Delocalization of Muonium in NaCl

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The spin dynamics of muonium diffusing in NaCl have been investigated using the technique of muon-spin relaxation. An effective coupling constant (δ_{ex}) for the nuclear hyperfine interaction and the correlation time for motion were determined from measurements of the muon-spin-relaxation rate. At temperatures below 200 K, δ_{ex} is sharply reduced below that expected from the known hyperfine structure of interstitial hydrogen, providing clear evidence for delocalization of muonium.

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Since the positive muon has a mass about $\frac{1}{9}$ that of a proton, its motion in a crystalline lattice is thought to be fundamentally different from that of heavier atoms due to enhanced quantum-mechanical effects. For example, the muon hop rate in Cu *increases* with *decreasing* temperature below a temperature $T^* \approx 50$ K.[1] This behavior can be explained qualitatively by theories of the motion of small polarons, although quantitative agreement with the data was not achieved until Kondo and Yamada included the effects of the conduction electrons.[2,3] Recently we have studied the diffusion of isolated muonium atoms ($\mu^+ e^-$) in the ionic crystal KCl, where the effect of conduction electrons is absent.[4] As predicted by theory, the exponent α characterizing the temperature dependence ($\approx T^{-\alpha}$) of the quantum diffusion rate below T^* was considerably larger than for muons in metals.

Another interesting aspect of quantum diffusion occurs when the mean free path before scattering by phonons becomes longer than a lattice constant. Then the simple picture of a localized particle tunneling from one site to the next must be replaced by one in which the muon wave function is coherent over several interstitial sites. A distinctive feature of such spatial delocalization is that the magnetic interaction between the muon and nuclear spins is averaged over all nuclei in the region of coherence. This leads to a net reduction in the effective strength of the interaction by a factor $(N/n)^{1/2}$,[5,6] where n is the number of nearest neighbors for a localized muon and N is number of nuclei within the region of coherence. Estimates of the temperature at which such delocalization occurs are less than 1 mK for muons in Cu.[2] However, the delocalization can occur at much higher temperatures if the matrix element for tunneling is large, such as would be the case if there is a delay to self-trapping and the formation of a small polaron. In this Letter we report measurements which show that the nuclear hyperfine (nhf) interaction of muonium in NaCl is reduced by at least a factor of 4 below 200 K, providing clear evidence for such quantum-mechanical delocalization.

It is known from previous work that muons implanted into alkali halides form muonium centers ($\mu^+ e^-$) with a high probability. Comparison of the muon hyperfine parameters with those of the proton indicates that muonium occupies the same tetrahedral interstitial (or *T*) site as atomic hydrogen.[7] This is expected since the adiabatic potential-energy surfaces for muonium and hydrogen are virtually identical. The spin Hamiltonian for muonium or hydrogen localized at the *T* site in alkali halides is of the following form:[8,9]

$$\mathcal{H}/h = A_\mu \mathbf{S}_\mu \cdot \mathbf{S}_e + g_e \mu_B \mathbf{S}_e \cdot \mathbf{B} + g_\mu \mu_\mu \mathbf{S}_\mu \cdot \mathbf{B} + \sum [g_i \mu_i \mathbf{I}_i \cdot \mathbf{B} + (a-b)\mathbf{I}_i \cdot \mathbf{S}_e + 3b I_i^{\hat{z}} S_e^{\hat{z}}] , \quad (1)$$

where $\mathbf{B}$ is the external field, $\mathbf{S}_\mu$, $\mathbf{S}_e$, and $\mathbf{I}_i$ are spins for muon, electron, and nuclei, A_μ is the isotropic muon hf parameter, a and b are isotropic and dipolar nhf parameters, and $\hat{\mathbf{z}}$, the muon-nuclear vector, is the symmetry axis for the nuclear hyperfine interaction. (The small nuclear quadrupolar interactions of strength ≤ 1 MHz are neglected.) Although the nhf parameters for muonium have not been measured directly, they can be inferred from those for hydrogen and deuterium,[8,10] where only small differences on the order of 5% are expected due the effect of zero-point motion. As in most alkali halides the largest nhf parameters in NaCl and KCl are for the four neighboring halide nuclei closest to the proton (muon).

