# Influence of Impurities on Short Range Electron Transport in GaAs

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The influence of Cr impurities on muonium atom formation in GaAs has been studied using muon spin relaxation techniques with alternating electric fields. The results suggest that electron transport to and capture by the muon is suppressed by capture/scattering on intervening Cr centers. The length scale involved is estimated to be about $3 \times 10^{-6}$ cm. This offers an opportunity to study electron transport to positive centers in semiconductors on a microscopic scale.

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The electronic structure and dynamics of isolated atomic hydrogen (H) in semiconductors is of fundamental interest since it is the simplest and the lightest interstitial impurity. Hydrogen impurities in semiconductors are also of considerable technological interest because atomic hydrogen can very effectively "passivate" the electrical activity of shallow donors and acceptors [1] and thus dramatically alter the electrical and optical properties of the host.

Unfortunately, direct information on isolated hydrogen is extremely limited due to its high mobility and reactivity. Most of the experimental information on hydrogen atoms comes indirectly from studies of the muonium ($\mathrm{Mu} = \mu^+ e^-$) atom. Muonium has a reduced mass almost the same as that of H, so its atomic states and chemical interactions are literally those of a light hydrogen isotope ($m_\mu \simeq m_p/9$). The behavior of muonium can be followed through the parity-violating radioactive decay of muons in muon spin rotation/relaxation/resonance ($\mu$SR) techniques [2].

When employing muonium as a light hydrogen isotope, however, one should always bear in mind that hydrogen and muonium are introduced into a semiconductor in very different ways. Hydrogen is incorporated during the process of sample preparation and reaches thermal and chemical equilibrium long before measurements start, whereas muonium is observed starting a few nanoseconds after the injection of energetic (about 4 MeV) muons into the sample and only those states reached on the microsecond time scale of the muon lifetime can be studied [2]. As the energetic $\mu^+$ is slowed to an energy of a few tens of keV, inelastic muon scattering involves mainly the production of atomic excitations and ionizations. At lower energies, collective excitations and charge exchange become important. In insulators and semiconductors the positive muon can pick up an electron to form an isolated hydrogenlike muonium atom; generally the $\mu^+$ undergoes many cycles of electron capture and subsequent electron loss. If the last such collision leaves atomic Mu in its neutral charge state, muonium is said to have been formed *promptly*. If the $\mu^+$ thermalizes as a positive ion, leaving behind an ionization track of liberated electrons and ions, in many materials there is a high probability that some of the excess electrons generated in this track can reach the stopped muon and form muonium within the time range of a $\mu^+$SR experiment, which is set by a few times the muon lifetime ($\tau_\mu = 2.197 \times 10^{-6}$ s) [3]. This process of *delayed* muonium formation (DMF) is crucially dependent on the electron's interaction with its environment and especially on the electron mobility. The characteristic length scale of DMF is less than $10^{-4}$ cm [3]. This situation presents a unique opportunity for the study of electron transport to positive centers on a microscopic scale.

Studies of electron transport in semiconductors are of considerable theoretical and practical interest. Many solid state electronic devices are based on the effect of external electric fields on the carriers. Most of the experimental information on electron transport in semiconductors comes from measurements of the electrical current and conductivity. The macroscopic scale of these experiments inevitably involves electron interactions with various impurities present in the sample, even if these impurities are very dilute. In time-differential $\mu$SR experiments muons are implanted into the sample one at a time. This, along with the microscopic length scale for DMF, allows the study of electron transport to an isolated positive impurity in the "pure" crystal.

An essential feature of DMF is that the muon stops some distance from the free electrons created in its track; this property is the key to distinguishing experimentally between *delayed* and *prompt* muonium formation by applying external electric fields [4–6]. Relatively weak external electric fields ( $\sim 10^4$ V/cm) can sometimes overcome the muon-electron Coulomb attraction and thus reduce the probability of DMF, whereas electric fields of atomic strength ( $\sim 10^9$ V/cm) would be required to affect epithermal muonium formation.

