Physica B ▮ (▮▮▮▮) ▮▮▮–▮▮▮

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Possible donor and acceptor energies for Mu in ZnSe

R.L. Lichti [a,*], B.R. Carroll [a], J.E. Vernon [a], H.N. Bani-Salameh [a], K.H. Chow [b], I. Fan [b], M. Egilmez [b], R.C. Vilão [c], J.M. Gil [c], H.V. Alberto [c], J. Piroto Duarte [c], N. Ayres de Campos [c], S.P. Cottrell [d], S.F.J. Cox [d,e]

[a] *Department of Physics, Texas Tech University, Lubbock, TX 79409-1051, USA*
[b] *Department of Physics, University of Alberta, Edmonton, Canada T6G 2G7*
[c] *CEMDRX, Department of Physics, University of Coimbra, P-3004-516 Coimbra, Portugal*
[d] *STFC ISIS Facility, Rutherford Appleton Laboratory, Chilton OX11 0QX, UK*
[e] *Condensed Matter and Materials Physics, University College London, WC1E 6BT, UK*

ARTICLE INFO

Keywords:
Defect levels
Hydrogen
Muonium
ZnSe

ABSTRACT

Multiple charge-state transitions are observed for muonium in heavily compensated ZnSe. A paramagnetic resonance signal for the state known as Mu_{II} is present to ~350 K, but has decreased amplitude between 30 and ~200 K, disappearing completely in one sample. Satellite lines in the Mu_{II} spectrum identify it as Mu^0 at the T-site with Se neighbours. We obtain an ionization energy of ~0.4 eV for this Mu donor location. Loss of Mu_{II} and growth of a diamagnetic signal near 25 K had been assigned to electron capture by Mu^0, and its loss near 80 K to e^- emission from Mu^- to the conduction band. We offer an alternative explanation for the loss of Mu^- amplitude, and suggest that high-temperature growth of diamagnetic amplitude be associated with Mu acceptor ionization. This alternative model gives thermodynamic levels for Mu in ZnSe that fit well into the overall picture of H in semiconductors.

1. Introduction

Previous transverse-field muon spin rotation (μSR) measurements on ZnSe have demonstrated two separate isotropic paramagnetic signals from Mu^0 states [1]. One explanation for these two signals is immobile neutral muonium centres located at the two distinct tetrahedral interstitial (T-site) locations in this zincblende structured II–VI semiconductor. The temperature dependent spin precession data show a transition from one of these Mu^0 states, labelled as Mu_I, into the second one, labelled as Mu_{II}, below 50 K [1]. This transition has been confirmed by microwave resonance measurements on Mu_{II} and can be identified as a site change if separate T-sites is the correct explanation for two Mu^0 signals. Both the low-temperature resonance results and the original precession data show that the Mu_{II} amplitude decreases sharply with increasing temperature beginning just above this transition.

Similarly, both spin precession and RF resonance results for the diamagnetic muonium signals in ZnSe show an increase at relatively low temperatures, followed by a decrease that sets in below 100 K. We recently published an interpretation [2] of the low-temperature transitions that identifies the decrease in total Mu^0 amplitude and increase in diamagnetic fraction as an electron capture transition, resulting in a Mu^- final state. Ref. [2] also puts forward an interpretation of the subsequent decrease in diamagnetic amplitude as thermal promotion of an electron from Mu^- to the conduction band with an energy of ~100 meV. This identification, if correct, would indicate a Mu acceptor level approximately 0.1 eV below the conduction band in ZnSe.

The above interpretation includes an implicit identification of the Mu_{II} signal as arising from the T_{Zn} acceptor site, which should be the lower energy T-site for a simple Mu^0 atom in ZnSe. Different attempts to theoretically model the sites for hydrogen defect centres in ZnSe yield either the bond-centred (BC) location [3] or an AB_{Zn} antibonding site [4], off centre from T_{Zn}, as the lowest energy location for the neutral charge state of H. We do not observe a Mu^0_{BC} signal in ZnSe, and the extra zero-point energy likely centres Mu^0 at T_{Zn} in the latter situation.

