Formation and dynamics of muonium centres in semiconductors—a new approach

2004 J. Phys.: Condens. Matter 16 S4761

(http://iopscience.iop.org/0953-8984/16/40/018)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) S4761–S4778 PII: S0953-8984(04)84861-6

Formation and dynamics of muonium centres in semiconductors—a new approach

Vyacheslav G Storchak[1,4], **Dmitry G Eshchenko**[2] **and Jess H Brewer**[3]

[1] Kurchatov Institute, Kurchatov Square, 1 Moscow 123182, Russia
[2] Physik-Institut der Universität Zürich, CH-8057 Zürich, Switzerland
[3] Canadian Institute for Advanced Research and Department of Physics and Astronomy, University of British Columbia, Vancouver, BC, V6T 1Z1, Canada

E-mail: storchak@stor.polyn.kiae.su

Received 27 January 2004
Published 24 September 2004
Online at stacks.iop.org/JPhysCM/16/S4761
doi:10.1088/0953-8984/16/40/018

Abstract

Various processes of muonium atom formation in semiconductors via electron capture by a positive muon have been studied using μSR techniques, including those with applied electric field. Experiments in GaAs, GaP and CdS suggest that the electron is initially captured into a highly excited state, from which the cascade down to the muonium ground state goes through an intermediate weakly bound state determined by the electron effective mass and the dielectric constant of the host. The electronic structure of this weakly bound state is shown to be hydrogenic. The nature of the final (on the μSR timescale) muonium state depends on the energy releasing mechanisms in the cascade process. We suggest that muonium dynamics in semiconductors (including the effects of electric and magnetic fields and temperature) reflect the electron dynamics in weakly bound muonium state(s) in which the electron is delocalized over distances of about 100 Å.

1. Introduction

Any process of recombination in semiconductors requires the transfer of a huge amount of energy—approximately the band gap—to some type(s) of crystal excitations. The question is, which excitations? Releasing this energy into the phonon subsystem is strongly suppressed, as it requires simultaneous emission of an enormous number of phonons. Therefore any subdivision of the recombination energy into smaller steps—e.g. via an intermediate state in the gap—increases the probability of recombination significantly. Energy levels associated with dopants and defects may thus assist in the formation of shallow centres; however, phonons cannot readily absorb enough energy for the formation of deep centres.

[4] Author to whom any correspondence should be addressed.

The pioneering work of Shockley and Read [1] and Hall [2] in the early 1950s suggested that the recombination of electrons and holes in solids could best be understood in terms of the mutual capture of an electron and a hole at a localization site ('recombination centre') in the crystal. The first step—electron capture by an attractive centre ('trapping centre')—is an important process on its own. The distinction between a trap and a recombination centre is a quantitative rather than a qualitative one. For the sake of definiteness the following picture is accepted: an electron is captured at a centre; if the electron stays for some mean lifetime in the captured state and is then ejected (e.g. thermally), the centre is regarded as a *trap*. If, however, a hole is trapped at the same centre before thermal ejection of the electron can occur, recombination will take place and the centre may be regarded as a *recombination centre*. Indeed it was found [3] that Cu and Ni impurities in germanium behave as recombination centres at room temperature, whereas at lower temperatures Cu behaves as a trap [4].

In μ^+SR experiments one accumulates individual $\mu^+ \rightarrow e^+\nu_e\bar{\nu}_\mu$ decay events into a time spectrum that reveals the time-dependent spin polarization of positive muons stopped in the sample. Each incoming 4 MeV muon creates an ionization track of excess electrons and ions liberated during the μ^+ thermalization process. Experiments in insulating [5–9] and semiconducting media (Si [10], GaAs [11, 12], GaP [13] and CdS [14]) have shown that the ionization track products are very close to the thermalized muon. (The characteristic distance is about 10^{-6}–10^{-5} cm.) Some of the excess electrons generated in the end of the μ^+ track are mobile enough to reach and be *captured* by the thermalized muon to form a muonium ($Mu = \mu^+e^-$) atom. This process of '*delayed*' muonium formation (DMF) [15] may be treated as trapping of excess electrons by an attractive centre. As an analogue of Cu impurities in germanium, Mu (or a filled trap) is typically found at lower temperatures, while a diamagnetic state (which could be an ionized trap or, alternatively, a recombination centre) is observed at higher temperatures.

The phenomenological description of an impurity as a trap or a recombination centre makes use of the cross section for the capture of an electron or a hole. The 'giant' capture cross sections (up to 10^{-12} cm^2) observed for a wide variety of Coulomb attractive centres in semiconductors at low temperatures by the end of 1950s were puzzling: these cross sections were found to be several orders of magnitude higher than the geometrical cross sections for electrons localized at the centre. Not only was there no explanation for the experimental cross sections, but the energy transfer mechanism was unknown: many of these centres involve binding energies an order of magnitude higher than the Debye energy.

In solving this problem a decisive role was played by the idea of Lax [16, 17] that, instead of being captured directly into the ground state, the electron is captured into one of the highly excited states with much larger radii, and then cascades down. The key point here is that the electron must not only come to the vicinity of the centre, but it must also on arrival perform the unlikely task of depositing perhaps many times the Debye energy, requiring the simultaneous production of many phonons. Whereas multiphonon transitions to the ground state of the trap yield cross sections five to ten orders of magnitude too small [18], capture into excited states with a large radius followed by a cascade of *one-phonon transitions* leads to cross sections of the right order of magnitude [17].

This cascade model correctly predicts the temperature dependence of the 'giant' cross sections. The initial capture involves one phonon and takes place into one of the very excited orbitals. Subsequent collisions may eject the electron or cause it to increase its binding energy. The 'sticking probability', or probability of eventual capture into the ground state, becomes significant for binding energies of order kT. As the temperature is reduced, capture into orbits of larger radius becomes effective and the cross section therefore increases rapidly with decreasing temperature. Using Lax's cascade model, Abakumov and Yassievich [19] found

that the capture cross section for an isolated attractive centre can be expressed as

$$\sigma = \frac{4}{3}\frac{\pi}{\ell_0} r_{\mathrm{T}}^3, \tag{1}$$

where $r_{\mathrm{T}} = e^2/\epsilon kT$ is the characteristic capture radius at temperature T, ϵ is the dielectric constant, $\ell_0 = v\tau_{\mathrm{E}}$, v is the electron's velocity and τ_{E} is its relaxation time in energy space.

Equation (1) has a transparent physical meaning in the framework of the classical paper of Thompson [20]: an electron is captured if (a) it enters a sphere of radius r_{T} about the trap; and (b) it loses its energy. The probability of energy transfer is expressed by a factor r_{T}/ℓ_0. The temperature dependence $\sigma \propto T^{-3}$, as well as the actual cross section values derived from equation (1), are found to be in good agreement with various experimental data on electron capture in Ge and Si into both shallow and deep attractive centres [21–23].

It has been customary to treat the dynamics of muonium centres in semiconductors in terms of the lowest electronic states (or long-lived metastable states) without explicitly considering the details of how these states are initially formed. Only recently have we begun to examine the muonium formation processes in detail with experiments designed to modify the final stages of muon implantation and thermalization. Specifically, we have sought to probe interactions between the muon and the carriers released during its implantation, particularly the initial capture of an electron to form an atomic muonium defect state.

The phenomenon of *delayed* muonium formation (DMF) implies that as the electron approaches the stopped muon it may be captured initially into a highly excited electronic state with mesoscopic-sized orbits. Electron capture by a deep-level impurity is assumed to proceed by capture into an excited electronic state followed by a cascade to the lowest energy level. Since, within the effective mass model, any positively charged impurity can have a series of weakly bound hydrogenic states (WBS), the initial capture may be into one of these states rather than into a deep state. The key point here is that these WBS formed on initial capture should be much more susceptible to effects of temperature, electric or magnetic fields because their binding energy is much less than that of muonium in any deep state.

