Quantum Diffusion of Muonium in KCl

R. F. Kiefl, R. Kadono, J. H. Brewer, G. M. Luke,[a] and H. K. Yen
TRIUMF and Department of Physics, University of British Columbia, Vancouver, Canada V6T 2A3

M. Celio
Physik-Institut der Universität Zürich, CH-8001 Zürich, Switzerland

E. J. Ansaldo
Physics Department, University of Saskatchewan, Saskatchewan, Canada S7N 0K3
(Received 28 November 1988)

The diffusion rate of muonium in an insulator, KCl, has been determined from measurements of muon spin relaxation induced by motion in the presence of nuclear hyperfine interactions. The crossover from stochastic to coherent hopping occurs at about 70 K, as evidenced by a dramatic rise in the hop rate at lower temperatures. The coherent hop rate rises much more rapidly with decreasing temperature than for muon diffusion in metals, as predicted by current theories on the diffusion of light interstitials in the absence of conduction electrons.

PACS numbers: 66.30.Jt, 61.70.Bv, 76.75.+i

The diffusion of light interstitials at low temperature has attracted wide interest because of the intrinsic quantum mechanical nature of the transport mechanism. The theory of the diffusion of a light interstitial with its attendant lattice distortion should follow from the theory of small-polaron diffusion.[1,2] At high temperatures the transport mechanism for small polarons is phonon-assisted tunneling, which is a stochastic thermally activated process. One of the most interesting consequences of small-polaron theory is the prediction of a minimum in the hop rate at a temperature T^*. Below this temperature the mobility increases with decreasing temperature due to coherent hopping, a process in which the particle tunnels to a neighboring site without change in the phonon occupation numbers. At still lower temperatures, the hopping picture becomes inappropriate as the particle becomes delocalized. It was pointed out later that the coherent hopping rate would be limited by quadratic terms in the particle-lattice potential.[3] Inclusion of these terms leads to a reduction of T^* and a diffusion constant which follows an inverse power law $T^{-\alpha}$, where α is some large number (as large as 9 for a perfect fcc lattice).[3,4]

The positive muon has a mass only $\frac{1}{9}$ th that of a proton and is therefore ideal for testing quantum theories of diffusion. Measurements of muon diffusion in copper[5-8] and aluminum[9] have confirmed that there is a minimum of the hopping rate at around 50 K for Cu and 5 K for Al, but α was measured to be only 0.6–0.7.[7,9] A similar exponent has been observed for hydrogen tunneling around substitutional oxygen in Nb.[10] Recently, Kondo[11] and Yamada[12] independently showed that, as a consequence of Anderson's orthogonality theorem,[13] the conduction electrons in a metal serve to reduce the tunneling matrix for a charged interstitial and to weaken the temperature dependence of the diffusion rate so that $0 \leq \alpha \leq 1$.

In this paper we present measurements of the diffusion rate of isolated muonium atoms (μ^+e^-) in an ionic insulator (KCl), in which there are no conduction electrons. A dramatic increase in the hop rate is observed below 70 K, which we attribute to the onset of coherent diffusion. The exponent α in the coherent region is at least 5 times larger than for muon diffusion in metals as predicted by current theories on the diffusion of light interstitials.

The spin Hamiltonian for muonium or hydrogen at the tetrahedral interstitial site in KCl is of the following form[14]:

$$\mathcal{H}/h = A\mathbf{S}_\mu \cdot \mathbf{S}_e + \gamma_e \mathbf{S}_e \cdot \mathbf{B} + \gamma_\mu \mathbf{S}_\mu \cdot \mathbf{B} + \sum [\gamma_i \mathbf{S}_i \cdot \mathbf{B} + \mathbf{S}_i \cdot \hat{\mathbf{C}}_i \cdot \mathbf{S}_e] , \quad (1)$$

where A is the muon hyperfine parameter, $\hat{\mathbf{C}}_i$ is a tensor describing the nuclear hyperfine interaction of neighboring nucleus i, and $\mathbf{B}$ is the external field. From previous muon-spin-relaxation (μSR) measurements,[15] it is known that A is about 4270 MHz, corresponding to about 95% of the vacuum value. ESR and electron-nuclear double resonance results on the analogous hydrogen center[14] have shown that the dominant nuclear hyperfine interaction is with the four nearest-neighbor spin-$\frac{3}{2}$ Cl nuclei, for which the isotropic part of $\hat{\mathbf{C}}$ is about 25 MHz. [The Cl nuclear quadrupolar interaction, which is not included in Eq. (1), is only a few MHz and is unimportant in the present study.] If the muonium is stationary and $\mathbf{B}$ is applied along the direction of initial muon polarization (LF-μSR), the muon spin polarization evolves in time according to a function, $P_z(t)$, which consists of unresolved high-frequency oscillations