In most semiconductors two quite different types of muonium centers coexist with the diamagnetic state (or states) of the muon [7,8]. These centers are characterized by their different muon-electron hyperfine interactions. So-called "normal" muonium has an isotropic hyperfine interaction with a hyperfine coupling about half as strong as that in the free muonium atom and is located at the tetrahedral interstitial site; it is therefore denoted $\mathrm{Mu}_{\mathrm{T}}^0$. "Anomalous" or "bond-centered" muonium, with a small anisotropic hyperfine interaction, is located near the center of the relaxed crystal bond and is thus denoted $\mathrm{Mu}_{\mathrm{BC}}^0$.

Recent experiments with semi-insulating GaAs [9] have shown complete suppression of the $\mathrm{Mu}_{\mathrm{BC}}^0$ signal by an electric field. This fact is illustrated in Fig. 1. One can see a large multifrequency muonium signal for $E = 0$; this beating is completely absent in electric field $E = 20$ kV/cm.

There are two possible explanations for the suppression of the $\mathrm{Mu}_{\mathrm{BC}}^0$ signal by an external electric field. The first is electrostatic ionization of an otherwise bound muonium center. Alternatively, the external electric field may prevent transport of the initially distant electron to the muon. The latter DMF mechanism has been observed in many insulators [3].

The characteristic electric field ($E_{\mathrm{char}}$) required to appreciably change the muonium formation probability is measured to be about 5 kV/cm in semi-insulating GaAs [9]. To ionize ground-state $\mathrm{Mu}_{\mathrm{BC}}^0$ muonium, atomic-scale electric fields ( $\sim 10^9$ V/cm) would be required. On the other hand, due to the large dielectric constant and a very small electron effective mass in the $\Gamma$ valley ($m^* \sim 0.07 m_e$), in GaAs a positive ion and a light electron can form a *very* weakly bound ($U = -7 \times 10^{-3}$ eV) and macroscopic-sized ($a_0 = 8.3 \times 10^{-7}$ cm) *shallow-donor-like* state [10]. The electric field $E_i$ required to ionize this state can be estimated by equating the bias across the orbit, $2eE_i a_0$, to the binding energy [11]. This rough estimate gives $E_i \sim 5$ kV/cm, in good agreement with the $E_{\mathrm{char}}$ observed experimentally. Electric fields of this magnitude are known to shorten the exciton lifetime in GaAs [12]. Thus the model of electrostatic ionization is compatible with ionization from this shallow state.

In the alternative model one envisions initially "distant" free electrons moving under the influence of the muon's Coulomb field plus a constant external electric field to (re)combine with the muon or with parent positive ions. At low temperature, where the electron mobility is very high, this motion is closer to ballistic than to classical viscous flow. From the characteristic field one can estimate the typical length scale of the interaction: $R_{\mathrm{char}} \sim \sqrt{e/(\epsilon E_{\mathrm{char}})} \sim 10^{-6}$ cm, where $\epsilon = 11.6$ is the dielectric constant of GaAs. On the other hand, the mean free path of a band electron in GaAs at 50 K is estimated to be $\ell = (b/e)\sqrt{3k_{\mathrm{B}}Tm^*} \sim 6 \times 10^{-6}$ cm (where $b \sim 1\text{–}2 \times 10^4\ \mathrm{cm}^2/\mathrm{V\,s}$ is the electron mobility), which is greater than $R_{\mathrm{char}}$. From this estimate it is clear that even if an electron starts far from the muon, under the process of recombination it will eventually form (or at least pass through) the macroscopic-sized state mentioned above. An external electric field will bias the potential shape. In a weak external electric field, the electron "falls to the muon" *via* the shallow state. If the external electric field is higher than $E_i$, the shallow bound state never forms (and so neither does any deeper state) and the electron escapes. Thus, in this model, an electric field of about $E_i$ will prevent muonium formation with initially well-separated track electrons.