In this paper we present a number of experimental results and their interpretation using the cascade model, which suggests that the dynamics of muonium centres in semiconductors is to a great extent determined by electron dynamics in WBS. We show that these initial events in the DMF process can no longer be ignored in studies of muonium centres.

2. The weakly bound muonium state in semiconductors

Muonium centres in semiconductors have been studied extensively for more than four decades. The typical justification for these studies comes from the idea that using the muonium atom as a light hydrogen isotope one can model the dynamics of the *isolated* H atom, whose observation is restricted because of its high reactivity. Although the μ^+ is almost an order of magnitude lighter than the proton, it is so much heavier than the electron that the Mu reduced mass is almost the same as that of the hydrogen atom. Therefore, Mu has almost the same ionization potential and electronic structure as the H atom. For this reason muonium may properly be considered a light hydrogen isotope; as such, and with due regard to isotope effects, muonium is expected to provide an experimentally accessible model for hydrogen defect centres in matter.

Early muonium studies considerably modified established views concerning the stable sites and electronic structure of hydrogen in semiconductors such as Si, Ge and GaAs [24]; muonium states were discovered for which the site and local electronic structure differed considerably from those of the expected trapped-atom state. We refer in particular to the so-called anomalous (or bond-centred) muonium state $\mathrm{Mu}_{\mathrm{BC}}^0$ in Si, GaAs etc, now understood

to have a somewhat extended electron distribution associated with a bond-centre site, and a defect energy level that nonetheless lies quite deep in the energy gap; in Si in particular, Mu^0_{BC} is suggested to provide a donor level 210 meV below the conduction band [25].

More recently these studies have moved on from spectroscopy to dynamics, revealing a largely unanticipated interplay of site and charge state suggested to be relevant to the deep-level electrical activity of hydrogen in these materials [26, 27].

Shallow muonium states (with binding energies of about 20 meV) have recently been found [28] in wide gap (notably II–VI) semiconductors. Stretching the analogy between muonium and hydrogen, these results were interpreted as evidence that hydrogen may act as a donor, rather than as a neutralizing centre, in certain materials.

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 a few nanoseconds after the injection of very energetic muons into the sample and only those states reached on the microsecond timescale of the muon lifetime can be studied [29].

As the energetic μ^+ 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 hydrogen-like muonium atom; generally the μ^+ 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 μ^+ 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 μ^+SR experiment, which is set by a few times the muon lifetime ($\tau_\mu = 2.197 \times 10^{-6}$ s) [15]. This process of *delayed* muonium formation (DMF) is crucially dependent on the electron's interaction with its environment and especially on the *electron mobility*. Recent experiments in insulating and semiconducting media [5–14] have led to a major breakthrough in understanding of the muon's interactions with the products of its track—in fact, it is found that these products may determine much of the subsequent behaviour of muonium/muon states in insulators and semiconductors.

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* Mu formation by applying external electric fields [5, 30]. Relatively weak external electric fields ($\sim 10^4$ V cm^{-1}) 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^{-1}) would be required to affect prompt (epithermal) Mu formation.

In most semiconductors two quite different types of muonium centres coexist with the diamagnetic state (or states) of the muon [24]. These centres 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 Mu atom and is located at the tetrahedral interstitial site; it is therefore denoted Mu^0_T. 'Anomalous' or 'bond-centred' muonium, with a small anisotropic hyperfine interaction, is located near the centre of the relaxed crystal bond and is thus denoted Mu^0_{BC}.

Recent experiments with semi-insulating GaAs [11, 12] have shown complete suppression of the Mu^0_{BC} signal by an electric field. This phenomenon is illustrated in figure 1, which shows the electric field dependence of the diamagnetic asymmetry and the sum of Mu^0_{BC} asymmetries in semi-insulating GaAs at 10 K. Both directions of the electric field ($E > 0$ corresponding

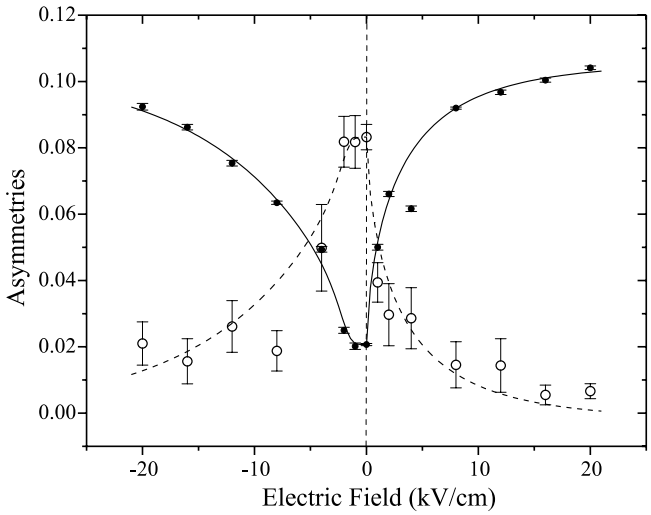

Figure 1. Electric field dependence of the diamagnetic asymmetry (filled circles) and the sum of Mu^0_{BC} asymmetries (open circles) in GaAs at $T = 10$ K.

to the direction parallel to the incoming muon momentum) eventually cause a sharp *decrease* of the Mu^0_{BC} signal accompanied by a corresponding *increase* in the diamagnetic amplitude. The characteristic electric field is estimated to be about $E_{char} \approx 5$ kV cm^{-1}.

In semiconductors, due to the low effective mass of the electron and the high dielectric constant, an electron and a positively charged centre can form a hydrogenic WBS with mesoscopic-sized orbits. In GaAs, the binding energy of a shallow donor state formed by positive ion and a light electron in the Γ-valley is known [31] to amount to $U \approx 7$ meV (the exciton state in GaAs has a similar U [32]) while the characteristic radius of such a state is $a \approx 8 \times 10^{-7}$ cm [31]. The electric field E_i required to ionize this state can be estimated by equating the bias across the orbit, $2eE_ia$, to the binding energy [33]. This rough estimate gives $E_i \sim 5$ kV cm^{-1}, in good agreement with that observed experimentally [11, 12]. To ionize ground-state Mu^0_{BC} muonium, atomic-scale electric fields ($\sim 10^9$ V cm^{-1}) would be required.

At low temperature, where the electron mobility is very high, electron motion is closer to ballistic than to classical viscous flow. From the characteristic field one can estimate the typical length scale of the interaction: $R_{char} \sim \sqrt{e/(\epsilon E_{char})} \sim 10^{-6}$ 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 $\ell = (b/e)\sqrt{3k_BTm^*} \sim 6 \times 10^{-6}$ cm (where $b \sim 1$–2×10^4 cm^2 V^{-1} s^{-1} is the electron mobility), which is greater than R_{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) a mesoscopic-sized shallow quantum state—i.e. the WBS mentioned above.

An external electric field will bias the shape of the Coulomb potential. In a weak external electric field, the electron 'falls to the muon' *through* this WBS. If the external electric field is higher than E_i, the WBS never forms (and so neither does any deeper state) and the electron escapes.

Thus, formation of Mu^0_{BC} in GaAs may be expected to proceed through the intermediate weakly bound Mu state (WBS), a metastable precursor for the final deep state [11, 12].

