Magnetic freezeout of electrons into muonium atoms in GaAs

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(Received 6 December 2004; published 16 March 2005)

High-field muon-spin-resonance techniques have been used to study muonium atom formation via electron capture by a positive muon implanted into GaAs with Cr impurities in magnetic fields up to 7 T. The distribution of muon polarization between neutral atoms and charged states is found to depend strongly on magnetic field when the energy of the electron's lowest-order conduction band Landau level becomes comparable to the characteristic binding energy of the electron in a weakly bound muonium atom. This effect is discussed in terms of magnetic freezeout of free electrons into weakly bound muonium states.

DOI: 10.1103/PhysRevB.71.113202 PACS number(s): 72.20.Jv, 36.10.-k, 76.75.+i

Electron localization in disordered systems has been the subject of intense study, particularly in doped semiconductors (see, e.g., Refs. 1 and 2), where localization may occur by formation of shallow bound states on impurities. Since atomic hydrogen (H) is the lightest dopant in semiconductors, its electronic structure and dynamics are of special interest. Nevertheless, very little is known about the isolated H impurity in bulk semiconductors, due to its high mobility and reactivity; most of our accumulated knowledge about H in semiconductors concerns hydrogen-impurity complexes, in which H removes electrically active levels from the band gap.[3] Fortunately the muonium ($\mathrm{Mu}=\mu^+e^-$) atom, a light isotope of H ($m_\mu \simeq m_p/9$), has provided a wealth of information about isolated hydrogen through the experimental techniques of muon-spin rotation, relaxation, and resonance (μSR),[4,5] which can be carried out in the dilute limit of a single muon in the sample at a time, thus avoiding any complications related to impurity-impurity interactions or formation of an impurity band.

An additional mechanism for electron localization is "magnetic freezeout" from the conduction band when strong magnetic fields act on shallow (hydrogenlike) impurity states. Unfortunately, for comparable Coulomb and magnetic interactions, the behavior of even the hydrogen (or Mu) atom with the simplest form of Hamiltonian remains an unsolved problem, because this Hamiltonian is nonseparable, the Coulomb symmetry being broken by the action of an external magnetic field of different symmetry but similar strength. Due to the absence of an exact solution for this problem, certain approximations have been made at low and high magnetic fields; thus the correspondence of energy states between the low-field and high-field limits has attracted considerable attention. For strictly two-dimensional systems, the situation is much simpler due to the removal of one degree of freedom. In this case the correspondence can be established with no ambiguity.[6] Magneto-optical investigations of impurities in quantum wells (at either the center or the edge of the well) show that the presence of a magnetic field enhances their binding energy.[7] However, as in other cases of "man-made" quantum structures, the geometry of a given situation is decisive for its behavior: in three dimensions, the assigned correspondence between low-field and high-field limits of excited states shows an apparent discrepancy with experimental results.[8]

It has been suggested that in bulk semiconductors the presence of an external magnetic field also enhances the binding energy U of the impurity atom.[9] This effect can be understood in terms of competition between the Coulomb energy and the magnetic energy. The Rydberg energy of a hydrogenic atom with an effective electron mass m^* and a screened nuclear charge e/ϵ (ϵ being the dielectric constant) is

$$R_y = \frac{m^* e^4}{2\hbar^2 \epsilon^2}. \tag{1}$$

The strength of a magnetic field H, on the other hand, can be characterized by the shift of the band edge due to the field, i.e., the zero-point energy of the lowest Landau level, given by (neglecting electron spin)

$$\frac{1}{2}\hbar\omega_c = \frac{e\hbar}{2m^* c} H. \tag{2}$$

The comparison of Eqs. (1) and (2) can also be interpreted in terms of the two kinds of orbital radius, i.e., the effective Bohr radius

$$a^* = \frac{\hbar^2 \epsilon}{m^* e^2} \tag{3}$$

and the cyclotron radius

$$\ell = \left(\frac{\hbar c}{eH}\right)^{1/2}. \tag{4}$$

Yafet *et al.*[9] showed that when the magnetic field is strong enough that $\frac{1}{2}\hbar\omega_c$ is comparable to or larger than R_y, a considerable compression of the electronic wave function of the atomic state occurs because its orbital radius tends to decrease in accordance with Eq. (4) as the field is increased. This shrinkage of the wave function in turn causes a stronger binding of the electron by the attractive Coulomb potential, and thus results in an increase of the binding energy. This effect can be observed as a decrease in the number of free carriers as they are "frozen out" of the lowest-order conduction band Landau level into localized states with a binding energy U that increases with magnetic field.