In this contribution, we present microwave resonance data that identifies Mu_{II} as the T-site with Se nearest neighbours, which means this signal is from a donor site in ZnSe rather than an acceptor location. This requires some reinterpretation of previous transition assignments. We obtain an energy of 0.4 eV associated with the eventual disappearance of the resonance signal from Mu_{II} near 350 K, which we suggest is $Mu^0_{II} \rightarrow Mu^+_{II} + e^-_C$. This assignment places the donor level for the T_{Se} site at $E_C - 0.4$ eV. We also offer a second interpretation of the low-temperature Mu charge-state dynamics, and suggest a

* Corresponding author. Tel.: +1 806 742 3697; fax: +1 806 742 1182.
E-mail address: roger.lichti@ttu.edu (R.L. Lichti).

0921-4526/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2008.11.161

transition at high temperatures as a possibility for Mu acceptor ionization. This alternative model gives Mu defect levels in ZnSe that correlate well with results in other semiconductors [5].

2. Experimental data and discussion

The important new experimental data on which we base a re-interpretation of state and transition identities in ZnSe are microwave resonance results obtained at TRIUMF using the M20 beamline. Two samples of ZnSe were examined, one obtained from Crystec and the second from Alpha Aesar. Both were heavily compensated, having a net electron concentration at 300 K of below $10^{10}\,cm^{-3}$ [6]. Annealing of a piece of the Crystec sample in a Zn atmosphere to remove compensating vacancies resulted in increased diamagnetic fraction suggesting an n-type concentration approaching $10^{12}\,cm^{-3}$, giving an estimate of the lower limit for (uncompensated) accidental donor concentration in that particular sample.

Most of the microwave resonance data were taken at a frequency of about 1.2 GHz with power levels that were just above that required to saturate the Mu_{II} signal because we were primarily interested in the variation of the Mu_{II} fraction with temperature. However, because our initial model of Mu properties in ZnSe had immobile Mu^0 centres at separate T-sites, particularly at low temperatures, we took some spectra at low power levels to look for structure that might reveal nuclear hyperfine couplings with the nearest Zn or Se neighbours.

Fig. 1 is a composite spectrum of several runs at temperatures near 15 K. There are two strong satellite lines, along with two much weaker lines having approximately twice the splitting. The basic structure and relative amplitudes are close to what one expects for couplings to the 7.6% abundant spin $\frac{1}{2}$ ^{77}Se neighbours to the T_{Se} site. The alternative T_{Zn} location for Mu_{II} would have a completely different nuclear hyperfine structure associated with the 4.1% abundant ^{67}Zn isotope which has $I=\frac{5}{2}$. Details of the modelling of the spectrum in Fig. 1 are to be reported elsewhere, but the identification as arising from T_{Se} is solid. Various tests at different frequencies and power levels excluded other explanations. This clearly identifies the Mu_{II} signal as coming from the T_{Se} donor location in ZnSe, rather than the T_{Zn} acceptor site expected to be the lower energy location for an isotropic Mu^0.

Fig. 2 shows the resonance amplitudes associated with the spectrum of Fig. 1 as a function of temperature. These data correlate with the fraction of muons forming the metastable T_{Se} donor in the ZnSe sample from Crystec. We have confirmed that

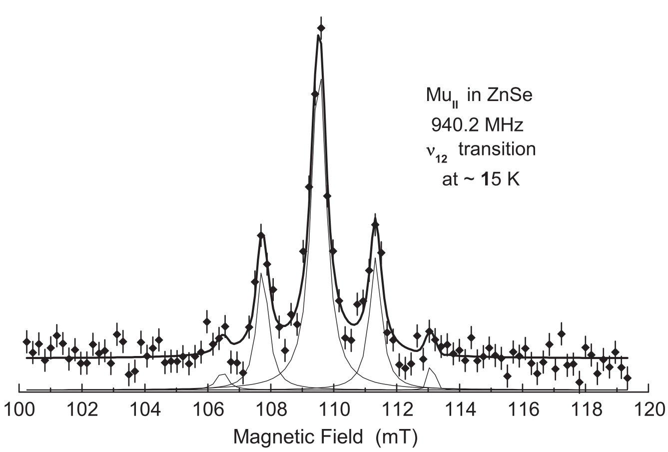

Fig. 1. The microwave resonance spectrum from the isotropic Mu_{II} state in ZnSe. Satellite lines are identified as nuclear hyperfine coupling to ^{77}Se neighbours, implying that the Mu_{II} site is T_{Se}.