It is important to recognize that this muonium WBS is *not* the same as any of the previously studied Mu states in semiconductors. This is truly a fascinating observation—the involvement

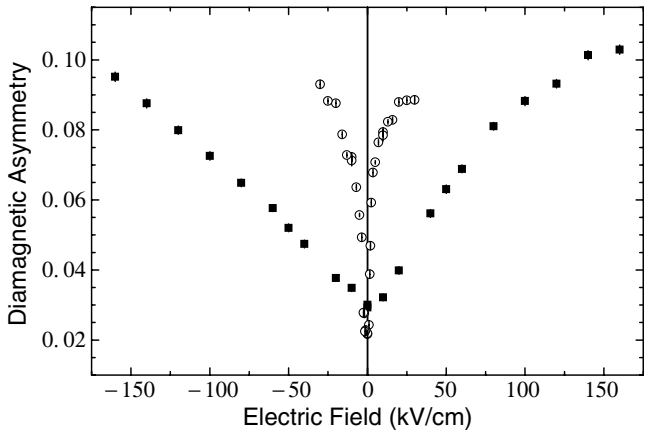

Figure 2. Electric field dependence of the diamagnetic asymmetry in a transverse magnetic field of $B = 51$ G for semi-insulating GaAs (10 K, open circles) and GaP (100 K, filled squares). In both cases the temperature is well below that causing 'ionization' of Mu in zero electric field.

of the WBS may in fact be a general phenomenon governing muonium formation in condensed matter! Electron capture (from the ionization track) by a positive muon into a very excited state, followed by a cascade down through WBS to form a deep-level Mu state, is consistent with Lax's vision of electron capture in solids [17].

In order to understand the mechanism of energy loss in the muonium cascade we must first examine the electronic structure of the WBS.

3. Electronic structure of the weakly bound muonium state

In GaAs, the binding energy derived from the characteristic electric field required to 'ionize' the weakly bound Mu state is the same as for an electron bound to any other positive centre. This binding energy is determined by the electron effective mass and the dielectric constant of the medium.

If the scenario for muonium formation described in section 2 has general validity in solids, the binding energy as well as the characteristic radius of the electron orbit (and therefore the characteristic electric field) of this intermediate weakly bound Mu state formed on initial capture should scale with the electron effective mass and dielectric constant of the host.

Here we present experimental evidence that formation of the final (deep) Mu state in GaP also proceeds through an intermediate Mu WBS [13]. The characteristics of this shallow Mu state are found to be in good agreement with those expected for a hydrogenic atom within the effective mass approximation. Comparing the characteristic fields required to prohibit formation of the muonium ground state in GaAs and GaP demonstrates that they scale with the electron effective mass and dielectric constant of the host very much as expected for initial electron capture into the $n = 1$ orbital of a hydrogenic state associated with a positive muon.

The electric field dependence of the diamagnetic asymmetry in GaP is shown in figure 2, along with that observed in semi-insulating GaAs. Less detailed measurements in GaP at $T = 20$ K give virtually the same electric field dependence as at $T = 100$ K.

The large difference in electric field dependences for GaP and GaAs—the characteristic electric fields differ by an order of magnitude (about 50 kV cm^{-1} in GaP versus about 5 kV cm^{-1} in GaAs)—cannot be attributed to 'ionization' of the final (deep) muonium states.

First, the electric field strength is 4–5 orders of magnitude less than atomic fields. Second, both muonium centres in GaP have hyperfine constants quite close to those for their counterparts in GaAs [34]. Therefore we conclude that it is not 'ionization' of the final Mu state which is observed in either case, but rather field 'ionization' (actually *prevention of formation*) of a weakly bound precursor (WBS) to the deep muonium final state.

We argue further that this muonium WBS is well described within the effective mass approximation of the hydrogenic model commonly used for shallow donors [31]. Specifically, in that model the characteristic electric field for ionization, estimated by equating the bias across the orbit to the binding energy [33], may be expressed as

$$E_{\mathrm{i}} = \frac{1}{4}\frac{e^5}{\hbar^4}\frac{m_*^2}{\epsilon^3} = \left(\frac{m_*}{m}\right)^2 \frac{1}{\epsilon^3} 1.9 \times 10^9 \text{ V cm}^{-1}, \tag{2}$$

where e is the electron charge, and m_* is the effective mass of the electron. The ratio $(m_*/m)^2/\epsilon^3$ makes E_{i} in semiconductors about five orders of magnitude less than atomic-scale electric fields. In the case of GaP with effective electron mass $m_* = 0.17m$ and dielectric constant $\epsilon = 10.7$, the characteristic field is $E_{\mathrm{i}} = 50$ kV cm^{-1}, in very good agreement with the experimental value [13]. Comparison with GaAs ($m_* = 0.067m$ and $\epsilon = 12.9$) where $E_{\mathrm{i}} = 5$ kV cm^{-1} [12] allows us to conclude that the electric field required to 'ionize' this Mu WBS scales with the electron effective mass and the dielectric constant of the host, as expected for a hydrogenic state.

The characteristic radius of the electron orbit within this model,

$$a = \frac{\hbar^2}{e^2}\frac{\epsilon}{m_*} = \frac{m}{m_*}\epsilon a_0, \tag{3}$$

is 0.28×10^{-6} cm in GaP and 0.83×10^{-6} cm in GaAs. These values are about two orders of magnitude larger than the Bohr radius a_0. This fact justifies the use of the hydrogenic model, as both the electron effective mass and the dielectric constant are essentially macroscopic characteristics of the medium.

The binding energy of such a WBS,

$$U = \frac{e^4}{2\hbar^2}\frac{m_*}{\epsilon^2} = \frac{m_*}{m}\frac{1}{\epsilon^2} \times 13.6 \text{ eV}, \tag{4}$$

is 23 and 7 meV for GaP and GaAs, respectively. Both shallow donors and excitons in GaAs have a binding energy near 7 meV [31], in good agreement with the hydrogenic model. In GaP, the exciton binding energy is 21 meV [35], again close to the estimate from the hydrogenic model. In both semiconductors, the estimated binding energies for WBS are about three orders of magnitude less than the atomic value, which suggests that this state should be relatively easy to ionize thermally.

In conclusion, these results imply that deep-level Mu formation in GaP (as well as in GaAs) proceeds through a weakly bound intermediate muonium state. Comparing the results in GaP and GaAs we find that the characteristic electric fields for ionization of this WBS (as well as estimated values for characteristic radii and binding energies) scale with the electron effective mass and dielectric constant of the medium as expected for a hydrogenic effective-mass state.

4. Energy releasing mechanism for Mu atom formation

To understand the process of electron capture by a positive attractive centre in a semiconductor, μSR experiments using *external electric fields* have proved very useful [12, 13]: with

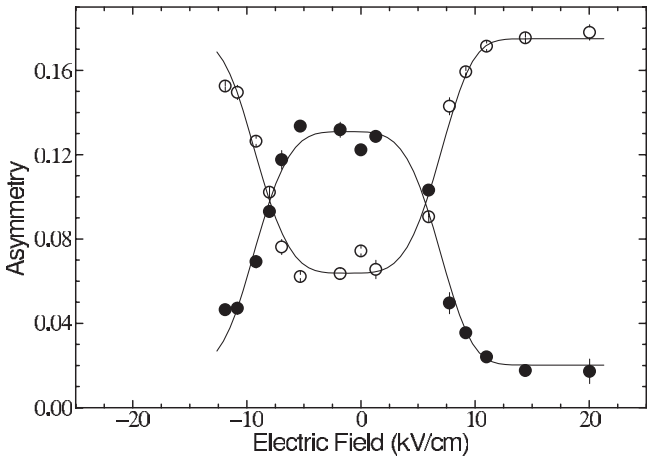

Figure 3. Electric field dependence of the diamagnetic asymmetry (open circles) and muonium asymmetry (filled circles) in intrinsic polycrystalline CdS at $T = 11$ K. The curves are to guide the eye.

increasing electric field, those excited states for which the bias across the orbit is bigger than the binding energy [33],

$$2Eea_n > U_n, \tag{5}$$

(where a_n is the radius and U_n is the binding energy of the nth excited state) are removed from the excitation spectrum and the number of 'valid' excited states is decreased. Therefore, by scanning the electric field at any given temperature one can find the 'bottleneck' excited state governing eventual electron capture to the ground muonium state.