In bulk semiconductors, electron localization is typically studied using "electrical" techniques such as measurements of magnetoresistance or Hall coefficient (see, e.g., Ref. 1). For example, in InSb an increase of the Hall coefficient at low temperature and high magnetic field[10] was interpreted in terms of the magnetic freezeout effect.[9] In these experiments, however, the conclusion of electron localization is based indirectly on measuring properties of the remaining delocalized electrons available for conduction.

Processes of muonium atom formation, on the other hand, offer a direct way to study localization of the electron through its capture by a positive muon. In a μ^+SR experiment one accumulates $\sim 10^7$ individual $\mu^+ \to e^+ \nu_e \overline{\nu_\mu}$ events into a time spectrum that reveals the evolution of the spin polarization of positive muons stopped in the sample. Each incoming 4 MeV muon leaves behind an ionization track of excess electrons and ions liberated during the μ^+ thermalization process. Experiments in insulating[11–13] and semiconducting[14–17] media have shown that the last few ionization track products are initially about 10^{-6}–10^{-5} cm from the thermalized muon. Thus some of the excess electrons generated in the end of the μ^+ track may reach the thermalized muon and form a muonium atom, if they are mobile enough.

The above mechanism of delayed muonium formation (DMF) should be distinguished from prompt muonium formation, which may take place at epithermal energies. The essential difference is that in the former, the electrons start out spatially separated from the thermalized muon, while in the latter one assumes direct electron capture into an atomic state whose size is on the order of the Bohr radius. This difference is essential for distinguishing experimentally between delayed and prompt Mu formation by applying external electric fields:[14–17] relatively weak external electric fields ($\sim$10–100 kV/cm) are sufficient to overcome a long-range muon-electron Coulomb attraction and thus reduce (or even eliminate) the possibility of DMF, whereas electric fields of atomic scale ($\sim 10^6$ kV/cm—the electric field of a point charge at a distance comparable to the Bohr radius) would be required to affect prompt Mu formation.

The process of DMF may be treated as capture of excess electrons by an attractive center. This capture, however, does not occur directly into a highly localized deep state. The "giant" capture cross sections (up to 10^{-12} cm^2) observed for a wide variety of Coulomb attractive centers in semiconductors at low temperatures are found to be several orders of magnitude higher than the geometrical cross sections for electrons localized at the center. It is now well established[18] that instead of being captured directly into the ground state, the electron is initially captured into one of the highly excited states with much larger radii, and then cascades down. In semiconductors with low electron effective mass and high dielectric constant, an electron and a positively charged center can form a hydrogenlike weakly bound state with macroscopic-sized orbits. In GaAs, the binding energy of such a shallow donor (in the $n=1$ state) is $U \approx 7$ meV while its characteristic radius is $a \approx 8 \times 10^{-7}$ cm.[19] Since, within the effective mass model of a shallow donor, any positively charged impurity can have the same series of weakly bound hydrogenic states, the initial capture may be into one of these states rather than into a deep (ground) state. In DMF, therefore, as the electron approaches the stopped muon its initial capture is expected to be into an excited electronic state rather than into the ground state.

In this Brief Report we present the results of our study of magnetic freezeout of electrons into weakly bound muonium states in GaAs in magnetic fields up to 7 T.

Time-differential μSR experiments were performed on the M15 surface muon channel at TRIUMF using the "HiTime" apparatus with a nominal time resolution of 48.8×10^{-12} s. (The actual time resolution is $\sim$150 ps.) We used a Cr-doped GaAs wafer with its (100) axis parallel to the muon beam and perpendicular to the magnetic field.

With the magnetic field $\boldsymbol{H}$ applied perpendicular to the initial muon-spin polarization, two classes of muon states—diamagnetic (charged, usually a "bare" μ^+) and paramagnetic (neutral, usually a Mu atom)—can easily be distinguished by their distinctive precession signals. In vacuum, a Mu atom precesses in very weak ($H \sim 0.01$ mT) transverse magnetic field at a characteristic triplet muonium Larmor frequency $\nu_{\rm Mu} \approx -103\ \nu_\mu$, where $\nu_\mu = (\gamma_\mu / 2\pi) B$ is the Larmor frequency of a muon in a diamagnetic environment and $\gamma_\mu = 2\pi \times 135.538\,79$ MHz/T is the muon magnetogyric ratio. At higher magnetic fields, Mu precession in vacuum splits into two lines, their separation determined by the muon-electron hyperfine interaction frequency $A_0 = 4463$ MHz.

