a simultaneous fit of Celio's model to the three spectra (see text).

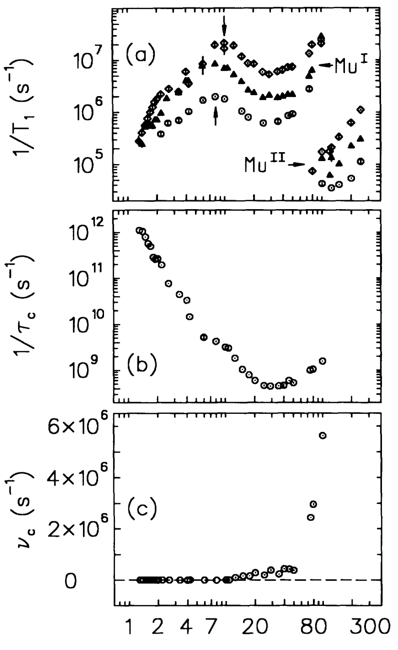

FIG. 2. Temperature dependence of (a) the average relaxation rate $1/T_1$, (b) the inverse correlation time $1/\tau_c$ associated with Mu$^{\mathrm{I}}$ motion, and (c) the Mu$^{\mathrm{I}}$ to Mu$^{\mathrm{II}}$ conversion rate ν_c in CuCl. Diamonds, triangles, and circles in (a) correspond to $B=0.1$, 0.2, and 0.4 T, respectively. The unmarked arrows indicate T_1 minima.

portant since they provide a reliable way to estimate δ_{ex} and calibrate the scale for $1/\tau_c$. For example, at $T=10$ K and $B=0.1$ T one may assume to a good approximation that $1/\tau_c = 3.164\times10^9$ s^{-1}, the value of ω_{12} calculated using the hf parameter for Mu^I in CuCl [9]. Inserting this into Celio's model [12] yields $\delta_{ex}=236(2)$ MHz. For comparison, the isotropic part of the static ^{63}Cu nhf interaction of Mu^I is 60.07(4) MHz [10], indicating that the fluctuating and static parts of the Cu nhf interaction are of the same order of magnitude. Note the slight movement of the T_1 minimum to lower temperatures in the $B=0.4$ T data (circles) which confirms that $1/\tau_c$ increases as the temperature is lowered. Near 100 K there is a rapid increase and subsequent discontinuity in the relaxation rate which is attributed to the known Mu^I to Mu^{II} transition [9]. The small relaxation rate of Mu^{II} and its gradual increase at higher temperatures indicates that Mu^{II} is quasistationary on the time scale of the muon lifetime.

The parameters $1/\tau_c$ and δ_{ex} were evaluated at each temperature by fitting the three time spectra simultaneously (Fig. 1). Since δ_{ex} showed no systematic trend as a function of temperature and because the two parameters are correlated, the data were refitted with δ_{ex} fixed at the value estimated at the T_1 minimum as described above. Above 10 K, a simple trapping model [14] was used to describe the Mu^I to Mu^{II} transition [Fig. 2(c)]. Our best estimates for $1/\tau_c$ are shown in Fig. 2(b). Note the minimum in $1/\tau_c$ at the crossover temperature T_X of about 30 K, which separates thermally activated motion at higher temperatures, attributed to phonon-assisted tunneling, from straight tunneling at lower temperatures, which is impeded by phonons. As the temperature falls from 30 to 1 K the fitted value of $1/\tau_c$ increases according to an approximate power law $T^{-\alpha}$ with $\alpha=2.7(1)$, which is close to that observed for long-range quantum diffusion of muonium in insulators such as KCl [15,16]. Below about 5 K, the fits to the model became increasingly worse with decreasing temperature. At each temperature, the theoretical average relaxation rate at the highest of the three fields was too small, while at the lowest field it was too large. This is an indication that the simple hopping picture may be breaking down as one would expect at very low temperatures where coherence effects should become important. Also at sufficiently low temperatures where k_BT is less than the tunnel splitting there may not be enough thermal energy to localize the particle at a single site.

Figure 3 shows the "quenching curves" in CuCl at $T=1$ K (predominantly Mu^I, open circles) and $T=150$ K (predominantly Mu^{II}, solid circles). The measured quantity P_0 is proportional to the amplitude of the relaxing signal in Fig. 1. The dot-dashed line (a) is a simulation assuming that the nhf interaction is averaged to zero due to fast long-range diffusion, whereas the dashed line (b) was calculated assuming a nonvanishing component of the nhf interaction, such as one would expect for local tunneling or for a quasistationary center. It is evident that the measured quenching curves for both Mu^I and Mu^{II} are of type b. The small discrepancy between curve b and the data is attributed to the fact that in the calculation the model system was muonium interacting with four Cu neighbors only, while in reality there is a nhf interaction with the six next-nearest Cl neighbors as well [10]. There is also a systematic uncertainty due to the slight increase of the experimental asymmetry with increasing field.

