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Location of the H[+/−] level: Experimental limits for muonium

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Abstract

The defect energy levels for muonium, a light pseudo-isotope of hydrogen, are investigated to define the equivalent of the H[+/−] level which is predicted to be fixed at a universal energy. Existing results for Mu at donor and acceptor sites in silicon tentatively place Mu[+/−] approximately 0.5 eV above the predicted hydrogen level. Measured donor ionization energies in other materials in which two neutral Mu centers are observed define a range for the Mu acceptor energies. We discuss possible reinterpretation of known energies and the current state of investigations to obtain these muonium acceptor levels in order to further refine a determination of the Mu[+/−] energy.

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Keywords: Hydrogen; Muonium; Defect levels

1. Introduction

Despite the scarcity of direct experimental results for isolated hydrogen impurities in most semiconductor materials, considerable knowledge of the sites, local physical and electronic structures, and energy levels associated with these hydrogen defects has been accumulated from theoretical modeling [1] and experimental results for the muonium 'isotope' [2,3]. Hydrogen is generally accepted to be a negative-U defect, which implies that the neutral center is never the dominant charge-state under thermodynamic equilibrium, and the defect's ionic state switches directly from positive to negative as the Fermi energy crosses a level defined as H[+/−] at the mid-point between the traditional donor H[+/0] and acceptor H[0/−] levels. Van de Walle and Neugebauer [4] predict that H[+/−] lies at zero on the electrochemical scale, roughly 4.5 eV below vacuum, independent of the host material. The electrical properties of H impurities are then predicted based on where this level falls within the band and gap energy alignments for a specific material. Similar predictions can be inferred from the work of Zunger and co-workers [5,6]. We have been investigating the muonium isotope of H as an experimental test of universality and to accurately determine the equivalent Mu[+/−] energy. In this contribution, we discuss the present state of these investigations.

An initial success for the above theoretical treatments was a prediction of materials in which hydrogen should have shallow-donor dopant properties, specifically materials where H[+/−] is above the conduction band minimum. Shallow, effective-mass donor Mu^0 centers were almost immediately observed for ZnO [7] and InN [8], two materials in that category, effectively verifying that Mu has the predicted properties. Shallow Mu^0 signals were also found in a number of other semiconductors [9], but in each case there was strong evidence that only Mu[+/0] is conduction band resonant. The limits on Mu[+/−] from observed Mu shallow donors yields E_C for ZnO as a lower limit and E_C for CdTe as an upper limit giving a range of only ~0.4 eV in the band alignments of Ref. [5].

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Muonium is formed by implantation of approximately 4.1 MeV positive muons, which parity violation conveniently delivers with 100% spin polarization. Experimental time scales are limited by the 2.2 μs muon lifetime. We can observe states that are formed very quickly, either epithermally or in the final stages of thermalization, and live longer than a few precession periods. Thus, metastable muonium sites and charge-states are present in the data, especially at low temperatures. The effective zero-time populations of the as-implanted states are extremely non-equilibrium, and the temperature dependence of the observed signals and transition dynamics will reflect conversions among the available sites and charge-states. This evolution of Mu states, observed in the temperature dependences, takes the system toward equilibrium and is governed by the same energetics that define the eventual thermodynamic equilibrium.

In covalent elemental semiconductors, the bond-centered (BC) location is the donor site and the tetrahedral interstitial (T-site) region is the acceptor location. In cubic III–V or II–VI compounds, the inequivalent T-sites take on separate donor and acceptor characteristics due to the bond ionicity. Hexagonal compounds provide more site options, thus assigning donor and acceptor sites becomes more difficult.