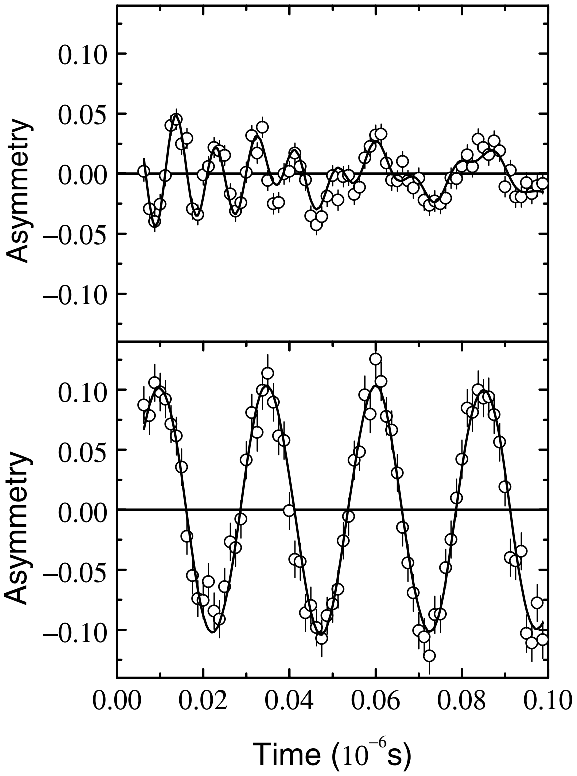

FIG. 1. Experimental $\mu$SR spectra in intrinsic GaAs at $T = 10$ K in a transverse magnetic field $B = 3$ kG. Top panel: zero electric field. The theoretical curve is the sum of several muonium frequencies plus a small diamagnetic signal. Bottom panel: external electric field $E = 20$ kV/cm. Only the diamagnetic signal is present.

In any case, experiments [9] suggest that $\mathrm{Mu}_{\mathrm{BC}}^0$ in GaAs is formed through an intermediate shallow state.

The same idea of an intermediate shallow state was proposed for muonium formation in CdS from measurements of its precession frequency shift due to atomic diamagnetism [13]. The question of whether this shallow state is formed *via* electron transport to the muon remains open.

In this Letter we report direct evidence that formation of the $\mathrm{Mu}^0_{\mathrm{BC}}$ muonium center in GaAs proceeds *via* transport of initially separated (by distances of more than $3 \times 10^{-6}$ cm) excess electrons to the muon. To demonstrate this we carried out experiments in GaAs samples with Cr impurities. The idea of the experiment was to place an impurity between the electron and the muon and thus influence electron transport to the muon.

Time-differential $\mu$SR experiments were performed on the M20 surface muon channel at TRIUMF. We tested two samples: GaAs with $n_{\mathrm{Cr}} < 5 \times 10^{15}$ cm$^{-3}$ and a sample with a chromium concentration of $n_{\mathrm{Cr}} = 3 \times 10^{16}$ cm$^{-3}$. Both samples were grown by the Czochralski technique with appropriate doping. The resulting Cr concentration was determined by mass spectrometry. The samples were oriented with their (100) symmetry axis parallel to the muon beam. Both surfaces of each sample were covered with vapor-deposited silver electrodes to a thickness of a few nm. Experimental data were obtained using a newly developed technique of $\mu$SR measurements in frequently switched external electric fields. We use this technique to avoid accumulation of space charge near the sample surfaces [9].

From experiments in high transverse magnetic field [9] it is known that the decrease of the $\mathrm{Mu}^0_{\mathrm{BC}}$ amplitude with electric field is accompanied by a corresponding increase of the diamagnetic amplitude. This fact is illustrated at the top of Fig. 2.