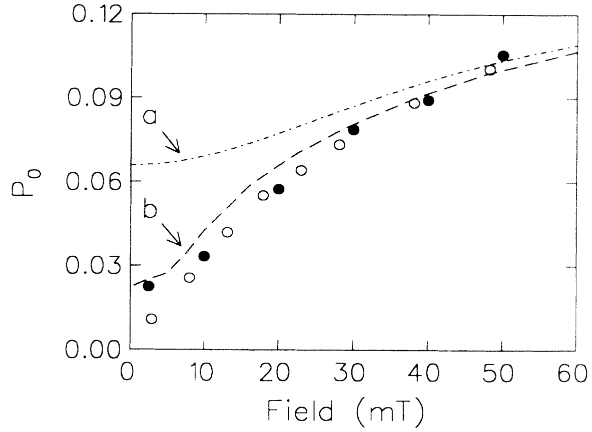

FIG. 3. Measured quenching curves in CuCl at $T=1$ K (predominantly Mu^I, open circles) and $T=150$ K (predominantly Mu^{II}, solid circles). The two lines, a and b, are calculated quenching curves: a, assuming the nhf interaction is averaged to zero due to fast long-range diffusion, and b, assuming there is a nonvanishing time-averaged component of the nhf interaction. For both calculations, the hf parameter for Mu^I was used. For b, a nhf interaction with four ^{63}Cu nuclei was assumed, using the nhf parameters for Mu^I.

Thus the current data strongly suggest a model in which Mu^I tunnels locally around a T_{Cu} site, while Mu^{II} is quasistationary at the T_{Cu} site itself. *Ab initio* calculations of the adiabatic energy surface for atomic hydrogen or muonium in other tetrahedrally coordinated semiconductors often find stationary points with the proton or muon displaced from the T site towards one of the four nearest host atoms [17]. These are defined to be the antibonding (AB) sites. Most authors agree that there is a shallow energy maximum between two AB sites within the same cage, while the energy increases sharply as the proton or muon approaches the region between two adjacent cages. In such a picture, it is clear that Mu^I would be tunneling among the four AB sites surrounding the T_{Cu} site. It is noteworthy that, based on chemical arguments, Cox and Symons [18] suggested two possible modes of local tunneling for muonium in CuCl before any experimental evidence for the mobility of Mu^I or the bulk of the results of the potential energy surface calculations became available. In their model, one of the two modes corresponds to the intracage tunneling described above, while the other mode involves the four AB sites surrounding a single Cu atom. The latter tunneling mode can be ruled out for both Mu^{I} and $\mathrm{Mu}^{\mathrm{II}}$ since it leads to an isotropic nhf interaction with the central Cu atom, which is inconsistent with the μLCR data.

We argue that the local tunneling of Mu^{I} is a nonadiabatic process, i.e., the lattice is essentially undistorted and does not follow the motion of the muon. Thus the metastability of Mu^{I} is a *consequence* of the local tunneling which dynamically prevents a decay to the stable $\mathrm{Mu}^{\mathrm{II}}$ at low temperatures. In this picture, $\mathrm{Mu}^{\mathrm{II}}$ is accompanied by an inward lattice relaxation of the four nearest-neighbor Cu atoms such that a single minimum in the potential energy occurs at the T_{Cu} site, thus suppressing the tunneling.

Such a model can explain many of the observed features of Mu^{I} and $\mathrm{Mu}^{\mathrm{II}}$: the similar and isotropic hf interactions, the metastability of Mu^{I}, the fact that both centers are located at the same site, and the apparent lack of motion associated with $\mathrm{Mu}^{\mathrm{II}}$. Finally we note that we have previously reported longitudinal spin relaxation in KCl [15] and NaCl [16] and attributed it to long-range diffusion. In the case of KCl the agreement between the fluctuating nhf field with that expected from ESR data on hydrogen is strong evidence that the motion was correctly ascribed to long-range diffusion. This is supported by the striking agreement with detailed theoretical calculations by Kagan and Prokofev based upon the assumption of long-range diffusion [7]. However, in the case of NaCl, where a significant reduction in the magnitude of the fluctuating nhf field is observed at low temperatures, the motion may be more complicated [7].

In conclusion, we have reported a detailed study of the spin dynamics of the Mu^{I} and $\mathrm{Mu}^{\mathrm{II}}$ centers in CuCl. We find that the metastable Mu^{I} tunnels locally around a T_{Cu} site, while the stable $\mathrm{Mu}^{\mathrm{II}}$ is quasistationary on the time scale of the muon lifetime, also at the T_{Cu} site. This is the centerpiece of a new model that can explain many of the previously puzzling properties of Mu^{I} and $\mathrm{Mu}^{\mathrm{II}}$ observed in earlier experiments.

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