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2004 J. Phys.: Condens. Matter 16 325

(http://iopscience.iop.org/0953-8984/16/3/012)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) 325–331 PII: S0953-8984(04)70765-1

Location of the hydrogen donor in InN: evidence from muonium results

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Received 17 October 2003
Published 9 January 2004
Online at stacks.iop.org/JPhysCM/16/325 (DOI: 10.1088/0953-8984/16/3/012)

Abstract

Muon spin depolarization measurements in a zero applied magnetic field confirm the existence of a shallow muonium (Mu) donor in InN, consistent with earlier transverse-field muon spin precession results. The zero-field data imply two Mu^+ centres in InN, similar to those associated with channel and cage sites in GaN. The zero-field results provide strong evidence that the shallow Mu^0 ionizes to Mu^+ at its lowest-energy location. We argue that data on Mu in the III–V nitrides, taken in total, support the assignment of a wurtzite channel location to the shallow hydrogen donor in InN. The present results yield 15.4 ± 2 meV below the conduction band edge for the donor level depth.

1. Introduction

Recent theoretical [1] and experimental [2, 3] evidence indicates that hydrogen acts as a shallow donor in InN and in a number of the wide-gap II–VI compounds [4–7]. This behaviour as an n-type dopant is in sharp contrast to the well-established properties of hydrogen in most semiconductors, where it is a deep compensating impurity and passivating agent. Hydrogen is commonly used to remove the electrical and optical activity of many unintentional impurities and extended defects in semiconducting materials and device structures. It is therefore important to understand this recently discovered electrical activity of hydrogen in materials that are being developed for future electrical and optical applications. Specifically, in the III–V nitrides, the current understanding is that hydrogen retains its typical compensating and passivating characteristics in GaN and AlN, but its shallow-donor properties in InN dictate that its use as a passivation agent in nitride alloys containing an indium component must be carefully evaluated and monitored.

We recently established that the muonium analogue of hydrogen yields a shallow state in InN [2], consistent with the theoretical prediction of shallow-donor behaviour for hydrogen [1].

0953-8984/04/030325+07$30.00

Muonium is formed when a positive muon is implanted into a semiconductor. It functions as a very light hydrogen isotope and the short muon lifetime ($\tau_\mu = 2.2\ \mu$s) means that it nearly always exists as an isolated atomic impurity. Measurements of muonium behaviour have provided much of the existing experimental evidence on the properties of isolated hydrogen impurities in many semiconducting materials where direct study of the equivalent states of H is exceedingly difficult. The mass ratio ($m_{\mathrm{Mu}} \simeq (1/9)m_{\mathrm{H}}$) implies that caution is needed when transferring physical properties related to defect motion from Mu to H; however, their electrical properties should be essentially identical.

The experimental techniques [8] used to study muonium are variants of magnetic resonance methods that make use of the unique muon formation and decay characteristics. In a typical experiment 100% spin-polarized muons are implanted into the host material and the time-dependent asymmetry of the positron emission from the muon decay process is collected as the raw data. The emission is preferentially along the muon spin direction; these data are thus very sensitive to magnetic interactions between the muon spin and its immediate surroundings in the host crystalline environment. In the initial report [2] of a shallow-donor Mu^0 state in InN and its ionization characteristics, we used the spin-precession signal in an external magnetic field applied normal to the initial spin direction. This type of measurement is known as muon spin rotation (μSR)—a notation now commonly used for the full range of muon spin research techniques.

Muons are implanted with relatively large energies (typically ~4.1 MeV) and immediately following thermalization various metastable sites may be occupied. We commonly assume that the muonium sites and charge states observed at the lowest temperatures are characteristic of the starting conditions at any other temperature. Except perhaps at very high temperatures, the muonium system essentially never reaches thermodynamic equilibrium within the experimental time range of several muon lifetimes. Transitions that are observed at any temperature are those which move the system from as-implanted conditions toward equilibrium. When using muonium observations to infer electrical properties of hydrogen, as in the current situation, the metastability makes it critical to establish that the relevant behaviour is in fact associated with the lowest-energy site for the appropriate Mu charge state. The only Mu^0 state that is detected in InN has the hyperfine characteristics of a shallow donor. The experiments described in this paper were undertaken specifically to determine whether or not this Mu^0 centre is associated with the lowest-energy site for Mu^+, as opposed to a metastable location.