New experiments were performed in a weak transverse magnetic field of 100 G. At that field the $\mathrm{Mu}^0_{\mathrm{BC}}$ signal relaxes too fast to be observed and the $\mathrm{Mu}^0_{\mathrm{T}}$ frequencies are too high for the finite time resolution of the spectrometer; thus the only observable signal is the diamagnetic one. Therefore the experimental asymmetry [2] was fitted to a single diamagnetic signal:

$$A_0 P(t) = A_D \exp(-\lambda_D t) \cos(\omega_\mu t + \varphi_D), \tag{1}$$

where $A_0$ is a normalization factor (the maximum muon decay asymmetry); $A_D$, $\lambda_D$, $\omega_\mu$, and $\varphi_D$ are the diamagnetic asymmetry, relaxation rate, frequency, and the initial phase, respectively. Bearing in mind the results in the high magnetic field (see top of Fig. 2), experiments in the weak magnetic field give complete information about $\mathrm{Mu}^0_{\mathrm{BC}}$ formation.

The electric field dependences of the diamagnetic amplitudes in GaAs samples with Cr impurities at $T = 50$ K are shown at the bottom of Fig. 2. The maximum electric field of ±25 kV/cm was limited by electric breakdown of the sample. Although the two data sets are at different temperatures and are taken with a different $E$-field switching period, they are directly comparable: experimental checks show the diamagnetic amplitude to be independent of both temperature (up to above 50 K) and switching period (up to 10 s). One can notice a clear difference between the two samples at low electric fields ($|E| < 10$ kV/cm), whereas at high fields the data practically coincide. A possible explanation of the different low field behavior in the dirty sample could be the following. The initial spatial distribution of track products is not likely to depend on such a dilute concentration of impurities. The characteristic distance between Cr centers in the dirty sample is $R_{\mathrm{Cr}} = n_{\mathrm{Cr}}^{-1/3} \sim 3 \times 10^{-6}$ cm. This is larger than the radius $a_0 = 8.3 \times 10^{-7}$ cm of the shallow state. Therefore, in the dirty sample Cr impurities can scatter or even capture track electrons which were initially located further than $R_{\mathrm{Cr}}$ from the stopped muon, and the probability of muonium formation will be less than in the pure crystal.

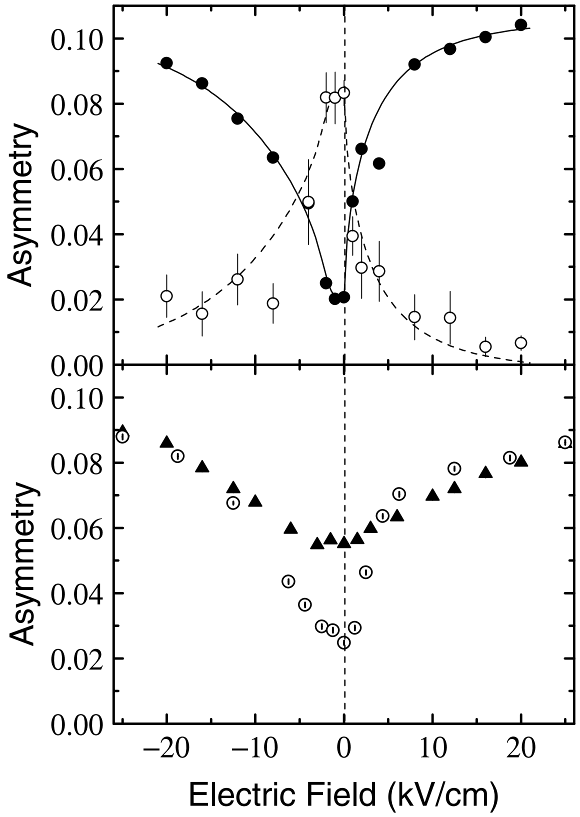

FIG. 2. Top panel: electric field dependence of the diamagnetic asymmetry (filled circles) and the sum of $\mathrm{Mu}^0_{\mathrm{BC}}$ asymmetries (open circles) in GaAs at $T = 10$ K. Positive electric field is in the direction of the initial muon beam momentum. The half-period of the alternating electric field is 0.005 s. The lines are to guide the eye. Bottom panel: electric field dependence of the diamagnetic asymmetries at $T = 50$ K in GaAs with $n_{\mathrm{Cr}} < 5 \times 10^{15}$ cm$^{-3}$ (circles) and $n_{\mathrm{Cr}} = 3 \times 10^{16}$ cm$^{-3}$ (triangles). The half-period of the alternating field is 5 s.