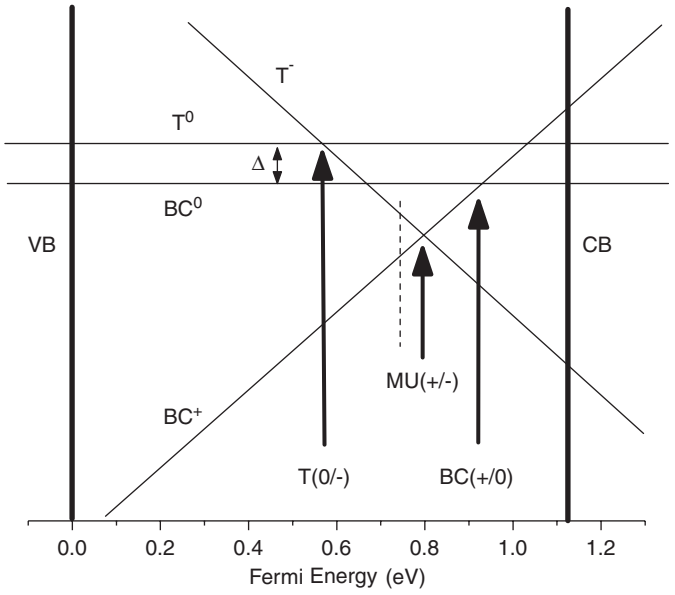

Fig. 1. Formation energy of Mu states in silicon based on experimental results. Measured energies are identified by long vertical arrows. Obtaining the Mu[+/−] level requires a midpoint adjustment of $\Delta/2$ due to Mu^0 site metastability.

2. Results for deep-level Mu centers

The best situation for experimentally defining the Mu[+/−] energy level is in materials where two deep localized Mu^0 centers are present. We have selected five semiconductors, all with cubic diamond or zincblende structures, as strong candidates for obtaining energy levels associated with donor and acceptor sites. These are Si, Ge, GaAs, and GaP, each with both Mu^0_{BC} and Mu^0_T readily identifiable via their very different hyperfine interactions and resulting muon spin precession signals, along with ZnSe in which two separate T-site Mu^0 signals were recently observed [10].

Fig. 1 is a Mu formation energy diagram scaled to reflect experimental results for silicon [11,12]. It displays some of the difficulties in translating the Mu results into the theoretical framework used to discuss equilibrium expectations for hydrogen. Most notably, translating the single-site energies into a Mu[+/−] level requires a mid-point correction of $\Delta/2$ to account for Mu^0 site metastability. Unfortunately, the metastability energy Δ is not accurately known experimentally for any of these materials.

The relevant energies measured in muonium experiments are from single-site ionization processes

$$Mu^0_{BC} \rightarrow Mu^+_{BC} + e^- \quad (1)$$

and either

$$Mu^0_T \rightarrow Mu^-_T + h^+ \quad (2)$$

or

$$Mu^-_T \rightarrow Mu^0_T + e^-. \quad (3)$$

The dynamics of these transitions yield an activation energy interpreted as $E_C - BC[+/0]$ since the e^- goes to the conduction band minimum (not to the Fermi level as in equilibrium population analysis), or place the T[0/−] energy relative to one of the band edges depending on whether Process (2) or (3) is active.

Silicon: Silicon is currently the only semiconductor for which the defect energy levels associated with both the donor and acceptor sites have been determined with any degree of confidence. The best current measurement of the Mu^0_{BC} ionization energy is from the increase in Mu^+ amplitude in RF final-state analysis [11] and places BC[+/0] at $0.21 \pm .01$ eV below the conduction band edge. Since BC is accepted as the lowest-energy site for Mu^0 at low temperatures, this identifies the Mu[+/0] deep-donor energy.

Our placement of the T[−/0] level is based on Process (3) acting on Mu^-_T as half of a rapid T-site electron capture—loss cycle in n-type samples [12]. An average of the results from two samples gives an energy of 0.56 ± 0.03 eV, placing the T-site acceptor level near mid-gap.

These energies yield negative U for Mu in Si provided that Δ is less than 0.35 eV. We have used an estimate of roughly half that, 0.15–0.20 eV, for the Mu^0 metastability energy, which then places Mu[+/−] at approximately 4.0 eV below vacuum within the band alignments of Ref. [4]. A conservative accuracy estimate of ±0.1 eV takes in nearly the full range of Δ that retains negative U and has

the BC site lowest for Mu^0, along with the statistical uncertainties in the measured ionization energies.

Germanium: The T and BC sites for Mu^0 are very nearly at equal energies both in theory [13] and experiment [14], thus we can approximate Δ as zero. The Mu^0 signals disappear below 100 K due to bi-directional Mu^0 site changes. Ionization for each Mu^0 center to Mu^+_{BC} is claimed as half of an electron loss—recapture cycle identified in longitudinal relaxation measurements. A simple interpretation of the resulting energies [14] places the BC[+/0] level at 0.215 eV below E_C and the $T^0 - BC^+$ crossing point at 0.175 eV below E_C, giving 0.04 eV for Δ at 200–300 K compared to 0.01–0.03 eV below 100 K from various data sets assuming Mu^0 site-change transitions.