For the Mu^+ ionized state, the relaxation rate (or linewidth) of the resulting diamagnetic frequency signal is characteristic of the Mu^+ site via local nuclear dipolar fields from neighbouring host nuclei. The precession signal from a shallow-donor Mu^0 state has two lines split symmetrically from this diamagnetic frequency, the satellites reflecting whether the muonium electron has its spin up or down in the applied magnetic field (see for example [7]). The very small value of this hyperfine splitting and the temperature dependence for the disappearance of the Mu^0 precession signal constitute strong evidence for the shallow-donor character of Mu in InN as previously detailed [2]. However, those results did not identify a site for the shallow Mu^0, and also did not fully characterize the ionized Mu^+.

In both GaN and AlN, previous μSR results showed two different Mu^+ centres [9–11]; one that is quite mobile and assigned to sites within unblocked channels along the *c*-axis of the wurtzite structure, and a second that is immobile at low temperatures, either located at a site within the blocked (cage) regions of the structure or trapped at an impurity or extended defect. Results for GaN imply a cage site while those for AlN are much more consistent with a defect-related location for the static Mu^+ centre [10, 11]. In GaN and AlN, temperature dependences suggest that the mobile centre is the lowest-energy state for Mu^+. Assignment

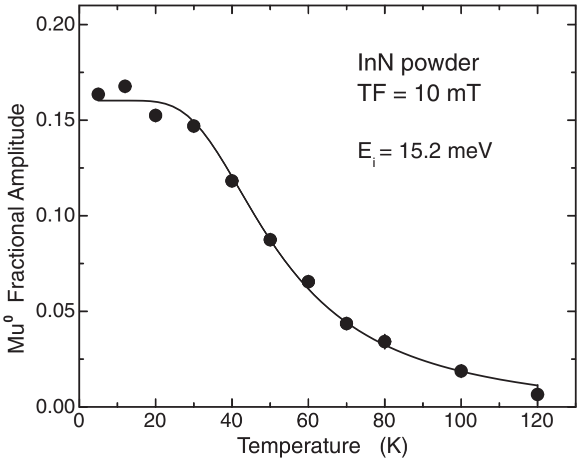

Figure 1. Fractional amplitudes for the shallow Mu^0 spin-precession signal in InN from an analysis including two Mu$^+$ states as separate signals.

to the wurtzite channel is based on theoretical results [12, 13], plus the fact that relaxation signals from other states have been correlated with level-crossing resonances that identify the other candidate sites [11]. Such level-crossing features are a signature of a stationary centre; they broaden and disappear as site-to-site motion increases, so are not expected to occur for a highly mobile state.

The diamagnetic spin-precession results for InN at temperatures well above the shallow Mu^0 ionization also suggest two Mu$^+$ locations. In the previous report on the Mu^0 characteristics [2], these states were treated as a single signal with the low-temperature lineshape fixed to the fitted result above the ionization region.

2. Data and analysis

In an attempt to resolve the two Mu$^+$ signals and refine our characterization of the Mu^0 shallow donor, we have undertaken additional higher-statistics spin-precession measurements. At temperatures above the Mu^0 ionization, these new data more clearly show two diamagnetic signals with significantly different relaxation rates. Figure 1 shows the temperature dependence for the shallow Mu^0 signal amplitude from an analysis of the high-statistics spin-precession data with the two Mu$^+$ states treated as separate signals. In the specific analysis shown, the fractional amplitude and relaxation rate for the static Mu$^+$ signal were fixed to average values (50.2% and 297 kHz, respectively) obtained from fits with these parameters free, and the (powder-averaged) Mu^0 hyperfine constant was set to 96 kHz. This procedure significantly reduced the scatter in Mu^0 amplitudes. The curve in figure 1 is a fit to the resulting amplitudes and gives an ionization energy of 15.2 ± 0.4 meV. The uncertainty is at least a factor of four larger when the fixed parameters are allowed to vary. This particular set of parameters closely mirrors those from analysis of zero-field depolarization data discussed below.