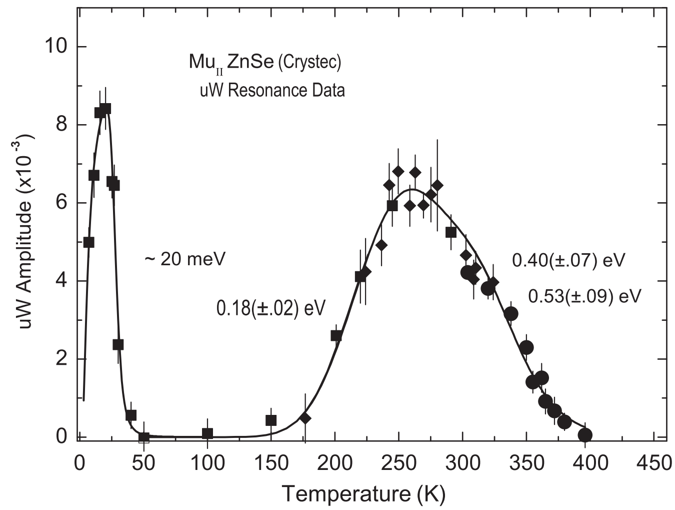

Fig. 2. The microwave resonance amplitudes from the isotropic Mu_{II} state in ZnSe. The higher temperature decrease has two energy components associated with competing Mu^0 site changes and T_{Se} donor ionization.

the characteristic nuclear hyperfine satellites are present in both of the temperature regions where this signal is found, although the widths of these satellites broaden above approximately 250 K, near the second peak in amplitude with increasing temperature. We note that amplitudes for similar spectra from the Alpha Aesar sample do not decrease all the way to zero in the 50–150 K region, consistent with its lower electron concentration and an assignment of electron capture by a Mu^0 centre for the 30 K transition.

Fits to the low-temperature peak, assuming either growth and loss of the monitored Mu_{II} signal or alternatively a transition from Mu_I to Mu_{II} along with a competing second transition out of Mu_I, yields a characteristic energy for the signal loss near 30 K that is extremely close to the ionization energy for the unintentional halogen donors that make ZnSe typically n-type. Because we have shown that the observed signal is from a Mu donor site, it is logical that the low-temperature disappearance of this signal is due to electron capture by the precursor state, especially if Mu_I is associated with the T_{Zn} acceptor site. The high-field muon spin precession results [1] related to the conversion from one Mu^0 to the other imply a faster transition out of Mu_I than into Mu_{II} providing additional evidence for a second exit route from Mu_I, consistent with this argument regarding transition assignments. If the electron capture is by Mu_{II}, then a site change must accompany the capture so that the resulting Mu^- would be at a stable location. That seems unlikely for a relatively immobile defect such as Mu^-, especially given that the capturing centre Mu_{II} is immobile at the unstable T-site for a Mu^-. Therefore, in the present model, we can reasonably assign the low-temperature formation of a diamagnetic state to electron capture by the Mu^0 acceptor at T_{Zn} and associate that state with Mu_I. The end result is a Mu^- at its most stable location without the necessity of a site change. Alternatively, Mu_I could be a low-temperature tunnelling state that visits both T-sites, with the same end results when Mu^0 localizes to an individual T-site.

According to several pieces of evidence [2,6,7], a diamagnetic state is formed consistent with electron capture at low temperatures. This state then disappears by about 80 K with a characteristic energy of 0.10 eV. In Ref. [2] we took the simplest approach, assigning this transition to thermal promotion of an electron from Mu^- to the conduction band. This implies a Mu acceptor level close to E_C, contrary to theoretical expectations [8] which has the *thermodynamic* acceptor level near or below mid-gap in ZnSe. We must consider whether this level high in the gap represents the primary acceptor level, or whether an alternative assignment is needed for the corresponding transition.