In order to deduce the energy loss mechanism in the cascade process, we compare electric field effects in GaAs with those in CdS. The remarkable feature of the muonium state observed in CdS [28] is that the hyperfine interaction A is extremely small, amounting to only about 10^{-4} of the vacuum value. Muonium and diamagnetic signals in CdS are temperature dependent [28]: at low temperatures the muonium signal dominates, but the diamagnetic fraction increases at the expense of the muonium fraction as the temperature is increased, although the temperature dependence is weak up to 15 K. To reduce the influence of thermal processes, the electric field experiments were performed at 11 K.

Both muonium and diamagnetic signals in CdS are strongly influenced by the external electric field (see figure 3). Application of the electric field in either direction eventually causes a *decrease* of the muonium amplitude accompanied by a corresponding *increase* in the diamagnetic amplitude. From figure 3 one can estimate the characteristic electric field to be $E_{\rm char} \sim 8$ kV cm^{-1}.

In GaAs [12], the characteristic electric field was determined to be $E_{\rm char}^{\rm GaAs} \sim 5$ kV cm^{-1}. Electrons are very light in GaAs; that is why even the ground hydrogenic state in GaAs is rather shallow, with energy $U_1 = -13.6(m^*/m\epsilon^2)$ eV $\simeq -7 \times 10^{-3}$ eV. Note that this energy is less than the Debye temperature $\Theta_{\rm D} = 344$ K in GaAs [36]. Therefore an electron can easily lose its energy by a one-phonon emission cascade process starting from the bottom of the conduction band and going down through a sequence of excited hydrogenic states.

By increasing the external electric field E one steadily removes excited states with quantum numbers n, according to the expression

$$E_n = \frac{1}{n^4}\left(\frac{m^*}{m}\right)^2\left(\frac{1}{\epsilon^3}\right)\frac{e^5m^2}{4\hbar^4} < E \tag{6}$$

for successive thresholds in electric field. Equation (6) is directly derived from equation (5) by substituting the appropriate expressions for the radius and the energy of the excited state with quantum number n within the hydrogenic model [13]. At low fields, electron transitions from the conduction band to states with small quantum numbers are still possible via one-phonon emission. In GaAs the situation becomes critical when the lowest hydrogenic state with $n = 1$ is ionized in electric fields higher than $E_1 \sim 5$ kV cm^{-1}. In this case the cross section for electron capture by the muon is dramatically reduced and muonium formation is prohibited.

The electron effective mass is rather large in CdS ($m^* = 0.2m$ [37]) while the dielectric constant ($\epsilon = 9.1$ [38]) is smaller than in GaAs. This should result in a much deeper hydrogenic state in CdS ($U_1 = -13.6(m^*/m\epsilon^2)$ eV $\simeq -3.5 \times 10^{-2}$ eV) compared with GaAs, with a correspondingly larger electric field required to ionize the lowest hydrogenic state with $n = 1$ ($E_1 \sim 100$ kV cm^{-1}). This value is clearly inconsistent with the $E_{\rm char} \sim 8$ kV cm^{-1} observed experimentally (see figure 3). However, the electric field required to ionize the first *excited* hydrogenic state (the state with quantum number $n = 2$) in CdS is $E_2 = E_1/16 \sim 6$ kV cm^{-1} (see equation (6)), much closer to the experimental value.

This result can be explained by considering the cascade model for electron capture by a positive centre [17]. The Debye temperature $\Theta_{\rm D} = 250$–300 K in CdS [39] is smaller than the binding energy of the ground hydrogenic state $-U_1 \simeq 3.5 \times 10^{-2}$ eV $= 390$ K, so an electron transition directly from the conduction band to the $n = 1$ level by emitting one phonon is unlikely. The binding energy of the level with $n = 2$ is $-U_2 = -U_1/4 \simeq 100$ K, which is smaller than the Debye temperature; thus electron transitions with emission of one phonon from the conduction band (or from any level with $n > 2$) to the level with $n = 2$ are possible. By increasing a still relatively small electric field one steadily removes excited states from the hydrogenic excitation spectrum (see equation (6)); however, electrons can still be captured by one-phonon emission to one of the un-ionized levels. The cross section for electron capture (or muonium formation) is dramatically reduced when the last state for which one-phonon transitions from the conduction band are possible is removed from the excitation spectrum. In the case of CdS, this 'bottleneck' of the capture process is the first excited hydrogenic level (the level with $n = 2$ in our notation).

Thus the interplay between the electron energy spectrum and the Debye temperature may result in a situation where the electron cannot be captured directly to the lowest hydrogenic state but can still be captured into an excited hydrogenic state. The excited states will then determine the temperature dependence of the muonium fraction: the electron is more likely to be thermally ionized from one of the excited states than from the deep one. This scenario of muonium ionization is supported by the observation of a remarkable shift in the muon precession frequency in CdS around the ionization temperature due to atomic diamagnetism [40]. The interpretation of the value of this shift involves an excited hydrogenic state with mesoscopic-sized electronic orbits that scale as n^2. Note that the characteristic size of the electron orbit extracted from the diamagnetic shift ($a \sim 100a_0$, where a_0 is the Bohr radius) is also consistent with an $n = 2$ excited muonium state.

It should also be noted that the *ground* muonium state in CdS (which has not been detected so far) may be as deep as ground Mu states in Si or GaAs. The ground state hydrogenic muon–electron complex (the shallow state with $n = 1$ in our notation) detected in CdS [28] may simply be a very long-lived precursor for the deep Mu state.

No matter how long the lifetime of any WBS, it is expected to be much more susceptible to the influence of ambient conditions—temperature and electromagnetic fields—than the ground Mu state. Effects of temperature on the various 'deep' Mu states have been studied for about 40 years, but as far the authors know these effects have never been attributed to WBS. As we have seen, recent studies of the effects of *electric* field on the formation and dynamics of Mu states in solids have clearly indicated that these effects are associated with WBS rather than with the ground Mu state. Below we present experimental evidence that the effects of *magnetic* field should also be attributed to WBS rather than to the ground Mu state.

5. Magnetic freeze-out of electrons into Mu atoms

The problem of weakly bound atoms in a magnetic field, at its simplest, concerns the dynamics of the electron when submitted to the joint actions of Coulomb and magnetic fields of comparable strength. In spite of intense studies, the behaviour of even the hydrogen (or muonium) atom with the simplest form of Hamiltonian [41]

$$\mathcal{H} = \frac{p^2}{2} - \frac{1}{r} + \frac{\vec{L}\cdot\vec{B}}{2} + \frac{\left(x^2+y^2\right)B^2}{8} \tag{7}$$

remains an unsolved problem for comparable Coulomb and magnetic interactions. Here the third and last terms represent the Zeeman and diamagnetic interactions, respectively; $\vec{L}$ is the angular momentum; the external magnetic field $\vec{B}$ is given in atomic units (2.35×10^5 T) and is taken to be in the $\hat{z}$ direction.

The last term in this Hamiltonian gives rise to the diamagnetism of weakly bound electronic systems, theoretically established by Landau [42]. Experimental evidence for the diamagnetic shift in atomic spectra was found for Na atoms and the existence of individual diamagnetic levels was observed for highly excited Ba atoms [43]. For the weakly bound Mu atom the diamagnetic shift was observed in CdS [40]. For the sake of brevity we will not discuss this effect here; instead we direct the reader to the original papers.