The muon spin depolarization function in zero external magnetic field represents a much more sensitive technique to separate the two Mu$^+$ signals than does transverse-field (TF) μSR. It also yields an oscillating signal at the hyperfine frequency for the shallow Mu^0 state. We thus chose to use zero-field depolarization along with the high-statistics precession data. Above roughly 150 K, the zero-field results show dynamics related to Mu$^+$ motion and detrapping

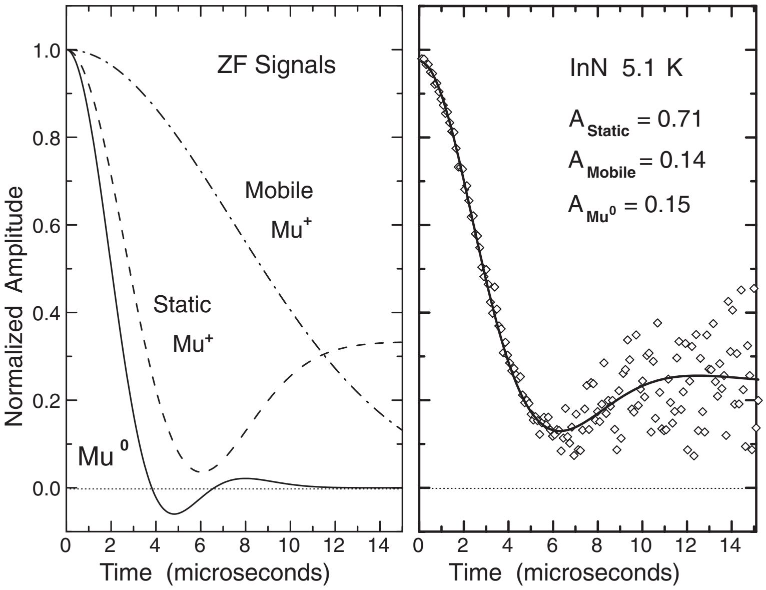

Figure 2. Comparison of the zero-field (ZF) depolarization functions for the three Mu centres in InN as determined prior to final signal separation, along with the fitted result for the 5.1 K data. The fractional yield (A) for each state is listed in the figure.

transitions; these will be reported in detail in a separate publication. Here we concentrate on data identifying the slowly relaxing signal as coming from the more stable Mu^{+} state and on the ionization region for the shallow Mu^{0}. All zero-field measurements reported here were made on the same powdered InN sample used for the spin-precession experiments.

As with the spin-precession data, the zero-field technique has some difficulty in cleanly distinguishing between signals with similar relaxation signatures. This is true in the present case for the static Mu^{+} and the shallow Mu^{0} states, leading to significant scatter and rather large error bars when relaxation parameters are all left free. Analysis of the zero-field data thus proceeded in several steps to refine the signal separation, with relaxation rates for the three signals eventually fixed to their free-fit averages, either singly or in pairs. Figure 2 displays the low-temperature zero-field relaxation signatures for the three signals involved along with the fitted result for the 5 K data. The apparent fast relaxation for the Mu^{0} signal reflects the spread of hyperfine frequencies in the unresolved powder pattern. The actual Mu^{0} relaxation rate increases above 30 K as a result of the ionization process, which improves the signal separation, while rate constants for the two Mu^{+} signals do not change significantly below room temperature.

Figure 3 shows the temperature-dependent amplitudes for the three zero-field signals when the two Mu^{+} rate constants are held constant at 294 and 92 kHz, the same values used in figure 2. The logarithmic temperature scale for figure 3 was chosen to emphasize the Mu^{0} ionization region. A major conclusion from this analysis is that the Mu^{0} signal is strongly correlated with the more slowly relaxing Mu^{+}. This outcome is very robust, independent of precise values for the relaxation rates. The decrease in Mu^{0} amplitude and increase in weakly relaxing Mu^{+} amplitude are each governed by the Mu^{0} ionization energy. A simultaneous fit to the two curves with both the ionization energy and prefactor shared yields 15.7 ± 1.7 meV.