Hole capture is usually the best alternative to thermal loss of an electron, but on first thought this seems unlikely in an n-type material, except perhaps with optical excitation. However, both of the examined samples have a very low electron concentration at 300 K, so low in fact that the initial hypothesis of electron capture at low temperatures would not appear reasonable. More careful consideration of sample characteristics reveals that these ZnSe samples are heavily compensated by zinc vacancies with an ionization energy of 218 meV [9]. The low-temperature quasi-Fermi level governing hole concentrations under implantation conditions would be very close to the 0.10 eV found for the loss of Mu^- signal. An alternative explanation for this loss is that the electron capture process is simply shut off when the compensating V_{Zn} acceptors ionize near 100 K, reducing the concentration of available electrons by 1–2 orders of magnitude.

Returning to Fig. 2, the Mu_{II} resonance amplitude increases between about 180 and 250 K with an energy of ~0.18 eV. This energy could represent a site change barrier for Mu^0, or some other more complicated set of dynamics. It is not consistent with a simple thermal loss of a Mu^- electron even in the model of Ref. [2]; however, a site change would also be required within that picture in order to end up at T_{Se}. Some knowledge of the direct precursor will likely be required before the process(es) related to this transition energy can be identified.

The Mu_{II} resonance disappears near 350 K with the signature of two separate processes having energies of approximately 0.40 and 0.53 eV. Additional qualitative results show that the Se satellite lines broaden and disappear much more rapidly than the main peak, suggesting motion or a site change transition for Mu_{II} competing with Mu donor ionization. A second weak resonance having a higher hyperfine constant appears for the highest few temperatures at which Mu_{II} is also observed, leading us to associate the larger energy with a site change, leaving 0.40(±.07) eV to be assigned to ionization of the T_{Se} muonium donor in ZnSe. This site is metastable for both Mu^0 and Mu^+; therefore some adjustment should be needed to reach the correct thermodynamic donor level from the one at $E_C - 0.40$ eV associated with the metastable T_{Se} donor. Adjustments for metastability of the two charge states will be in opposite directions, thus the overall correction ought to be relatively small. We can thus conclude that the Mu donor level in ZnSe is considerably deeper than the previously claimed acceptor level.

Based on this result for a Mu donor in ZnSe, and results for other semiconductors [5] that support negative U for muonium impurities and a common energy for the mid-point between the acceptor and donor levels, one can expect the acceptor level for Mu in ZnSe to be below mid-gap with an acceptor ionization energy of more than an eV. A large amplitude transition with increasing diamagnetic fraction exists in ZnSe that has the appropriate energy characteristics. Fig. 3 shows the prompt diamagnetic fraction in low-field spin precession measurements. The growth in amplitude above 650 K yields an average energy of 1.44(±.15) eV for the fits shown. Various other data including RF-μSR resonance amplitudes also show a high-temperature transition, but those data sets also show a number of small amplitude transitions which impinge on this one, complicating the analysis. Those data yield somewhat smaller energies near 1.2 eV but with larger error bars and visibly poorer fits. Note that the data for the Alpha Aesar sample have a small increase between 400 and 500 K that matches the 0.4 eV obtained for T_{Se} donor ionization in the microwave results, adding to our confidence in the assignment of ionization versus site change for that energy.

An open question regarding the behaviour of Mu in ZnSe is the lack of observation at higher temperatures of the Mu^0 signal from the T_{Zn} acceptor site, especially between 350 and 600 K. This site is expected to be the lowest energy location for the neutral charge state and should have a larger hyperfine constant than the Mu^0 donor at T_{Se} [10]. A direct correlation between a signal from this missing Mu^0 acceptor state and the data of Fig. 3 would confirm the tentative acceptor ionization assignment put forward here for the high-temperature growth of diamagnetic amplitude. There is a significant missing fraction in the relevant temperature region. Identification of this missing state and characterization of its dynamics remains one of several important pieces of unfinished business related to Mu in ZnSe.