Difficulties arise because the Hamiltonian (7) is nonseparable, the Coulomb symmetry being broken by the action of an external field of different symmetry but similar strength. In the two perturbation limits when either the magnetic or the Coulomb interaction is dominant, the eigenvalues can easily be found and yield the Landau and Rydberg spectra, respectively. In the intermediate regime, however, where both interactions are comparable, a perturbation treatment is not appropriate. Since the full Hamiltonian is not separable, determination of the eigenvalues becomes extremely difficult; it is this region of the spectrum that is of particular interest, since it is here that the overall structure changes from Landau-like to Rydberg-like as the electron is captured by an attractive centre.

It has been suggested that in bulk semiconductors the presence of an external magnetic field enhances the binding energy of the impurity atom [44]. The point here is the effect of competition between the magnetic energy and the Coulomb energy. The characteristic Coulomb interaction arises from a charged impurity centre with a binding energy expressed by equation (4). The strength of a magnetic field B, on the other hand, may 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

$$\frac{1}{2}\hbar\omega_c = \left(\frac{e\hbar}{2m^*c}\right)B. \tag{8}$$

The comparison of (4) and (8) can also be interpreted in terms of the two kinds of orbital radius, i.e. the effective Bohr radius expressed by equation (3) and the cyclotron radius

$$r_c = \left(\frac{\hbar c}{eB}\right)^{1/2}, \tag{9}$$

respectively.

Yafet *et al* [44] showed that when the magnetic field is strong enough that $\frac{1}{2}\hbar\omega_c$ is comparable to or larger than U, a considerable compression of the electronic wavefunction of the atomic state occurs because its orbital radius tends to decrease in accordance with (9) as the field is increased. This shrinkage of the wavefunction in turn causes the electron to be more strongly bound by the attractive Coulomb potential, thus resulting in an increase of the binding energy. This effect can be observed as a decrease in the number of conduction carriers as they are frozen out of the lowest-order conduction band Landau level into localized states with binding energies that increase with magnetic field.

Of relevance to the present work is the fact that electrons (and holes) created during the process of muon implantation and thermalization are available for interaction and capture, regardless of temperature or doping.

As we have seen, in DMF the electron may be captured initially into a weakly bound muonium state. Studies of GaAs and GaP in particular imply validity of the effective mass approximation within the hydrogenic model as a description of the muonium WBS formed on initial capture of an electron by a positive muon.

The formation of this weakly bound muonium centre may serve as a model for the process of electron localization by any attractive centre. Delayed muonium formation via capture of a free electron by a positive muon offers us an opportunity to study the elementary act of a metal–insulator transition.

These studies are carried out in the extremely dilute limit of a single impurity in the sample (in μSR techniques one follows the behaviour of every muon one at a time), thus avoiding complications related to impurity–impurity interactions or formation of an impurity band.

Here we present the results of our study of magnetic freezing out of electrons into muonium atoms in GaAs in magnetic fields up to 7 T.

Our experiments in electric field [12] have shown that the formation of the Mu^0_{BC} ground state in GaAs proceeds through a weakly bound intermediate state with a binding energy of about 7 meV. A reverse process of Mu^0_{BC} thermal ionization is unlikely to take place from the ground state itself, but suppression of the final Mu^0_{BC} yield may occur via thermal ionization of the intermediate weakly bound state.

At low temperature, virtually no diamagnetic fraction is formed upon muon implantation into semi-insulating GaAs, the entire muon polarization being distributed in almost equal amounts between Mu^0_{BC} and Mu^0_T states. Therefore, the magnetic freeze-out effect, which should show up as a decrease of the diamagnetic fraction of muon polarization, cannot be studied at low T. It can, however, be studied in semi-insulating GaAs at higher temperatures (about 200 K), where the diamagnetic fraction starts to grow at the expense of the Mu^0_{BC} fraction. In semi-insulating GaAs, the relaxation rate of the Mu^0_{BC} signal becomes faster than 10^8 MHz at about 160 K and thus unobservable at higher temperatures. 'Ionization' of Mu^0_{BC} in GaAs is accompanied by an increase of the diamagnetic fraction (diamagnetic polarization) [24].

Figure 4 presents the magnetic field dependence of the diamagnetic fraction in a semi-insulating GaAs sample at $T = 190$ K. The diamagnetic signal in GaAs is normalized to that in Ag in order to take into account effects of the finite time resolution of the spectrometer. (It is known that in Ag 100% of the muon polarization is diamagnetic.) The data are normalized at every temperature point.

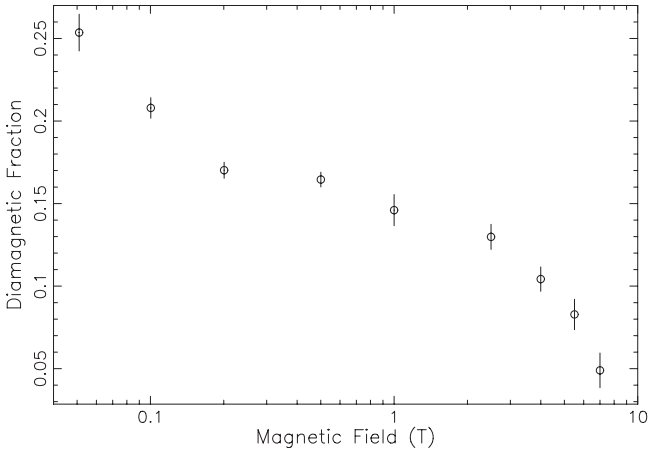

Figure 4. Magnetic field dependence of the diamagnetic fraction in semi-insulating GaAs at $T = 190$ K.

The reduction of the diamagnetic polarization at high magnetic field may be explained by magnetic freezing out of free electrons into muonium atom energy levels when the characteristic energy of the lowest-order conduction band Landau level becomes comparable to the binding energy of the weakly bound muonium atom. Within the hydrogenic model, an estimate of the magnetic field B_0 required for $\frac{1}{2}\hbar\omega_c$ to match R_y in the ground state of the weakly bound muonium atom in GaAs yields

$$B_0 = \frac{e^3 m^* c}{\hbar \epsilon^2} = \left(\frac{m^*}{m}\right)^2 \frac{1}{\epsilon^2} \times B_a \approx 6.7 \text{ T}, \tag{10}$$

where $B_a \approx 2.2 \times 10^5$ T is the atomic scale magnetic field.

This value of B_0 is characteristic of the $n = 1$ shallow donor state in GaAs [45]. Since in delayed muonium formation the electron may be captured initially into an excited electronic state, one may expect a reduction of the characteristic magnetic field required for a magnetic freeze-out effect in a weakly bound muonium atom. This circumstance may explain the reduction of the diamagnetic fraction with a corresponding increase of the Mu^0_{BC} fraction at magnetic fields almost an order of magnitude less than B_0 (see figure 4).

It is worth noting that even B_0 is about five orders of magnitude less than the magnetic field (B_a) required to affect the ground state of muonium or hydrogen in vacuum in the same manner. Thus the effect of the magnetic field seems to be associated with muonium WBS rather than any deep muonium states. Accordingly, the characteristic electric field required to 'ionize' a muonium atom in GaAs, GaP or CdS is about 4–5 orders of magnitude less than the atomic scale electric field [12–14]. It is therefore more consistent that 'ionization' of Mu^0_{BC}, either thermally or by electric field, takes place from the weakly bound muonium state rather than from the deep state.