The thermal transition in Mu^{+} amplitudes starting just below 200 K implies that the faster relaxing signal is from a metastable Mu^{+} and that the slowly relaxing signal represents the

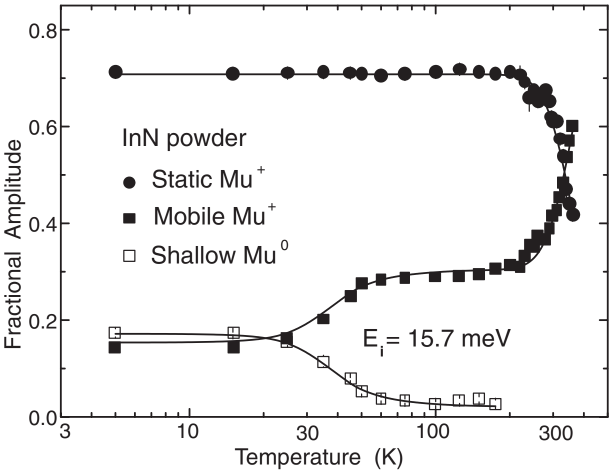

Figure 3. Zero-field fractional amplitudes for the shallow Mu^0 (open symbols) and two Mu^+ (filled symbols) centres in InN.

lowest-energy Mu^+ state. The fit to the transition out of the static Mu^+ state shown in figure 3 assumed a single complete transition into the mobile ground state and yields an energy barrier of about 240 meV. However, details of this transition do not appear to represent a single trap site with a sharply defined barrier energy. Thus more than one metastable Mu^+ state may be involved.

3. Discussion and conclusions

Based on the above analysis of zero-field data, we can confidently conclude that the shallow donor in InN is correlated with the lowest-energy Mu^+ state. This result significantly strengthens the argument that the experimental results for muonium independently imply that hydrogen has shallow-donor character in InN, in agreement with the theory [1].

If we rely on the very close similarity in character of the Mu^+ signals in all three III–V nitrides, we can draw additional conclusions regarding the likely location of the muonium donor in InN. While details are to be published elsewhere, the more rapidly relaxing zero-field Mu^+ signal in InN is correlated with a level-crossing resonance that identifies this signal as coming from an immobile centre with a nitrogen nearest neighbour, as also found for a static Mu^+ signal in GaN and AlN [11]. All three nitrides show the slowly relaxing signal that we assign to a mobile Mu^+; this signal appears to represent the lowest-energy state in each case. Correlation of this weakly relaxing signal with channel sites is strongest in GaN where level-crossing signatures for the other anticipated Mu^+ sites have been assigned [14]. We also rely quite heavily on theoretical results for H in GaN [12, 13] that predict H^+ to be the most mobile isolated H centre with its lowest-energy location at an N-related antibonding site in the channels. The combination of these various results makes assignment of a weakly relaxing diamagnetic signal to Mu^+ moving among channel sites very reasonable and consistent across the III–V nitrides. Thus, while the conclusion is not definite, all of the data are consistent with a ground-state Mu^+ that is mobile within the wurtzite channels in all three nitrides. Based on the relaxation rate for this signal, this Mu^+ centre is less mobile in InN than in the other two materials.

We further argue that at the low temperatures involved, the basic muon site should not change during ionization. That is, if the Mu^0 is associated with a channel site then ionization

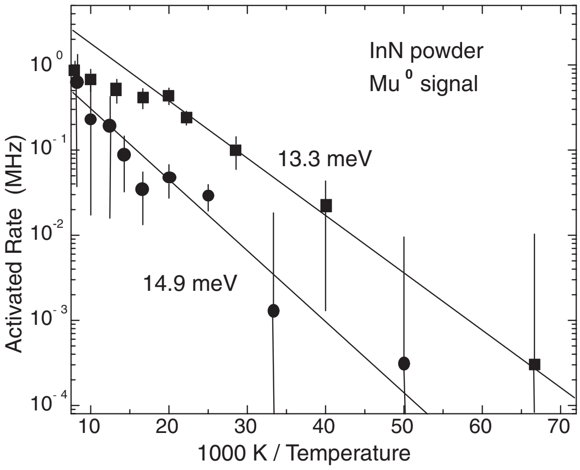

Figure 4. Relaxation rates for the Mu^0 signals in μSR spin precession (circles) and zero-field depolarization (squares) data for InN each give an additional measurement of the ionization energy.