We have recently shown that the muon T_1 spin-relaxation rate is a sensitive measure of the muonium diffusion rate.[4] The basic idea is that the nhf interaction produces an effective magnetic field on the unpaired electron which depends on the orientation of the nuclear

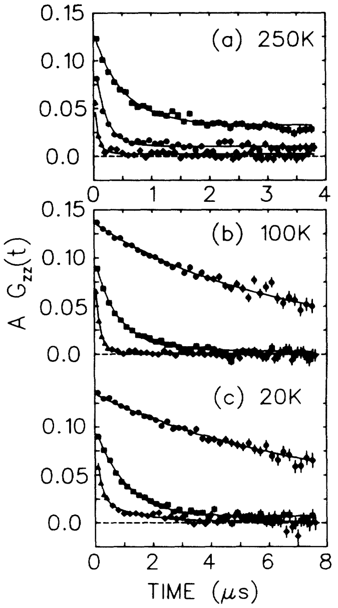

FIG. 1. The μSR time spectra in NaCl in magnetic field applied along the muon-spin-polarization direction. The solid lines are fitted curves. In (a) where $T=250$ K the magnetic fields are from top to bottom 0.3, 0.15, and 0.05 T. In (b) where $T=100$ K and in (c) where $T=20$ K the magnetic fields are from top to bottom 0.15, 0.05, and 0.02 T. Note the change in time scale compared with (a).

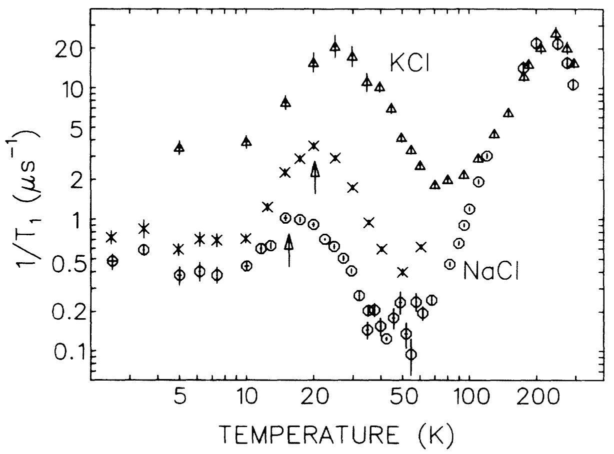

FIG. 2. Temperature dependence of the muon-spin-relaxation rate in NaCl and KCl in a magnetic field B applied along the muon-polarization direction. The crosses correspond to $B=0.02$ T in NaCl, the circles to $B=0.05$ T in NaCl, and the triangles to $B=0.02$ T in KCl. Arrows show T_1 minima at each field in NaCl.

spins. As the muonium diffuses the direction of this effective field fluctuates, thereby inducing transitions between the muonium hyperfine levels. From the resulting muon relaxation rate and after appropriate modeling of the spin dynamics using the Redfield equations of motion,[4,11] one can deduce an average electron-nuclear coupling constant δ_{ex} and the correlation time τ_c over which that interaction is constant. The general expression for the muon polarization is complicated. However, for the purpose of illustrating the essential features of our data it is useful to consider the idealized situation where $1/\tau_c$ is small with respect to all transition frequencies except the smallest intratriplet transition ω_{12}. Ignoring all higher-frequency transition leads to the muon-spin-relaxation rate

$$\frac{1}{T_1} \approx \left[1-\frac{x}{(1+x^2)^{1/2}}\right]\frac{\delta_{ex}^2\tau_c}{1+\omega_{12}^2\tau_c^2}, \tag{2}$$

$$\omega_{12}=\tfrac{1}{2}\omega_0[1+(\Gamma_-/\Gamma_+)x-(1+x^2)^{1/2}],$$

where $\Gamma_\pm=\frac{1}{2}(g_e\mu_B\pm g_\mu\mu_\mu)$, $\omega_0=2\pi A_\mu$, and $x=2\times\Gamma_+B/\omega_0$. The parameter δ_{ex} can be related to the nearest-neighbor halide nhf parameters a and b, with the result[12]

$$\delta_{ex}=(a^2+2b^2)^{1/2}[nI(I+1)/3]^{1/2}, \tag{3}$$

where the second factor is the mean-squared value of the component of total nuclear spin along the field for n nearest-neighbor nuclei with spin I.