6. General considerations

The results of different experiments in electric fields [12–14] (see sections 2–4) and magnetic fields (see section 5) suggest that the effects observed must be associated with highly excited muonium states rather than deep states. Indeed, to directly affect a deep muonium state,

electric and magnetic fields of atomic scale would be required ($\sim 10^9$ V cm^{-1} and $\sim 10^5$ T, respectively).

The binding energies for muonium WBS in GaAs [12], GaP [13] and CdS [14] are estimated to amount about 100 K. This value is more than an order of magnitude smaller than the binding energy of the ground Mu state. In particular, Mu^0_{BC} in Si lies deeper than 2000 K below the conduction band [25]. Therefore, it is more plausible that the thermal 'ionization' of muonium takes place from one of the weakly bound muonium precursor states rather than from any deep state. The excited states with electron orbits extended over distances 100 times the Bohr radius of the vacuum ground state then determine the temperature dependence of the muonium fraction (or the probability of electron capture by the positive muon). This conclusion is strongly supported by measurements of the muon precession frequency shift due to atomic diamagnetism in CdS at the edge of muonium ionization [40]. Thus not only effects of electric and magnetic fields but also effects of temperature may be associated with muonium WBS rather than deep states.

This is consistent with the cascade model for electron capture in solids [17]: initially captured into a very excited state, the electron is much more susceptible than in any deep state to the action of fields and temperature.

Since the cascade model turns out to give a consistent description of muonium formation and dynamics in solids, we need to explore it here in more detail. Special attention is devoted to limitations of the cascade model and the consequences of those limitations with respect to muonium dynamics in solids.

First, the cascade model assumes that the energy loss mechanism is elastic. It is suggested that the energy relaxation time is much less than that of the momentum. In other words, electrons are considered equally distributed over all degrees of freedom but the energy. This picture also suggests that energy relaxation may be treated as diffusion in energy space, which means that the energy transfer in one collision, ΔE, is much less than kT. For acoustic phonons in particular, if one works out both energy conservation and momentum conservation, it turns out that the phonon cannot transfer energy of the order kT in one collision. Instead, the energy transfer in one collision, $\Delta E = \sqrt{8m^*s^2kT}$ (where s is the velocity of sound), is much less than kT because the factor m^*s^2 turns out to be small compared with the typical experimental temperature. (For example, in GaAs $m^*s^2 \sim 0.5$ K.) In the case of electron scattering on acoustic phonons, this sets a limit for application of the cascade theory:

$$kT \gg m^*s^2. \tag{11}$$

In the opposite limiting case, the electron may be considered to be captured as the result of a single one-phonon event: at low temperature ($kT \ll m^*s^2$) electron–phonon scattering becomes essentially inelastic. In this case the problem of electron capture by a positive centre cannot be considered as diffusion in energy space, because the characteristic energy loss in a one-phonon emission event is of the order of m^*s^2. Therefore after a one-phonon emission event, any electron will find itself in a bound state with binding energy much higher than kT; electron ejection into the conduction band then becomes very unlikely and such carriers may be considered to be captured. In this case the capture process can be considered as a single-quantum transition from the conduction band into the bound state. The capture cross section for such a process [19],

$$\sigma \sim \left(\frac{e^2}{\epsilon kT}\right)\left(\frac{e^2}{\epsilon m^*s^2}\right)^2, \tag{12}$$

differs from expression (1) (which holds if $kT \gg m^*s^2$) by a factor $\sim (kT)^2/(m^*s^2)^2$. Thus, as the temperature drops below m^*s^2, the increase of σ slows down and σ becomes $\propto T^{-1}$ (versus $\sigma \propto T^{-3}$ at temperatures high enough that $kT \gg m^*s^2$).

In either case, the cross section increases rapidly with decreasing temperature, and therefore muonium formation via electron capture by a positive muon is favoured at low temperature, which is consistent with experimental results [24]. The transition from (12) to (1) should have no effect on the muonium formation process: either a single one-phonon capture event or a sequence of several one-phonon transitions down through the ladder of states into a WBS is completed with essentially the same result—the electron is captured into a muonium WBS.

It should be noted that the cascade model in its classical form [17] and the entire discussion here are both limited to consideration of *one-phonon* processes only. Processes with numbers of phonons higher than one are suppressed by a factor of $(\frac{T}{\Theta_D})^i$, where i is the number of phonons involved in a single transition. Furthermore, the fact that the muonium WBS with quantum number $n = 2$ acts as a bottleneck for muonium formation in CdS [14] is the experimental confirmation of the dominant role of one-phonon events in the capture process. Indeed, if two-phonon events (or any other processes which involve many phonons) were essential then the electron could be captured directly into the $n = 1$ WBS, which is obviously in contradiction with the experimental results at low temperature.

At higher temperatures, the cascade model breaks down when the thermal energy of an electron becomes higher than the typical distance between energy levels δE in the vicinity of the ionization threshold: an electron which gets into a very excited bound state of the attractive centre should be ejected back into the conduction band with high probability. In this case a direct capture of the electron from the conduction band into an $n = 1$ WBS may become essential. Binding energies of shallow donors in GaAs, Ge or Si are 70, 110 and about 400 K, respectively; the corresponding Debye energies are 340, 300 and 600 K [46]. Therefore, the direct capture process (although strongly suppressed even at temperatures as high as 100 K) is still possible.

In other words, the cascade model works when the characteristic phonon energy involved in the process of electron transition from the conduction band into a highly excited bound state ($\sqrt{8m^*s^2kT}$) is higher than δE. In the framework of the quasi-classical approximation, the distance between levels may be estimated using an expression for the density of states $R(E)$: $\delta E \approx R^{-1}(E)$. For the Coulomb centre the cascade model then works if [19]

$$kT \ll U^{3/4}\left(2m^*s^2\right)^{1/4}. \tag{13}$$

(At higher temperature, optical phonon transitions may become important.) It is worth noting that the inequality (13) is even stronger than necessary for the quasi-classical approximation to be justified. Indeed, the quasi-classical approximation is justified if the de Broglie wavelength of an electron (which is of the same order of magnitude as the wavelength of an emitted phonon) is less than the radius of the characteristic orbit ($r_T = e^2/\epsilon kT$; see equation (1)):

$$\frac{\hbar}{\sqrt{2m^*kT}} \ll \frac{e^2}{\epsilon kT}, \qquad \text{e.g. } kT \ll U. \tag{14}$$

The analysis of the experimental results, however, indicates that the cascade model adequately describes the capture cross sections even at temperatures as high as U [17]. The probability of a cascade capture involving a sequence of one-phonon events is estimated to be higher than that for a direct (single) one-phonon event [47] by a factor of

$$\frac{U^{7/2}}{(kT)^2\left(m^*s^2\right)^{3/2}}. \tag{15}$$

It is therefore obvious that, at temperatures below U, the cascade process is the dominant mechanism for electron capture by a positive centre.

