An Atom in the Bloch State

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(Received 8 April 1999)

A resonant enhancement of muon spin relaxation has been observed at a field where the muonium Zeeman splitting crosses a Van Hove singularity in the small polaron band for interstitial muonium in potassium chloride. This feature is predicted only for muonium in a coherent state near the bottom of the band and thus clearly establishes that a light interstitial atom such as muonium can exist in a Bloch state in an ordered crystalline host at low temperature.

PACS numbers: 66.35.+a, 61.72.–y, 76.75.+i

It is well established that electrons in crystalline solids behave not as particles colliding repeatedly with the host atoms, but as quantum mechanical waves extended over the entire crystal. This picture of electron waves, first pointed out by Bloch in 1928 and called the "Bloch state" since then, provides the fundamental basis for modern solid state physics. In view of this, how should one consider a light interstitial atom placed in similar conditions in a lattice? While it is possible in principle for an atom to be in a Bloch state, there are a number of factors which prevent such a coherent state from being realized in practice. However, we have now found that a muonium atom (effectively a light isotope of atomic hydrogen whose proton is substituted by a positive muon having 1/9 of the proton mass) is indeed in such a Bloch state in an ordinary crystalline host of potassium chloride (KCl) at very low temperatures (<10 mK). This new result opens up a path to the experimental study of a completely novel type of atomic state in crystalline solids.

Quantum diffusion is an interesting kinetic process in which an interstitial atomic particle migrates from site to site in a crystalline lattice by quantum mechanical tunneling. One of the most dramatic manifestations of quantum diffusion is that the diffusion rate increases with decreasing temperature, in contrast to the usual thermal diffusion. Quantum diffusion was first observed for the positive muon (μ^+) in metals and more recently for muonium (Mu) in ionic crystals [1]. In general, an atom placed in a crystalline solid strongly interacts with its host atoms to form the so-called "polaron state," i.e., a complex state associated with the deformation of the lattice (and also with perturbation of the conduction electrons in metals), thus making the interstitial atom less mobile than it would be in the absence of interaction. However, such a polaron state can have a finite tunneling matrix element, Δ, to the nearest neighbor sites, and the jump frequency (which is proportional to the diffusion rate) at a temperature T is

$$\nu(T) \simeq \frac{\Delta^2}{\Omega(T)}, \tag{1}$$

where $\Omega(T)$ is the damping factor (i.e., the width of the final state energy level) due to interaction with the phonon/electron bath and is proportional to a power of T [i.e., $\Omega(T) \propto T^{\alpha}$]. Since Δ does not depend on T in nonmetallic hosts, we may expect an inverse power law T dependence, $\nu(T) \propto T^{-\alpha}$, which is in excellent agreement with many experimental observations [1]. An example of diffusion of Mu in KCl is shown in Fig. 1 where the predominant phonon damping leads to a steep increase of jump frequency with decreasing T for $T <$ 80 K [2,3]. A further reduction of $\nu(T)$ due to the additional electron-muon polaron effect was also proved to be effective for μ^+ diffusion in metals [1,4].

This diffusion model, based on the situation where an atom is localized due to strong damping, is valid only when $\Omega(T) \gg \Delta$: The jump frequency cannot exceed the rate determined by Δ and thus the rate ν is predicted

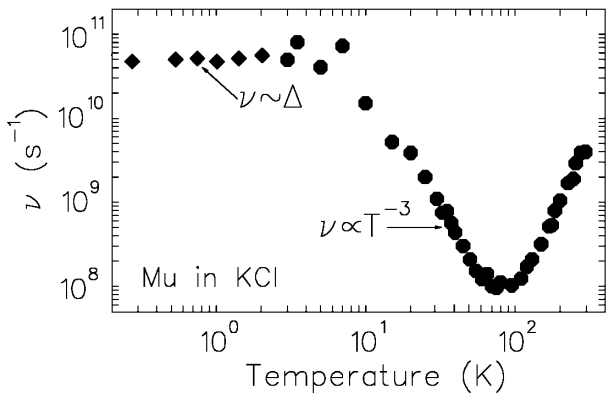

FIG. 1. Jump frequency, ν, of muonium atoms in KCl (circles from Ref. [3]; diamonds from Ref. [5]).

to level off for $\Omega(T) \ll \Delta$, i.e.,

$$\nu(T) \simeq \Delta\,. \tag{2}$$

As shown in Fig. 1 [5], this feature has also been confirmed in various nonmetallic systems and has been used to evaluate Δ in each case. However, it should be noted that a term such as "jump frequency" may lose its physical meaning in this situation. The issue becomes more critical when one considers how the jump frequency is determined experimentally.