should feed into the channel-related Mu$^+$ signal, and similarly if the shallow Mu^0 lies in the wurtzite cage or resides at some other trap site, the amplitude for the static Mu$^+$ signal should increase upon ionization. When taken in total, the data on muonium in the III–V nitrides supports assignment of the Mu shallow donor to a location within the channel regions of the wurtzite structure. One theoretical model places the lowest-energy Mu^0 location at a symmetric site in the centre of these channels [13].

Finally, we turn briefly to the question of the level depth for the Mu shallow donor in InN. Each of the temperature-dependent amplitude curves in figures 1 and 3 provides a measurement of the Mu^0 ionization energy. As judged by the ionization rates, only one cycle of electron capture and ionization takes place during the muon lifetime over most of the relevant temperature range. The energy obtained can therefore be interpreted as the depth of the shallow-donor energy level below the conduction band edge. The activated contribution to the Mu^0 relaxation rates (shown in figure 4) represents lifetime broadening, directly reflecting the ionization rate, and therefore yields an additional measurement of the Mu^0 ionization energy. In principle, this should be the best data from which to obtain an ionization energy, rather than the amplitudes. However, as has been the case for other Mu shallow donors, relaxation rates for Mu^0 in InN have large error bars or significant contributions from other mechanisms and, as a consequence, are less useful in this regard than the amplitude variations. The transverse-field activated rates yielded 14.9(±4.2) meV, consistent with the value obtained from the amplitudes (figure 1). In the zero-field case, the low-temperature rate constants are large due to the spread of hyperfine frequencies for the powder, and above 60 K both these rates and the residual Mu^0 amplitudes depend critically on values of fixed parameters. Thus the zero-field relaxation may not properly reflect the ionization process. Even with these concerns, the obtained value of 13.3 ± 2.8 meV is reasonably consistent with the other measurements of E_i.

The best value for the Mu^0 ionization energy obtained by combining results from the various data sets is $E_\mathrm{i} = 15.4(\pm 0.5)$ meV based on statistics for the displayed fits. A more realistic uncertainty is probably closer to ±2 meV if one considers the spread in parameters for all the fits undertaken in refinement of this analysis. The measured energy is interpreted as that required for an electron to be removed from the neutral Mu donor and placed at the bottom of the conduction band. It should therefore be a good value for the Mu(0/+) defect level position.

Since the muonium state occupations are essentially never at thermal equilibrium, the location of the Fermi level does not enter into this interpretation.

In conclusion, we have characterized the shallow-donor muonium defect centre identified in InN using muon spin depolarization data in zero applied magnetic field and high-statistics muon spin-precession measurements in a field of 10 mT applied perpendicular to the initial polarization direction. Consistent with results for the other III–V nitrides [11], these data imply the existence of two Mu^+ states for InN in addition to the shallow-donor Mu^0 present below 80 K. Analysis of the zero-field data implies that the Mu^0 state ionizes to only one of the two Mu^+ sites, leading to the strong conclusion that the shallow donor is associated with the lowest-energy Mu^+ location. Using the final fits from our signal-separation procedures for the various data sets, the combined results yield a shallow-donor ionization energy of 15.4 meV. We argue that this energy is a good measure of the depth of the Mu(0/+) donor level below the conduction band minimum. The present results, particularly the association of the neutral donor with the lowest-energy Mu^+ state, provide further evidence that the analogous atomic hydrogen impurity will be a shallow donor in InN, in contrast to the deep compensating impurity behaviour found in AlN and GaN.

Acknowledgments

This work was supported by the US National Science Foundation, the Robert A Welch Foundation, and the Engineering and Physical Sciences Research Council of the UK.

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