Electron capture by any centre may take place only when (and if) the electron approaches close enough to the centre. So far we have assumed that the redistribution of the carriers in space is fast enough that the electron concentration in the vicinity of the muon is well described by the Boltzmann distribution. In other words, it is assumed that the capture process (muonium formation) has no influence on the distribution of electron concentration in space. It is clear that such an assumption is correct if the capture rate is low with respect to the rate of electron arrival into the vicinity of the muon where the capture can take place. In such semiconductors as Si, Ge or GaAs this is typically the case. In semiconductors with low *electron mobility*, however, this is not the case, and the dynamics of the carriers in the vicinity of the centre may be the 'bottleneck' of the capture process. In this case the concentration of electrons around the centre turns out to be less than in cases governed by the Boltzmann distribution. This depletion has a significant influence on the capture process. The theory of recombination (or electron capture by a positive centre) under these conditions was first considered by Langevin [48] and then developed by Pekar [49, 50]. In particular, the theory shows that in cases where the limiting process is the electron transport, the carrier concentration turns out to be *uniform* in space instead of being Boltzmann-like. In such cases the theory predicts a capture coefficient c ($c = \sigma v$, where v is the velocity of the carrier) given by

$$c_{\mathrm{L}} = 4\pi \frac{eb}{\epsilon} \tag{16}$$

so that c_{L} is proportional to the electron mobility b. The remarkable feature of equation (16) is that it is independent of the capture mechanism itself. The only important point here is that capture of the carrier from the vicinity of the centre occurs faster than the arrival of such carriers into the said vicinity. As shown by Lax [17] for such semiconductors as Si or Ge, equation (16) gives values for the capture coefficient several orders of magnitude higher than experimental values. Therefore it is not diffusion which limits the capture of carriers in these semiconductors. Indeed, for electron capture in Si it was found that equation (16) predicts a c three orders of magnitude higher than that determined in the experiment [51, 52]. In CdS, however, equation (16) estimates $c = 10^{-6}$ cm^3 s^{-1} at 100 K, which is close to experimental values determined in this semiconductor [53, 54]. In CdS, therefore, it is suggested that electron transport to a positive centre is the limiting mechanism in the capture process.

The distinction between the Thompson model [20] and the Langevin approach [48] can be best understood in terms of the interplay of the electron mean free path ℓ and the characteristic orbit radius r_{T} (see equation (1)). If

$$\ell \gg r_{\mathrm{T}}, \tag{17}$$

the Thompson model applies, which assumes that the electron experiences quasi-free motion under the influence of the central potential with very few scattering events (ballistic regime). A free electron (i.e. an electron with positive energy) passes by the centre with very small probability of scattering by a third body (acoustic phonon) and being captured into a bound orbit. On the other hand, a bound electron is associated with some particular orbit for a long time until it experiences a scattering event which puts it into a different orbit. In the case of scattering by acoustic phonons, the ratio ℓ/r_{T} is temperature independent and the inequality (17) can be expressed as

$$\frac{e^2}{2\epsilon m^* s^2 \ell_0} \ll 1, \tag{18}$$

where ℓ_0 is the characteristic length for electron energy loss (see equation (1)). For Si, Ge and GaAs the left-hand side of inequality (18) is about 5×10^{-2}, 2×10^{-2} and 10^{-2}, respectively, while in CdS it is of the order of 1.

In the opposite limit

$$\ell \ll r_{\mathrm{T}}, \tag{19}$$

the electron transport mechanism is qualitatively different from that in the ballistic regime—it is diffusive. In the equilibrium case one may make use of the Einstein relation between the mobility b and the diffusion coefficient D, and rewrite equation (16) as $c_{\mathrm{L}} = 4\pi r_{\mathrm{T}} D$. Comparing this capture coefficient with that in the Thompson limit ($c_{\mathrm{T}} = 4\pi r_{\mathrm{T}}^3/3\tau_{\mathrm{E}}$), one finds that electron transport controls the capture process if

$$\sqrt{3D\tau_{\mathrm{E}}} \ll r_{\mathrm{T}}, \tag{20}$$

i.e. if the characteristic length for energy loss is much less than the characteristic capture radius.

The interplay of the electron mean free path and the capture radius may play an important role not only in the muonium formation process but also in determining spectroscopic characteristics of muonium centres in semiconductors. The entire discussion above is restricted to the process of electron capture into muonium WBS. The question of how it gets down into the deep state, in particular what energy transfer mechanisms are responsible for muonium transitions from WBS into the deep state, still remains an open problem.

Binding energies of muonium deep centres in semiconductors are much higher than those of muonium WBS (typically, 0.1–1 eV versus 0.01 eV). The energy differences between muonium WBS and muonium deep states are much higher than most Debye energies (typically several hundred kelvins). Therefore, having captured into a very excited muonium state and cascaded down to a muonium WBS via phonon emission, an electron cannot cascade further down into a deep muonium state via phonon emission. The multiphonon process into the deep state is severely suppressed by a factor $(T/\Theta_{\mathrm{D}})^i$, where i is $\sim 10^2$ at $T = 10$ K, because the typical energy transfer is $\sqrt{8m^*s^2kT}$ (see above).

Energy release through photon emission is also ineffective: the characteristic radiation time scales with the energy difference δE as $(\delta E)^{-4}$, and the characteristic time for deep state muonium formation with a binding energy of the order of 1 eV is estimated to be about 10^{-5} s, whereas the coherent muonium precession observed in magnetic fields as high as 7 T requires that the muonium formation time is at least an order of magnitude less than 10^{-11} s.

The only energy bath that can accept the energy difference between a muonium WBS and its deep state is the electron subsystem. We suggest that processes analogous to Auger recombination in semiconductors are responsible for muonium formation in the deep state. The elementary act of Auger recombination requires three particles to participate. If all these particles are free carriers then the Auger process has a certain energy threshold [55] as a consequence of momentum and energy conservation laws. Such a threshold makes the Auger mechanism ineffective at low temperatures.

Auger processes may also occur as an electron is captured by a positive centre; the releasing energy is then transferred to the second carrier. The mere presence of a heavy centre like the positive muon removes the restriction coming from the momentum conservation law, and therefore such processes can take place without any energy threshold. The absence of the energy threshold makes this process very effective even at low temperatures. Such processes were first observed in doped Ge crystals [56]. To date, a great body of information has been accumulated on Auger processes in different semiconductors (see e.g. [57]). In fact, at carrier concentrations above about 10^{14}–10^{15} cm^{-3} the Auger mechanism becomes the most efficient one in recombination processes which involve significant energy release [58, 59].

As the Auger mechanism is proportional to n^2 (see e.g. [60]) it is essential to have a high electron concentration n around the muon for these processes to be effective in the formation of a deep muonium state. It is known that ionization processes in the muon track may produce

electron concentrations of about 10^{16} cm^{-3} [12]. These electrons, if transported to the vicinity of the muon, may act as third bodies in Auger processes. Therefore, in semiconductors with *high electron mobility* (such as Si, Ge, GaAs, etc) where the inequality (17) holds true, the Thompson model may apply, and the Auger mechanism may be responsible for deep state muonium formation. In fact, the Auger mechanism may be responsible for deep muonium state formation in some insulators—solid phases of Ne, Ar, Kr and Xe—which possess electron mobilities close to those in semiconductors. That is why the formation of a multi-electron track is essential to DMF in these solids [9].

In semiconductors with *low electron mobility* (such as CdS, CdTe, GaN, etc) the Langevin model may apply, implying a depletion region around the muon. Then Auger processes are ineffective, there is essentially no energy releasing mechanism by which the muonium WBS can be transferred into a muonium deep state, and therefore the muonium WBS should live forever (on the μSR timescale). This conclusion is consistent with experimental findings [24, 28], bearing in mind that the WBS has such a weak hyperfine coupling between the muon and the electron that its precession signal is practically indistinguishable from that of a diamagnetic state.

Further experiments designed to

(a) stabilize muonium WBS in Si, GaAs or GaP at low temperature (where the electron supply to the muon may be suppressed), and
(b) force the muonium WBS in CdS to be transferred into a deep muonium state via artificial production of electron–hole pairs (by photoemission etc)

may help in understanding muonium formation and dynamics in semiconductors.

Acknowledgments

This work was supported by the Kurchatov Institute, the Canadian Institute for Advanced Research, the Natural Sciences and Engineering Research Council of Canada and the National Research Council of Canada. Two of us (VGS and DGE) were also supported by the USA NSF (DMR-0209727) and the Royal Society of London (through the International Award).