In the case of Mu, one measures the longitudinal muon spin relaxation rate $(1/T_1)$ induced by fluctuation of local magnetic fields $H(t)$ acting on the Mu orbital electron; i.e.,

$$T_1^{-1} \simeq \delta_{\rm ex}^2 \sum_{i,j} a_{ij} \int G(t) e^{i\omega_{ij}t}\, dt = \delta_{\rm ex}^2 \sum_{i,j} a_{ij} C(\omega_{ij})\,, \tag{3}$$

where $\delta_{\rm ex}$ is the rms value of the random local field [i.e., $\delta_{\rm ex}^2 = \langle H(0)^2 \rangle$], $G(t)$ is the time correlation, $C(\omega)$ is the corresponding spectral density, and ω_{ij} is the relevant Mu Zeeman frequency with the respective amplitude a_{ij} under an applied magnetic field. The random magnetic field produced by the nuclear moments, which are the main source of the local field, is short-ranged so that the fields experienced by the Mu after each jump (with a mean resident time $\tau_c = \nu^{-1}$) should be uncorrelated. This leads to an exponential time correlation function for the local field,

$$G(t) \equiv \frac{\langle H(t)H(0) \rangle}{\langle H(0)^2 \rangle} = \exp(-t/\tau_c)\,, \tag{4}$$

and subsequently to a Lorentzian spectral density for the relaxation [6],

$$C(\omega) = \frac{\tau_c}{1 + \omega^2 \tau_c^2} \equiv C_L(\omega)\,. \tag{5}$$

The jump frequencies for the data in Fig. 1 have been deduced by assuming this spectral density.

On the other hand, when $T \ll \Delta$, the only limiting factor is the mean free path of Mu l, and one should start from a delocalized (Bloch) state for $l \gg a$ (where a is the lattice constant), which is the eigenstate of energy and momentum $\varepsilon_{\mathbf{k}}$. In this case $G(t)$ is directly given by the time evolution of the Mu density matrix itself, and the corresponding spectral density should be expressed as

$$C(\omega) = \pi \rho(\hbar\omega + \varepsilon_{\mathbf{k}}) \equiv C_B(\omega)\,, \tag{6}$$

where $\rho(\varepsilon_{\mathbf{k}})$ is the density of states for Mu [7]. One of the most interesting features of the above prediction is that the spin relaxation occurs as a result of exchanging Zeeman energy $\hbar\omega$ with the Mu band energy, so that the rate may strongly reflect the shape of the Mu density of states $\rho(\varepsilon_{\mathbf{k}})$. In particular, one would expect a strong modulation of relaxation rate $(1/T_1)$ when the Zeeman frequency coincides with van Hove singularities; i.e.,

$$\omega \simeq 0,\ \frac{4}{3}\Delta_0,\ \frac{8}{3}\Delta_0,\ \text{or}\ 4\Delta_0\,, \tag{7}$$

for a band corresponding to a simple cubic lattice (where $\Delta_0 = \Delta/12$ for the simple cubic lattice). More specifically, the lowest Zeeman frequency ω_{12} has the predominant contribution to Eq. (3) and the most significant effect is observed as a peak of relaxation rate when

$$\omega_{12} \simeq \frac{4}{3}\Delta_0\,, \tag{8}$$

which is illustrated in Fig. 2. (Other singularities are more difficult to observe in the current conditions and therefore disregarded in the following discussion.) This is more or less similar to the situation for the de Haas-van Alphen effect, with the Landau level replaced by the Zeeman level. Thus we have the possibility to study the band structure of a muonium atom in a crystalline lattice by mapping out the field dependence of the muon spin relaxation. It is also important to note that the above prediction is valid only when the initial and final states of the relaxation process are both Bloch states (i.e., $T \ll \Delta$). In the case of a localized state, one must average the spectral density over $\varepsilon_{\mathbf{k}}$ to give $C(\omega) \propto \{\rho(\omega)\}^2$ [1,5]. This smears out the structure in the relaxation rate so that the difference between $C_L(\omega)$ and $C_B(\omega)$ becomes very subtle.

In order to examine the above prediction, we have measured the muon spin relaxation rate of the muonium atom in KCl at the RIKEN-RAL Muon Facility in the Rutherford Appleton Laboratory. While the details of