plus a static component whose amplitude increases with increasing magnetic field.[16] The spin dynamics for muonium diffusing in the presence of nuclear hyperfine interactions have recently been modeled by Celio.[17] The nuclear hyperfine interaction is simulated by an effective field acting on the electron, which is a good approximation provided the electron Zeeman interaction is much greater than the nuclear hyperfine interaction. The entire last term in square brackets in Eq. (1) is then replaced by $\delta_{ex}\mathbf{S}_e\cdot\mathbf{T}(t)$, where δ_{ex} is the strength of the effective Zeeman interaction and $\mathbf{T}(t)$ is the direction of the effective field, which is fluctuating with a correlation time τ_c corresponding to the mean time between hops. It was found that a τ_c equal to about 1.9×10^{-10} s with δ_{ex} about 60 MHz could explain room-temperature measurements of the linewidths in transverse field[18] and the time-averaged muon polarization in a longitudinal magnetic field.[19] Theory also predicts that motion will induce relaxation of the nonoscillating component of the muon polarization in a longitudinal field, which until now has not been reported. The essential point is that the fluctuating nuclear hyperfine field on the electron causes electron spin relaxation which in turn depolarizes the muon spin through the muon hyperfine interaction. Such muon spin relaxation in a longitudinal field is more sensitive to diffusion than are linewidth measurements in transverse field, although the latter are essential to identify unambiguously the relaxation mechanism.

The present experiment was performed on the M15 beam line at TRIUMF which provides a beam of 100%-spin-polarized positive muons of momentum 28.6 MeV/c. Muons were stopped in a single crystal of KCl measuring 30 mm diam by 5 mm thick obtained from the Harshaw Chemical Co. Conventional LF-μSR spectra were taken with an external magnetic field applied along a [110] crystalline direction. Positrons from muon decay are emitted preferentially along the instantaneous direction of muon polarization[20] so that the time-differential μSR spectrum, after correction for instrumental asymmetry, is of the following form:

$$S_{\rm asy}(t)=\frac{F(t)-R(t)}{F(t)+R(t)}=AP_z(t)\,,$$

where $F(t)$ and $R(t)$ refer to the positron events in the forward and rear telescopes at time t after the muon arrival, A is the maximum experimental asymmetry in muon decay, and $P_z(t)$ is the time-dependent muon polarization function. Typical spectra in a longitudinal magnetic field (50 and 150 mT) are shown in Fig. 1. The observed relaxation is attributed solely to the motion of interstitial muonium for the following reasons: (1) From previous work, the relaxation of the precession signals in transverse magnetic fields below 200 K can be completely quenched by the application of a large magnetic field of 1.2 T.[15] This is incompatible either with charge-exchange reactions seen at higher temperature,[21] or with spin-exchange reactions with paramagnetic impurities. It should be noted that the muonium atoms are studied one at a time so that there can be no interaction between the muonium atoms themselves. (2) The amplitude of the relaxing component (which corresponds to about an 80% muonium formation probability at 200 K) and its temperature dependence are in close agreement with the amplitude of the muonium precession signals seen in high transverse magnetic fields.[18] This confirms that the relaxing component reported here is due to the muonium seen in transverse field.

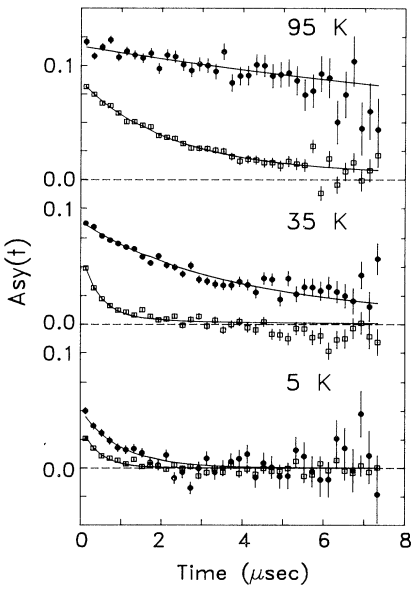

FIG. 1. Muon spin relaxation of muonium in KCl in a longitudinal magnetic field of 50 mT (open squares) and 150 mT (filled circles) applied along the muon polarization direction.

Good fits were obtained with the theoretical relaxation function which is, in general, a sum of three exponentials[22] depending on δ_{ex}, τ_c, and **B** (see Fig. 1). The coupling constant δ_{ex} and τ_c were deduced at several temperatures where data were taken at two different fields. The fitted δ_{ex} was statistically independent of temperature, yielding an average $\delta_{ex}=55(6)$ MHz which is consistent with the previous result at room temperature. The muonium hopping rate was then determined from a second analysis in which δ_{ex} was fixed at its average value. Note from Fig. 1 the consistency between the data at 50 and 150 mT, where the same δ_{ex} and τ_c account for the relaxation and relative amplitudes at the two fields.