Taking Mu[+/−] from Si and band alignments from Ref. [4], the above donor energy puts the acceptor level within the valence band. The longitudinal relaxation data that yielded the above energies also show a non-relaxing diamagnetic signal that disappears with an energy of 0.75 eV. It was originally assigned to a Mu-impurity complex; however, if this state is Mu^-_T and it disappears by Process (3), this would be consistent with the above energies placing T[−/0] about 0.08 eV below E_V at 350 K and the proper Mu[−/0] level just slightly higher, but still in the valence band.

We would then be left with the question of why a localized Mu^0_T should be observed at all. Germanium is one of the few materials for which H[+/−] is predicted to be in the valence band; however, it appears that Mu[+/−] lies in the gap although the acceptor level may be below the valence band maximum.

Gallium arsenide: The relaxation rates for Mu^0_{BC} in GaAs shown in Fig. 2a place the Mu[+/0] donor level at roughly 0.16 eV below E_C assuming the BC site lies lowest for Mu^0. Again, assuming the result for Mu[+/−] in silicon is universal and using the band alignments from Ref. [4], we estimate that the T-site acceptor level should be 0.3–0.6 eV above E_V.

There are two measured energies in GaAs which fall generally into that range; from Mu^0_T ionization as part of a charge cycle in 10^{15} cm^{-3} n-type GaAs [15], and an increase in diamagnetic amplitude in RF final-state analysis for several semi-insulating samples [16]. The extracted energies are 0.45 and 0.62 eV, respectively; however, in both cases the initial process assignment was e^- ionization to a metastable Mu^+ state that is mobile through the T_{As} sites in the relevant temperature region [17]. Reassignment of the final state to Mu^- and the transition to h^+ ionization, Process (2), may be compatible with the existing data in each case. We are currently seeking to make a more definitive identification of the diamagnetic final state. Several tests are available to confirm a Mu^-, which is expected to be stationary at a T_{Ga} location in the observed transition temperature range [18].

Gallium phosphide: We currently have less information on Mu in GaP than for any of the other materials. Preliminary analysis of recent Mu^0_{BC} relaxation data shown in Fig. 2b yield a Mu donor level of about 0.15 eV. No data currently exist relevant to the acceptor level, except that the Mu^0_T precession signals persist to above 300 K. Experiments are scheduled to pursue the acceptor energy by observing Mu^0_T hole ionization at higher temperatures. Our estimate of the appropriate energy gives a range of roughly 0.4–0.8 eV, but there is not yet an existing candidate for the Mu^0_T ionization transition in GaP.

Zinc selenide: Recent data on Mu in ZnSe show two separate Mu^0_T signals at low temperatures [10]. One interpretation involves a stationary Mu^0 at each T-site with Mu_I assigned to the T_{Se} donor site and Mu_{II} to the T_{Zn} acceptor site based on hyperfine interactions that agree well with calculated values [19]. Mu_I disappears below 50 K with roughly 40% showing up as Mu_{II}, implying a site change. The data suggest a second exit route, perhaps ionization, which would place a localized T_{Se} donor level just below E_C. Although the dynamics are complicated across the intervening region, Mu_{II} persists to above 400 K before disappearing, perhaps by ionization of the T_{Zn} acceptor state. Work continues to confirm or discredit the two T-site model for the observed signals, and to assign processes and extract accurate energies for all Mu^0 transitions.