On the other hand, electric fields higher than $E_i \sim 5$ kV/cm will prevent the electron from reaching the muon regardless of the presence of impurities, and the probability of muonium formation will be almost the same in any sample of GaAs.

The electric field dependence in the pure sample is almost the same as that measured in the semi-insulating sample (see Fig. 2). This fact implies that the process of muonium formation is independent of impurity concentration up to some level (about $10^{15}$ cm$^{-3}$).

The results obtained suggest a multielectron character of the muon track. Otherwise, if there were only a single electron near the muon, the significant influence of such dilute Cr impurities on muonium formation would lead to the inequality $R_e > R_{\mathrm{Cr}}$, where $R_e$ is the initial distance between the muon and the electron in the framework of a single electron model. Then $R_e \gg a_0$ and one should expect the influence of the external electric field to be significant at fields $e/\epsilon R_e^2 < 0.5$ kV/cm. This value is an order of magnitude less than the experimentally observed $E_{\mathrm{char}} = 5$ kV/cm. The reason for proposing a multielectron track and a detailed discussion of its structure can be found in [14].

The mechanism described is in qualitative agreement with the early work of the Zürich group [7]. In that study, high resistivity GaAs was irradiated with fast neutrons to a dose of $8 \times 10^{15}$ cm$^{-2}$. Such a dose creates approximately $1.5 \times 10^{17}$ cm$^{-3}$ antisite defects (As replacing Ga) [15]. This irradiation left the $\mathrm{Mu}_{\mathrm{T}}^0$ muonium signals unchanged but destroyed the $\mathrm{Mu}_{\mathrm{BC}}^0$ muonium state, transferring its polarization to the diamagnetic state. Annealing at 900 K restored both asymmetries to their unirradiated values. It was proposed that the antisite As defect could inhibit the formation of $\mathrm{Mu}_{\mathrm{BC}}^0$ by restricting the supply of electrons to the stopped muon. Note that the concentration of impurities in that experiment was close to the value $a_0^{-3} \sim 10^{18}$ cm$^{-3}$ needed to completely suppress transport of track electrons to the muon.

In conclusion, we have used the technique of muon spin rotation in alternating electric fields to study the influence of Cr impurities on the excess electron transport to muon centers in GaAs. Our results suggest that muonium formation proceeds *via* electron delivery to the stopped muon. This phenomenon allowed us to study electron transport in a semiconductor on the microscopic scale—another application of muonium as a unique and sensitive probe in condensed matter science. Just after muon implantation into the sample, the muon and its track electrons are separated by distances of more than $R_{\mathrm{char}} \sim 3 \times 10^{-6}$ cm. Under the influence of Coulomb attraction, track electrons approach the muon and/or their parent positive ions. For Cr concentrations of about $n_{\mathrm{Cr}} \sim 10^{16}$ cm$^{-3}$ or greater, electrons can be captured/scattered by Cr impurities on their way to the muon. Those electrons which avoid scattering by Cr impurities may form a short lived shallow muonium state with radius $a_0 \sim 10^{-6}$ cm—the precursor of the ground state of $\mathrm{Mu}_{\mathrm{BC}}^0$. External electric fields higher than $E_i \sim 5$ kV/cm prevent formation of this shallow state, thus diminishing the probability of $\mathrm{Mu}_{\mathrm{BC}}^0$ formation.

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