In semiconductors, different muonium states are observed with weaker hyperfine interactions than that for Mu in vacuum.[5] In GaAs two such centers are well studied: $\rm Mu_T$ with an isotropic hyperfine interaction about half that of a free Mu atom, located at the tetrahedral interstitial site, and $\rm Mu_{BC}$ or bond-centered muonium with a smaller ($\sim A_0/50$) and highly anisotropic hyperfine interaction. Both these Mu states are very strongly bound compared with the canonical shallow donor state. In Si and GaAs, formation of $\rm Mu_T$ is not affected by electric fields of up to 10^4 V/cm,[14,15] which implies that tetrahedral Mu may be formed epithermally. In contrast, an electric field of $\sim 10^4$ V/cm is sufficient to prohibit $\rm Mu_{BC}$ formation in GaAs, as expected for suppression of a shallow donor state in GaAs.[15] One may conclude that formation of the $\rm Mu_{BC}$ ground state in GaAs proceeds through a weakly bound intermediate state.

At low temperature, virtually no diamagnetic fraction is formed upon muon implantation in semi-insulating GaAs, the entire muon polarization being distributed with almost equal probability between $\rm Mu_{BC}$ and $\rm Mu_T$ states within $\sim$100 ps. Thus the magnetic freezeout effect, which should show up as a decrease in the diamagnetic fraction with a corresponding increase of the $\rm Mu_{BC}$ fraction, cannot be stud-

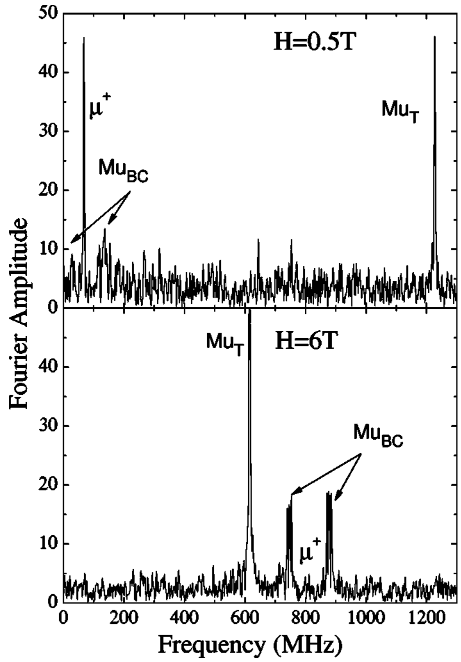

FIG. 1. Fourier amplitudes of muon and muonium signals in GaAs with $n=5\times10^{16}$ cm^{-3} concentration of Cr impurities at $T=15$ K in magnetic fields 0.5 (top) and 6 T (bottom). The high-frequency Mu_T line is also observed at 0.5 T, but is not shown here.

ied at low T. (The Mu_T state is not expected to be affected by magnetic fields much lower than the atomic scale, $H_a \approx 2.2\times10^5$ T, since it is thought to be formed epithermally.) Magnetic freezeout could be studied in semi-insulating GaAs at higher temperatures (about 200 K) where Mu_{BC} starts to disappear, leaving a diamagnetic μ^+ fraction; however, at such high temperatures $\mu^+ \leftrightarrow$Mu dynamics become complicated, involving apparent interconversions between different muon and muonium states.[20] Moreover, thermal activation of the various impurities inevitably present in any sample becomes significant at high temperature. We therefore restrict our studies to low temperature and use instead a GaAs sample with a concentration $n=5\times10^{16}$ cm^{-3} of Cr impurities. At this concentration, Cr impurities scatter or capture electrons from the muon's track, preventing DMF for some muons and restoring a modest diamagnetic fraction.[15] One can then monitor the effect of magnetic field on both diamagnetic and muonium signals in a rather "clean" situation: since electrons captured by Cr impurities are very strongly bound [their energy level is located exactly in the middle of the gap in GaAs (Ref. 21)], at low temperature neither intrinsic carriers nor shallow donor states[19,21] ($U\sim7$ meV) are present in significant numbers. What remains are free conduction band electrons liberated in the muon's track, which can be captured by the muon, initially into a series of weakly bound hydrogenlike energy levels of muonium.[16]

Figure 1 presents Fourier transforms showing diamagnetic (μ^+) and paramagnetic (Mu_{BC} and Mu_T) signals in GaAs in transverse magnetic fields of 0.5 and 6 T. The diamagnetic amplitude is dramatically reduced at higher magnetic field, with a corresponding increase of Mu_{BC} amplitudes. The actual amplitudes of high-frequency signals are higher than they appear in Fig. 1, because of the finite time resolution of the spectrometer. This instrumental effect is corrected by normalization of GaAs signals to the μ^+ amplitude in Ag.