The experiment was performed on the M15 beam line at TRIUMF, which provides a beam of 100% spin-polarized muons of momentum 28 MeV/c. Muons were stopped in a single crystal of NaCl measuring 30 mm in diameter by 5 mm thick obtained from the Harshaw Chemical Co. At each temperature conventional muon-spin-relaxation (μSR) spectra were taken with an external field applied along the initial muon-polarization direction and a [110] crystalline direction. The μSR technique, details of which can be found elsewhere,[13] measures directly the time evolution of the muonium polarization [$G_{zz}(t)$] on the time scale of the average muon lifetime (2.2 μs).

Typical μSR time spectra observed in NaCl are shown in Fig. 1. Note the high sensitivity of the muon-spin-relaxation rate to magnetic field and temperature. The temperature dependence of the average spin-relaxation rate for muonium in NaCl and KCl is plotted in Fig. 2. The nuclear hyperfine coupling constant δ_{ex} and $1/\tau_c$ [see Figs. 3(a) and 3(b), respectively] were determined by simultaneous fitting of the μSR time spectra taken at two or three external magnetic fields by the general expression for the muon spin relaxation derived from the Redfield equations. In the temperature range 20–200 K excellent fits to the data were obtained for the muon polarization assuming the muonium was freely diffusing for its entire lifetime [see, for example, Fig. 1(b)]. However, below 20 K and above 200 K, where the diffusion is fastest, a small nonrelaxing component of the muon polarization function was observed whose amplitude depended on magnetic field [see, for example, Fig. 1(a)]. This indicates that muonium in NaCl traps or reacts to form a diamagnetic center[14] in which there is no spin re-

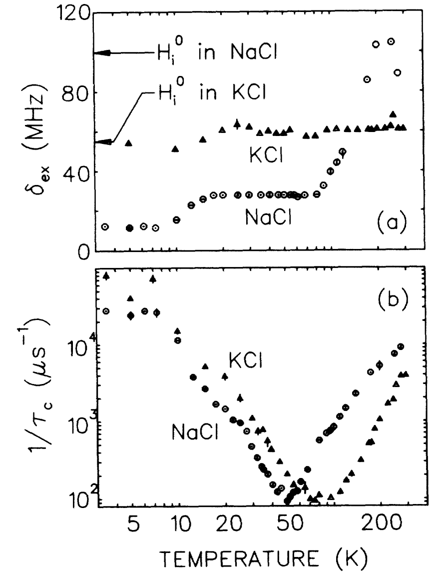

FIG. 3. Temperature dependence of (a) the effective nuclear hyperfine coupling constant δ_{ex} and (b) the inverse correlation time for muonium motion in NaCl (circles) and KCl (triangles). Arrows indicate the δ_{ex} expected for localized interstitial muonium or hydrogen H_i^0.

laxation. A simple two-state trapping model[15,16] was necessary to fit these data. The derived trapping rates reached about 0.4 μs^{-1} at the extreme temperature limits. Systematic errors introduced by such trapping are small since the fitted parameters are weakly correlated; i.e., the trapping (reaction) rate is determined by the nonrelaxing component in the time spectrum [see Fig. 1(a)] whereas δ_{ex} and τ_c are determined by the field dependence of the relaxation rate.