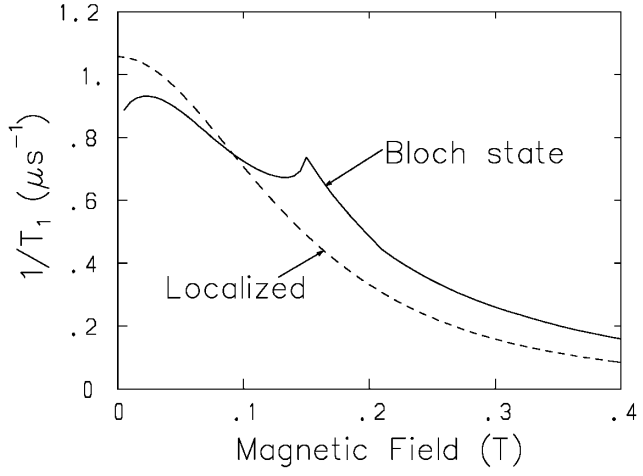

FIG. 2. Calculated spin relaxation rate $(1/T_1 \propto \sum_{i,j} a_{ij} C(\omega_{ij})$, where ω_{ij} is the transition frequency between relevant hyperfine levels) for the muonium atom in the Bloch state, assuming a simple cubic band with $\Delta_0 \simeq 0.09$ K (solid curve). Compared with the case for localized muonium (dashed curve), one can see a strong modulation reflecting the energy dependence of the Mu density of states. ($\delta_{\rm ex}$ was adjusted to simulate the result in Fig. 3 qualitatively.)

the experiment will be published elsewhere, we briefly point out the main distinction of the present experiment from those in the past. Namely, instead of using a bulk crystal, a mixture of freshly ground single crystal KCl and silver powder was molded into a sample holder with a small amount of grease to secure good thermal contact with the coldest part of the ^{3}He-^{4}He dilution refrigerator. Compared with using the bulk crystal, a crude estimation suggests that about 10^2 times improved efficiency was expected for cooling those ground crystals due to wider surface area. Except for this, conventional muon spin relaxation (μSR) measurements were performed under a longitudinal magnetic field (for KCl crystals in this condition the only muon spin relaxation comes from Mu). The μSR time spectra were analyzed by a single exponential decay $A(t) = A(0)\exp(-t/T_1)$.

The results are shown in Fig. 3, where one can notice a clear difference between the data at 3.9 K (Fig. 3a) and below 10 mK (Fig. 3b). In particular, there is a broad peak in the relaxation rate in Fig. 3b, which is absent in Fig. 3a. The spectral density in Fig. 3a is reproduced by assuming $C_L(\omega)$ plus a constant background relaxation ($\simeq 2.5 \times 10^{-5}$ s^{-1}), as shown by the solid curve. The magnitude of local field δ_{ex} ($\sim$1 mT) is about one-half of the value at higher temperature, which is similar to the situation in NaCl [3]. The same model, however, completely fails to fit the data in Fig. 3b because of the peak around 0.15 T. Since the peak structure seems to be more pronounced than that in Fig. 2, which was predicted for a specific case, we adopt a phenomenological model in which $C_B(\omega)$ is represented by the sum of a Lorentzian spectrum and a Gaussian peak. A fitting analysis with this model yields a fitted peak position at 0.16(1) T, corresponding to an energy of 0.11(1) K. This is close to the value of $\Delta_0 \simeq 0.15$ K estimated from the leveling off of the jump frequency and thus provides strong evidence that the peak originates from the energy band structure of the muonium atom in KCl. In other words, this peak structure in the spectral density below 10 mK is a clear signature that the muonium is in the Bloch state. The Lorentzian part is well reproduced by assuming the Bloch state with $\delta_{ex} \sim 1.2$ mT.

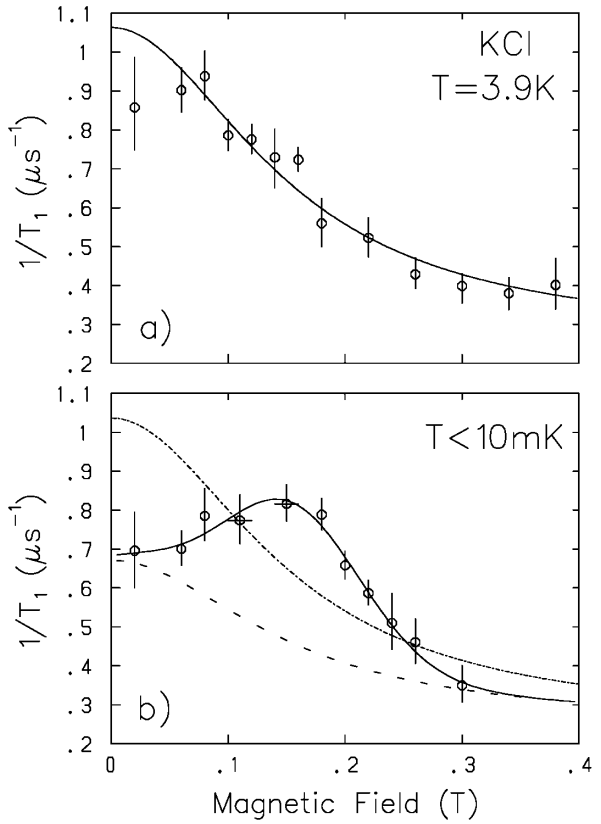

FIG. 3. Muon spin relaxation rate for muonium in KCl (a) at 3.9 K and (b) below 10 mK. For the solid curves, see the text. The dot-dashed curve in (b) is the best fit to a Lorentzian spectrum, whereas the dashed curve is the Lorentzian spectral component fitted in conjunction with a Gaussian peak around 0.15 T to give the solid curve.