The average muon relaxation rates and the fitted muonium hop rate are shown in Figs. 2(a) and 2(b), respectively. The weak field dependence in the relaxation below 20 K and the slight downturn in the relaxation rate at 50 mT are consequences of a T_1-minimum effect, often encountered in magnetic resonance experiments. In the present case, the T_1 minimum in the 50-mT data occurs at a temperature of 20 K where the average hop

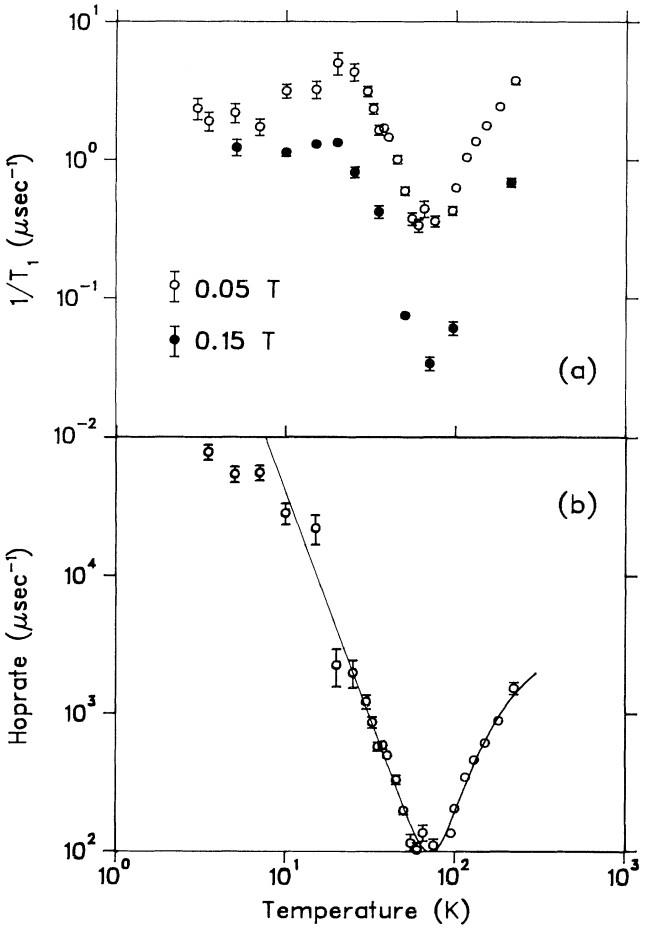

FIG. 2. Temperature dependence of (a) the average muon relaxation rate at 50 and 150 mT and (b) the extracted muonium hop rate.

rate is equal to $2\pi\nu_\mu^+$, where ν_μ^+ is the muonium transition frequency corresponding to a flip of the muon spin with the electron spin aligned with **B**. This feature in the data provides an absolute calibration of the hop rate at this temperature. The relaxation rate at 150 mT is insensitive to temperature below 20 K because the T_1 minimum is broader at this field and never quite reached. Thus, although the relaxation rate below 20 K is decreasing or leveling off, the hop rate is monotonically increasing. From Fig. 2(b) it is clear that the hop rate increases by almost 3 orders of magnitude between 70 and 5 K and that the muonium is moving considerably faster at 5 K than at room temperature. The curve in Fig. 2(b) is a fit by the function

$$\nu = \nu_1 \exp(-E_a/kT) + \nu_2 (T/\Theta_D)^{-\alpha}, \qquad (2)$$

over the temperature range 10–250 K with parameters $\nu_1 = 8.2(8) \times 10^9$ s^{-1}, $E_a/k = 388(12)$ K, $\nu_2 = 1.3(6) \times 10^6$ s^{-1}, $\alpha = 3.3(1)$. A Debye temperature (Θ_D) of 231 K was assumed. Note that the activation energy is smaller than that reported for atomic hydrogen in KCl (2300 K).[23] Since the zero-point energy for muonium is about 3 times that of hydrogen, one would expect a reduced barrier for muonium. However, if phonon-assisted tunneling dominates the muonium diffusion at high temperatures, as indicated by the observed minimum in the hop rate at $T^* = 70$ K, E_a reflects the lattice relaxation energy rather than the potential barrier between sites. It is interesting that the second term in Eq. (2) is completely absent for the heavier hydrogen atom, which is immobile below about 120 K.[23] The observed T^* and α are compatible with numerical calculations of the temperature dependence of the correlation time using typical parameters (see Figs. 4 and 5 in Ref. 4). However, it should be noted that the observed α must be considered a lower limit for an ideal crystal since strain fields from crystal imperfections are expected to limit the low-temperature diffusion by producing a potential-energy difference between sites on the order of the small-polaron bandwidth.[24] The observed leveling off of the hop rate below 10 K might be due to such strain fields.