Note that $1/T_1$ (see Fig. 2) and $1/\tau_c$ [see Fig. 3(b)] reach a minimum at a temperature T^* equal to about 50 and 70 K in NaCl and KCl, respectively. Near T^*, $1/T_1$ and $1/\tau_c$ are roughly proportional to one another as may be seen from Eq. (2) in the limit $\omega_{12}\tau_c \gg 1$. Below T^*, $1/\tau_c$ increases with *decreasing* temperature due to zero-phonon tunneling, whereas above T^*, $1/\tau_c$ increases with *increasing* temperature due to thermally activated hopping. On the other hand, $1/T_1$ passes through a maximum on both the high- and low-temperature sides of T^*. This is the familiar "T_1 minimum" effect which occurs when $\omega_{12}\tau_c = 1$ in Eq. (2). The observed shift of the T_1 minimum from 20 to 15 K with the change of field B from 0.02 to 0.05 T (see arrows in Fig. 2) clearly shows that $1/\tau_c$ continues to increase in NaCl with decreasing temperature.

There is an important difference in the temperature dependence of $1/T_1$ between NaCl and KCl (see Fig. 2). It follows from Eq. (2) that at a T_1 minimum $1/T_1 = \kappa\delta_{ex}^2$, where κ is independent of temperature. Thus $1/T_1$ should be equal at the two T_1 minima for fixed magnetic field, provided the effective nhf interaction is independent of temperature. This statement should be true independent of the detailed model of the hopping since the condition on τ_c at the T_1 minimum is temperature independent (for example, $\omega_{12}\tau_c = 1$). In KCl the relaxation rates at the two T_1 minima are approximately equal on both the high- and low-temperature sides of T^*, demonstrating that δ_{ex} is temperature independent. In NaCl, on the other hand, $1/T_1$ is an order of magnitude smaller at the low-temperature T_1 minimum (see Fig. 2). This is also clearly seen in the μSR time spectra at 250 and 20 K [see Figs. 1(a) and 1(c), respectively]. Thus in NaCl the effective nuclear hyperfine parameter (δ_{ex}) must be considerably less at 20 K than at 250 K.

The full temperature dependence δ_{ex} in NaCl and KCl is shown in Fig. 3(a). Note that in KCl δ_{ex} is almost temperature independent and in good agreement with that expected from the nhf parameters of hydrogen [indicated by an arrow in Fig. 3(a)]. This confirms that muonium in KCl is the localized analog of interstitial hydrogen. The same is true for muonium in NaCl above 200 K. However, there is a steplike reduction in δ_{ex} below 200 K in NaCl and indication of a further decrease below 20 K, although the fits for $T < 20$ K were not as good as at higher temperatures. These results lead us to conclude that there is a dramatic reduction in δ_{ex} for muonium diffusing in NaCl at low temperatures. Furthermore, the magnitude of δ_{ex} below 200 K is far less than expected for a spatially localized muonium center hopping between interstitial T sites.

The temperature dependence of A_μ is weak in NaCl[17] and almost the same as in KCl.[7] This implies that the observed sharp decrease in the nuclear hyperfine coupling in NaCl is not accompanied by any dramatic change in the muon hyperfine coupling, discrediting any explanation involving an electronic excitation. Considering the light mass of muonium, the natural explanation for the reduction of δ_{ex} is quantum-mechanical delocalization. The ratio of δ_{ex} between 200 and 20 K [(104 MHz)/(27.5 MHz)] suggests that the region of coherence encompasses at least 57 halide nuclei. The observation of delocalization at such high temperatures and its rapid variation with temperature at around 200 K are not easily explained within a simple small-polaron model for muonium. One possibility is that below 200 K there is a delay to the formation of a small polaron after the introduction of energetic muons.[18] This could result in an enhanced matrix element for tunneling within the large polaron and an averaging of the nuclear hyperfine interaction. Presumably, above 200 K the muonium localizes due to a collapse of the polaron. Finally, we note that an extended muon wave function has been proposed to explain experiments in pure bismuth,[19] although the evidence was not so clear.

In conclusion, muon-spin-relaxation measurements of muonium diffusion in NaCl indicate that there is a dramatic steplike reduction in the nuclear hyperfine interaction below 200 K, providing firm evidence for the quantum-mechanical delocalization of a light interstitial.

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