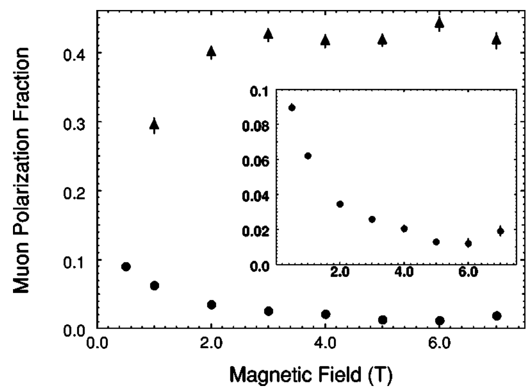

FIG. 2. Magnetic field dependence of the diamagnetic (circles) and Mu_{BC} (triangles) fractions in GaAs at $T=15$ K. Signal amplitudes are normalized to that in Ag at the same frequency. The inset shows the diamagnetic fraction on an expanded scale.

Figure 2 presents the magnetic field dependence of the diamagnetic and net Mu_{BC} asymmetries (amplitudes) in GaAs at $T=15$ K. One might suspect that the decrease of the diamagnetic fraction with field could be a result of dephasing: if Mu_{BC} atoms were to ionize after a mean lifetime τ, the subsequent μ^+ precession would have apparent initial phases spread over $\delta\phi \sim 2\pi\ \delta\nu\ \tau$, where $\delta\nu$ is the difference in precession frequencies of Mu_{BC} and the "bare" μ^+. This could explain a reduction of the diamagnetic polarization in low magnetic field. However, in fields of 0.5 T or higher ($\gamma_\mu B \gg 2\pi A_{BC}$) the Mu_{BC} frequencies are positioned symmetrically about the diamagnetic signal[5] $\left(\nu_{Mu_{BC}} \approx \nu_\mu \pm \frac{1}{2}A_{BC}\right)$, where A_{BC} is the hyperfine frequency of Mu_{BC}. Thus for all the fields shown in Fig. 2, the difference in precession frequencies $\delta\nu$ is independent of magnetic field and any dephasing associated with a Mu_{BC} precursor state cannot explain the reduction of the diamagnetic polarization at high magnetic field. Moreover, we do not expect ionization of the strongly bound Mu_{BC} center at temperatures as low as 15 K. In any case, a corresponding increase of the Mu_{BC} fraction with magnetic field is inconsistent with thermal ionization of that state.

This effect may, however, be explained by magnetic freezeout of free electrons into muonium atomic states when the characteristic energy of the lowest-order conduction band Landau level becomes comparable to the binding energy of the "shallow" muonium atom. Within the hydrogenic model, an estimate of the magnetic field required for $\frac{1}{2}\hbar\omega_c$ to match R_y for the $n=1$ state of the weakly bound muonium atom in GaAs yields

$$H_0 = \frac{e^3 m^* c}{\hbar \epsilon^2} = \frac{(m^*/m)^2}{\epsilon^2} H_a \approx 6.7\ \text{T}, \qquad (5)$$

where $\epsilon=12.9$ and $m^*=0.067m$. This value of H_0 is characteristic of the $n=1$ shallow donor state in GaAs;[22] in Fig. 2 the magnetic field required to begin reducing the diamagnetic fraction and enhancing the Mu_{BC} fraction appears to be about an order of magnitude smaller. However, in delayed muonium formation it is expected that the electron is captured initially into an excited electronic state, with binding energy $\sim kT$,[18] which in our case is about five times smaller than that given by Eq. (1). Accordingly [see Eq. (2)] the onset of the magnetic freezeout is seen at magnetic fields about five times lower than H_0.

Note that even H_0 is about five orders of magnitude smaller than H_a, the magnetic field required to affect the ground state of a muonium or hydrogen atom in the same manner. Therefore we suggest that it is not the ground Mu_{BC} state which is affected by the magnetic field but rather its weakly bound muonium precursor state. An increase of the probability of electron capture into this precursor state in high magnetic field causes an increase of Mu_{BC} fraction.

In conclusion, we have used a high-field μSR technique to detect magnetic freezeout of free electrons into atomic energy levels of a weakly bound muonium atom which is the "gateway state" for the deeply bound Mu_{BC} center.

This work was supported by the Canadian Institute for Advanced Research, the Natural Sciences and Engineering Research Council of Canada, the U.S. National Science Foundation Grant No. (DMR-0102862), and the Royal Society of London. We acknowledge discussion with R. F. Kiefl.

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