In conclusion, the diffusion rate of muonium in KCl has been determined from measurements of the muon spin relaxation rate in the presence of nuclear hyperfine interactions. We have observed a dramatic increase in the hop rate below 70 K, which is attributed to the onset of coherent hopping. Our most important result is that the temperature dependence of the coherent hop rate is much steeper than that observed for muon diffusion in metals, thus providing strong confirmation of current theories on diffusion of light interstitials.

We would like to acknowledge helpful discussions with Dr. Jun Kondo and also thank Keith Hoyle and Curtis Ballard for technical support. This work was supported by the National Research and Natural Sciences and Engineering Research Councils of Canada.

[a]Present address: Department of Physics, Columbia University, New York, NY 10027.

[1]T. Holstein, Ann. Phys. (N.Y.) **8**, 343 (1959).

[2]C. P. Flynn and A. M. Stoneham, Phys. Rev. B **1**, 3966 (1970).

[3]Yu Kagan and M. I. Klinger, J. Phys. C **7**, 2791 (1974).

[4]K. G. Petzinger, Phys. Rev. B **26**, 6530 (1982).

[5]C. W. Clawson, M. K. Crowe, S. S. Rosenblum, S. E. Kohn, C. Y. Huang, J. L. Smith, and J. H. Brewer, Phys. Rev. Lett. **51**, 114 (1983).

[6]R. Kadono, J. Imazato, K. Nishiyama, K. Nagamine, T. Yamazaki, D. Richter, and J.-M. Welter, Phys. Lett. **109A**, 61 (1985).

[7]R. Kadono, T. Matsuzaki, K. Nagamine, T. Yamazaki, D. Richter, and J.-M. Welter, Hyperfine Interact. **31**, 205 (1986); R. Kadono, J. Imazato, T. Matsuzaki, K. Nishiyama, K. Nagamine, T. Yamazaki, D. Richter, and J.-M. Welter, Phys. Rev. B **39**, 23 (1989).

[8]G. M. Luke, Ph.D. thesis, University of British Columbia,

1988 (unpublished).

[9]O. Hartmann, E. Karlson, E. Wäcklegard, R. Wäppling, D. Richter, R. Hempelmann, and T. O. Niinikoski, Phys. Rev. B **37**, 4425 (1988).

[10]D. Steinbinder, H. Wiff, A. Magreland, D. Richter, A.-J. Dianoux, and K. Neumaier, Europhys. Lett. **6**, 535 (1988).

[11]J. Kondo, Physica (Amsterdam) **125B**, 279 (1984), and **126B**, 377 (1984), and Hyperfine Interact. **31**, 117 (1986).

[12]K. Yamada, Prog. Theor. Phys. **72**, 195 (1984); K. Yamada, A. Sakurai, and S. Miyazawa, Prog. Theor. Phys. **73**, 1342 (1985).

[13]P. W. Anderson, Phys. Rev. **164**, 352 (1967).

[14]J. M. Spaeth, Phys. Status Solidi **34**, 171 (1969).

[15]R. F. Kiefl, E. Holzschuh, H. Keller, W. Kündig, P. F. Meier, B. D. Patterson, J. L. Schneider, K. W. Blazey, S. L. Rudaz, and A. B. Denison, Phys. Rev. Lett. **53**, 90 (1984).

[16]R. Beck, P. F. Meier, and A. Schenck, Z. Phys. B **22**, 109 (1975).

[17]M. Celio, Helv. Phys. Acta **60**, 600 (1987).

[18]Hp. Baumeler *et al.*, Hyperfine Interact. **32**, 659 (1986); Hp. Baumeler, Ph.D. thesis, University of Zurich, 1988 (unpublished).

[19]F. N. Gygax, A. Schenck, A. J. van der Wal, R. Koch, and A. Winnacker, Hyperfine Interact. **32**, 511 (1986).

[20]See, for example, A. Schenck, *Muon Spin Rotation Spectroscopy* (Hilger, Boston, 1985).

[21]K. Nishiyama, Y. Morozumi, T. Suzuki, and K. Nagamine, Phys. Lett. **111A**, 369 (1985); Y. Morozumi, K. Nishiyama, and K. Nagamine, Phys. Lett. A **118**, 93 (1986).

[22]H. K. Yen, M.Sc. thesis, University of British Columbia, 1988 (unpublished).

[23]M. Ikeya, L. O. Schwan, and T. Miki, Solid State Commun. **27**, 891 (1978).

[24]H. Sugimoto, J. Phys. Soc. Jpn. **55**, 1687 (1986).