References

[1] Shockley W and Read W T 1952 *Phys. Rev.* **87** 835
[2] Hall R N 1952 *Phys. Rev.* **87** 387
[3] Burton J A, Hall G W, Morin F J and Severiens J C 1953 *J. Phys. Chem.* **57** 853
[4] Shulman R G and Wyluda B J 1956 *Phys. Rev.* **102** 1455
[5] Storchak V G, Brewer J H and Morris G D 1995 *Phys. Rev. Lett.* **75** 2384
[6] Storchak V G, Brewer J H and Morris G D 1996 *Phys. Rev. Lett.* **76** 2969
[7] Storchak V G, Brewer J H, Morris G D, Arseneau D J and Senba M 1999 *Phys. Rev.* B **59** 10559
[8] Storchak V G, Eshchenko D G, Brewer J H, Morris G D, Cottrell S P and Cox S F J 2000 *Phys. Rev. Lett.* **85** 166
[9] Eshchenko D G, Storchak V G, Brewer J H, Morris G D, Cottrell S P and Cox S F J 2002 *Phys. Rev.* B **66** 035105
[10] Storchak V G, Cox S F J, Cottrell S P, Brewer J H, Morris G D, Arseneau D J and Hitti B 1997 *Phys. Rev. Lett.* **78** 2835
[11] Eshchenko D G, Storchak V G and Morris G D 1999 *Phys. Lett.* A **264** 226
[12] Eshchenko D G, Storchak V G, Brewer J H and Lichti R L 2002 *Phys. Rev. Lett.* **89** 226601
[13] Storchak V G, Eshchenko D G, Lichti R L and Brewer J H 2003 *Phys. Rev.* B **67** 121201
[14] Eshchenko D G, Storchak V G, Cottrell S P and Cox S F J 2003 *Phys. Rev.* B **68** 073201
[15] Storchak V G, Brewer J H and Eshchenko D G 1997 *Appl. Magn. Reson.* **13** 15
[16] Lax M 1959 *J. Phys. Chem. Solids* **8** 66

[17] Lax M 1960 *Phys. Rev.* **119** 1502
[18] Gummel H and Lax M 1957 *Ann. Phys.* **2** 28
[19] Abakumov V N and Yassievich I N 1976 *JETP* **71** 657
[20] Thompson J J 1924 *Phil. Mag.* **47** 337
[21] Koenig S H, Brown R D and Shillinger W 1962 *Phys. Rev.* **128** 1668
[22] Norton P, Braggins T and Levinstein H 1973 *Phys. Rev. Lett.* **30** 488
[23] Grimmeiss H G, Janzen E and Skarstam B 1980 *J. Appl. Phys.* **51** 4212
[24] Patterson B D 1988 *Rev. Mod. Phys.* **60** 69
[25] Kreitzman S R, Hitti B, Lichti R L, Estle T L and Chow K H 1995 *Phys. Rev.* B **51** 13117
[26] Chow K H, Hitti B and Kiefl R F 1998 *Identification of Defects in Semiconductors* (*Semiconductors and Semimetals* vol 51A) ed M Stavola (New York: Academic)
[27] Lichti R L 1999 *Hydrogen in Semiconductors* vol 2, ed N Nickel (San Diego, CA: Academic)
[28] Gil J M, Alberto H V, Vilao R C, Piroto Duarte J, Mendes P J, Ferreira L P, Aures de Campos N, Weidinger A, Krauser J, Niedermayer Ch and Cox S F J 1999 *Phys. Rev. Lett.* **83** 5294
Gil J M, Alberto H V, Vilao R C, Piroto Duarte J, Aures de Campos N, Weidinger A, Krauser J, Davis E A, Cottrell S P and Cox S F J 2001 *Phys. Rev.* B **64** 075205
[29] Schenck A 1986 *Muon Spin Rotation: Principles and Applications in Solid State Physics* (Bristol: Hilger)
Cox S F J 1987 *J. Phys. C: Solid State Phys.* **20** 3187
Brewer J H 1995 Muon spin rotation/relaxation/resonance *Encyclopedia of Applied Physics* ed G L Trigg (New York: VCH)
[30] Eshchenko D G 1996 *PhD Thesis* Kurchatov Institute, Moscow
[31] Animalu A O E 1977 *Intermediate Quantum Theory of Crystalline Solids* (Englewood Cliffs, NJ: Prentice-Hall)
[32] von Plessen G, Meier T, Koch M, Feldmann J, Thomas P, Koch S W, Goebel E O, Goossen K W, Kuo J M and Kopf R F 1996 *Phys. Rev.* B **53** 13688
[33] Knox R S 1963 *Theory of Excitons* (New York: Academic)
[34] Kiefl R F, Schneider J W, Keller H, Kundig W, Odermatt W, Patterson B D, Blazey K W, Estle T L and Rudaz S L 1985 *Phys. Rev.* B **32** 530
[35] Zhang X, Dou K, Hong Q and Balkanski M 1990 *Phys. Rev.* B **41** 1376
[36] Goryunova N A 1968 *Complex Diamond-Like Semiconductors* (Moscow: Sovetskoye Radio)
[37] Berchenko N N, Krevs V E and Sredin V G 1963 *Semiconductor Solid Solutions and their Applications* (Moscow: Voenizdat)
[38] Aven M and Prener J S (ed) 1967 *Physics and Chemistry of II–VI Compounds* (Amsterdam: North-Holland)
[39] Abrikosov N Kh 1967 *Semiconductors Compounds, their Manufacturing and Properties* (Moscow: Nauka)
[40] Storchak V G, Eshchenko D G, Cottrell S P, Cox S F J, Karlsson E, Waeppling R and Gil J M 2001 *Phys. Lett.* A **290** 181
[41] Gallagher T F 1994 *Rydberg Atoms* (Cambridge: Cambridge University Press)
[42] Landau L 1930 *Z. Phys.* **64** 629
[43] Garton W R S and Tomkins F S 1969 *Astrophys. J.* **158** 839
[44] Yafet Y, Keyes R W and Adams E N 1956 *J. Phys. Chem. Solids* **1** 137
[45] Zawadzki W, Pfeffer P, Najda S P, Yokoi H, Takeyama S and Miura N 1994 *Phys. Rev.* B **49** 1705
[46] Levinstein M, Rumyantsev S and Shur M 1996 *Semiconductor Parameters* (Singapore: World Scientific)
[47] Gummel H and Lax M 1955 *Phys. Rev.* **97** 1469
[48] Langevin M P 1903 *Ann. Chem. Phys.* **28** 289
Langevin M P 1903 *Ann. Chem. Phys.* **28** 433
[49] Pekar S I 1950 *JETP* **20** 267
[50] Pekar S I and Perlin Y E 1950 *JETP* **20** 271
[51] Preier H 1968 *J. Appl. Phys.* **39** 194
[52] Weber W H 1970 *Appl. Phys. Lett.* **16** 396
[53] Friedrich H 1964 *Acta Phys. Pol.* **26** 655
[54] Blazhko N A, Sal'kov E A and Khvostov V A 1977 *Phys. Tech. Semicond.* **11** 2278
[55] Beattie A R and Landsberg P T 1959 *J. Phys. Chem. Solids* **8** 73
[56] Karpova I V and Kalashnikov S G 1963 *Fiz. Tverd. Tela* **5** 301
[57] Landsberg P T and Robbins D J 1978 *Solid State Electron.* **21** 1289
[58] Bonch-Bruevitch V L and Gulyaev Yu V 1960 *Fiz. Tverd. Tela* **2** 465
[59] Robbins D J and Landsberg P T 1980 *J. Phys. C: Solid State Phys.* **13** 2425
[60] Bonch-Bruevitch V L and Kalashnikov S G 1977 *Physics of Semiconductors* (Moscow: Nauka)