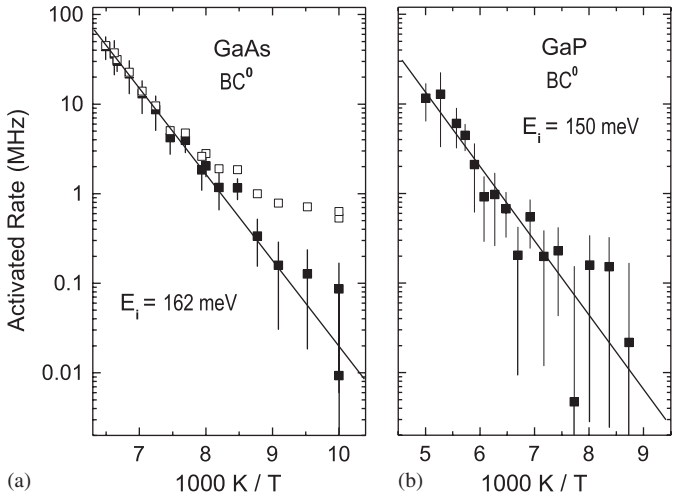

Fig. 2. Relaxation rates from recent high-field spin precession data for Mu^0_{BC} (a) in GaAs yield an ionization energy of ~0.16 eV, and (b) in GaP give ~0.15 eV when corrected for non-lifetime effects. Open squares in (a) are measured rates.

3. Discussion and preliminary conclusions

Fig. 3 provides a summary of the current knowledge of the muonium defect levels as outlined in the previous section. Site metastability for Mu^0 states is the largest source of uncertainty in the Mu[+/−] energy. Experimentally determining Δ poses a major challenge in any of these materials; although, we have tentative values at different temperatures for Ge. ZnSe also has a possibility of obtaining that energy, but in the other materials we must rely on calculated values.

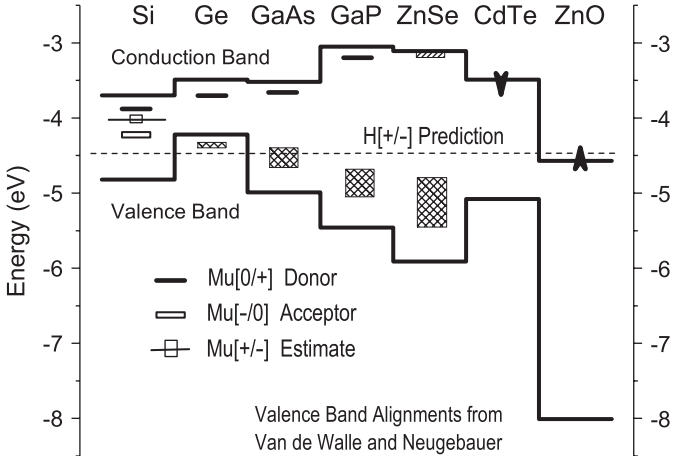

Fig. 3. Summary of experimental results for the defect levels of Mu in semiconductors within band alignments of Ref. [4], including limits from Mu shallow donors. Hatched boxes are search regions or as yet unconfirmed process assignments.

Unfinished business includes obtaining accurate energies for acceptor states, and verifying that measured energies come from acceptor ionization. Most of the acceptor levels should lie in the lower half of the gap based on Fig. 3, implying that Process (2) is most relevant. Definitively labeling the final state as Mu^- is the crucial experimental step in verifying such a hole ionization process and should be possible for GaAs and GaP where abundant nuclear moments can yield distinctive signatures for diamagnetic states.

Results available so far, including tentative acceptor energies, suggest that the muonium data may prove to be consistent with universality of the H[+/−] level. However, taking earlier results for silicon at face value, M[+/−] is higher than expected. Because the single-site donor or acceptor levels are determined by strictly electronic processes these energies ought to be essentially identical for H and Mu. If the sites are basically the same, the metastability energy for neutral centers is the main source for any significant differences between H[+/−] and Mu[+/−]. If one further assumes that the potential energy landscapes within which H or Mu reside are identical, the origin of these differences lies in the kinetic energies, which are certainly larger for Mu. The proper quantity to consider is the difference in the zero-point energy at the two sites for each species. This poses a significant problem for the current level of sophistication in modeling of quantum systems, and a full treatment will likely also need to consider the possibility of a difference in lattice relaxation surrounding H and Mu at fundamentally the same site, and corresponding differences in the potential functions.

In conclusion, in the near future we will be able to provide a placement of the Mu[+/−] defect level as an average for the materials considered here and perhaps a few others. The one case where data are most complete suggests that the level for Mu is about 0.5 eV above that predicted for H. Accurately modeling detailed differences in site geometries, potential functions, and particularly zero-point kinetic energies for Mu compared to H will need to be accomplished in order to determine whether half an eV upward is a reasonable adjustment in going from H[+/−] to the Mu[+/−] thermodynamic defect level.

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