The possibility of attributing the observed peak to anisotropic hyperfine structure is ruled out by the field dependence of the initial muon polarization $P_z(t)$. As shown in Fig. 4, the quenching pattern of the initial decay positron asymmetry $A(0)$ is in good agreement with the case of isotropic hyperfine structure with the known value of the muonium hyperfine parameter ($\omega_0 = 2\pi \times 4.28 \times 10^9$ s^{-1}); i.e.,

$$A(t \simeq 0) = A_0 \frac{\frac{1}{2} + x^2}{1 + \frac{\lambda}{\kappa} + x^2}, \qquad (9)$$

where A_0 is the total asymmetry, λ is the spin relaxation rate for the precursor state, κ is the transition rate to the final Mu state, and $x \simeq \gamma_e B/\omega_0$ with B being the applied magnetic field and γ_e the electron gyromagnetic ratio. The small A_0 ($\simeq$0.045) is due to the small fractional yield for muon stopping in the mixture of KCl and Ag

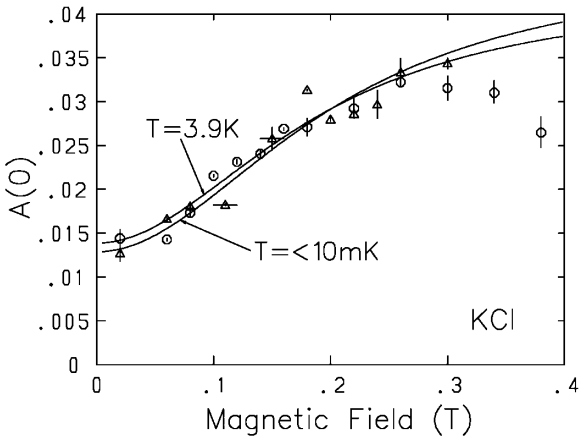

FIG. 4. Initial positron decay asymmetry $A(0)$ versus longitudinal field for muonium in KCl at 3.9 K (circles) and below 10 mK (triangles). Solid curves are results of fitting to Eq. (9) in the text.

powders. A slight complication arises in Eq. (9) due to the presence of an unknown precursor state undergoing fast spin relaxation, leading to loss of initial muon polarization in a time faster than the current minimum time resolution ($dt \geq 10^{-8}$ s). This is a feature commonly observed in alkali halides at low temperatures and is presumably due to fast spin exchange interaction with muon radiolysis products [8]. Equation (9) is valid in such a case, with the subsequent relaxation rate being close to the hyperfine parameter (i.e., $\lambda \sim \omega_0$). However, it seems that this process is terminated within time dt, leaving a virtually unaffected final Mu state for the current time scale of observation: The obtained ratio $\lambda/\kappa \simeq \sim 0.5-0.8$ means that the transition rate to the final state is of the same order of magnitude as ω_0. In any case, it must be stressed that the field dependence of the asymmetry in Eq. (9) is predominantly determined by the hyperfine parameter ω_0 and thereby provides a good measure for ω_0. Since the above model with identical ω_0 for both precursor and final Mu states is in excellent agreement with the data, we can conclude that the Mu hyperfine structure is unchanged and isotropic.

Finally, we discuss the reduction of δ_{ex} from the value seen at higher temperatures ($\simeq$2 mT). As mentioned earlier, this also occurs in the case of Mu in NaCl and may be interpreted by a similar scenario [3]. The important point here is that δ_{ex} reflects not simply the magnitude of the local fields themselves but is rather the parameter used to describe their dispersion {i.e., $= [\langle H(0)^2 \rangle]^{1/2}$}. While this value remains unchanged for localized Mu, it must be reduced by $N^{1/2}$ for a muonium simultaneously probing the local fields at N sites due to the effect of statistical averaging [9,10]. It is reasonable to make the interpretation that the effective value of δ_{ex} is reduced due to the coherence of the Mu wave function developing over multiple sites with decreasing temperature. It should be noted, however, that the position of the peak in the spectral density does not depend on the magnitude of δ_{ex} and thereby the interpretation of current data is hardly affected by the change of this parameter.

The present result demonstrates that one can potentially study the energy band structure of the "polaron band" for a hydrogen isotope in any crystalline solid where one finds stable muonium upon muon implantation. We believe that this will add an important new dimension to the study of atomic centers and point defects in solids.

We thank J. Kondo for illuminating discussions and for showing us his theoretical calculation prior to publication. Thanks are also given to the RIKEN staff for their technical support. This work was partially supported by a Monbusho Grant-in-Aid for Scientific Research on Priority Areas.

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