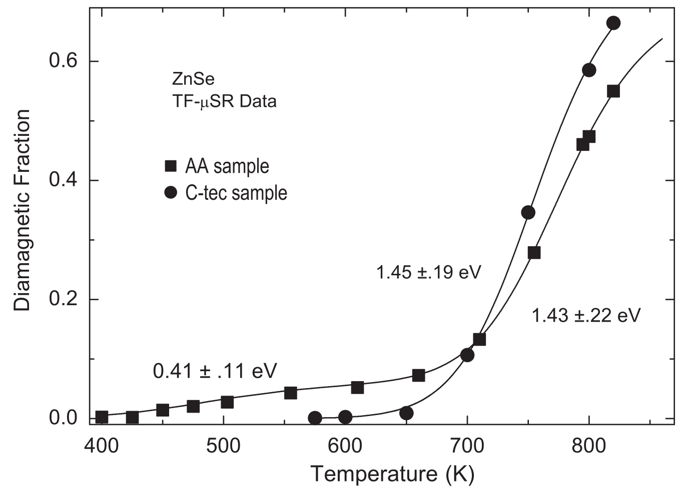

Fig. 3. High-temperature growth of the prompt diamagnetic amplitude in ZnSe offers an alternative signature for Mu acceptor ionization that results in Mu defect levels in agreement with results for other materials. Data from Ref. [7].

A second unanswered question is which process is related to the decrease in diamagnetic amplitude in the 60–100 K region for which we have offered an alternative explanation. If this is thermal loss of a electron from Mu^-, as proposed in Ref. [2], then one would expect that transition to trigger an electron capture/loss cycle which would cause depolarization that would be detectable in a magnetic field applied along the initial muon polarization direction. This charge cycle would likely involve only muons in the T_{Zn} site and the Mu^0 and Mu^- charge states at that location. Thus, there are experimental checks that may help define the relevant processes in that low-temperature region, as well as at higher temperatures. The temperature range between 100 and 200 K may then constitute a second region in which to search for the microwave resonance signal due to Mu^0 at T_{Zn} depending on results of the longitudinal depolarization measurements.

3. Conclusions

In conclusion, we have identified the Mu_{II} signal in ZnSe as coming from an immobile neutral muonium at the T-site with Se nearest neighbours. We have measured the ionization energy of this Mu donor state to be 0.40(±0.07) eV and expect the adjustment to reach the thermodynamic donor level for Mu in ZnSe to be relatively small. We propose the high-temperature growth of diamagnetic amplitude in ZnSe as the primary Mu acceptor ionization transition, and suggest an alternative explanation for the low-temperature Mu charge dynamics that implied an acceptor level high in the gap. This alternative model would yield Mu defect levels that fit nicely with the defect pinning results for muonium in other semiconductors [5], and more generally in

Please cite this article as: R.L. Lichti, et al., Physica B (2009), doi:10.1016/j.physb.2008.11.161

agreement with theoretical expectations of a 'universal' energy for the equilibrium $(+/-)$ charge-state transition level for hydrogen offered in Ref. [8].

Acknowledgements

This research was supported in part by the U.S. National Science Foundation, the RA Welch Foundation, the Natural Sciences and Engineering Research Council of Canada, the European Commission under the Sixth Framework Programme, and by FCT-Portugal.

References

[1] R.C. Vilão, et al., Phys. Rev. B 72 (2005) 235203.
[2] R.C. Vilão, et al., Phys. Rev. B 77 (2008) 235212.
[3] Ç. Kiliç, A. Zunger, Phys. Rev. B 68 (2002) 73.
[4] C.G. Van de Walle, Phys. Stat. Sol. (b) 229 (2002) 221.
[5] R.L. Lichti, K.H. Chow, S.F.J. Cox, Phys. Rev. Lett. 101 (2008) 136403; R.L. Lichti, K.H. Chow, S.F.J. Cox, Physica B, this issue, doi:10.1016/j.physb.2008.11.164.
[6] R.C. Vilão, et al., this issue, doi:10.1016/j.physb.2008.11.144.
[7] R.C. Vilão, Ph.D. Dissertation, University of Coimbra, 2007, unpublished.
[8] C.G. Van de Walle, J. Neugebauer, Nature (London) 423 (2003) 626.
[9] O. Madelung (Ed.), Properties of Semiconductors, second ed., Springer, Berlin, 2003.
[10] C.G. Van de Walle, P.E. Blöchl, Phys. Rev. B 47 (1993) 4244.

Please cite this article as: R.L. Lichti, et al., Physica B (2009), doi:10.1016/j.physb.2008.11.161