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Delayed electron capture and Mu^- formation in ZnSe

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ABSTRACT

We have investigated a single crystal of the wide bandgap II–VI semiconductor ZnSe. The sample was highly resistive due to heavy compensation of this n-type semiconductor. In low transverse fields, clear signs of conversion from a paramagnetic to a diamagnetic fraction are observed, at about 60 K. The data are interpreted as delayed electron capture by paramagnetic muonium, forming the negatively charged state Mu^-. The implications with respect to the electrical activity of muonium, and by analogy hydrogen, in this semiconductor are analyzed.

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1. Introduction

Hydrogen states in semiconductors have been extensively discussed in recent years, in particular in connection with the theoretically predicted universal constancy of the +/− charge state conversion level [1,2]. From the experimental side, muon studies using muonium as an analogue of hydrogen were the main source of information. In this context, the determination of the 0/− acceptor level in these semiconductors is of particular interest. We have recently presented rf-μSR measurements on ZnSe and ZnS which support the formation of negatively charged muonium in ZnSe and ZnS [3], and we have related the thermal instability of this state to its ionization to the conduction band, thus extracting the position of the acceptor −/0 level in ZnSe and ZnS if this association is valid. We now present transverse-field μSR measurements which strongly support the formation of negatively charged muonium in ZnSe.

The determination of the −/0 acceptor level is difficult, since the most common methods using implanted protons or implanted muons usually do not observe the negatively charged state, except in heavily doped samples [4,5], where the neutral state becomes unobservable due to fast charge-exchange processes. However, the presence of the acceptor configuration has often been proposed based upon physical arguments [6,7].

2. Experimental details and results

2.1. Experimental details

Standard transverse field μSR measurements [8] have been undertaken at the Laboratory for Muon Spectroscopy at the Paul Scherrer Institut, Switzerland, while the radio-frequency (rf) muon-spin resonance experiments were carried out at the ISIS Facility, Rutherford Appleton Laboratory, UK.

A monocrystalline sample, obtained commercially from Crystec (Ctec) of ZnSe was used. The room temperature resistivity was measured to be $\rho = 7 \times 10^9\,\Omega$cm. The high resistivity arises from an almost complete compensation of donors and acceptors, leaving only a small amount of surplus dopants of one kind to provide the mobile carriers (estimated to be in the order of $10^{10}\,cm^{-3}$ or below in this sample). ZnSe is known to present a strong tendency to grow n-type and a resistance to p-type doping [9,10]. Hence, it is reasonable to assume n-type conduction in this sample.

2.2. Delayed formation of the diamagnetic fraction

Fig. 1 shows the temperature dependence of the diamagnetic fraction in ZnSe, as observed by rf-μSR (Ref. [3]) and TF-μSR at 0.001 T. This is observed to grow up to 100% in the temperature region 30−60 K, in the rf measurements. However, in the transverse field measurements the corresponding growth occurs at a higher temperature and the maximum observed fraction does not exceed 25%. This is a clear sign of delayed formation of the diamagnetic fraction.

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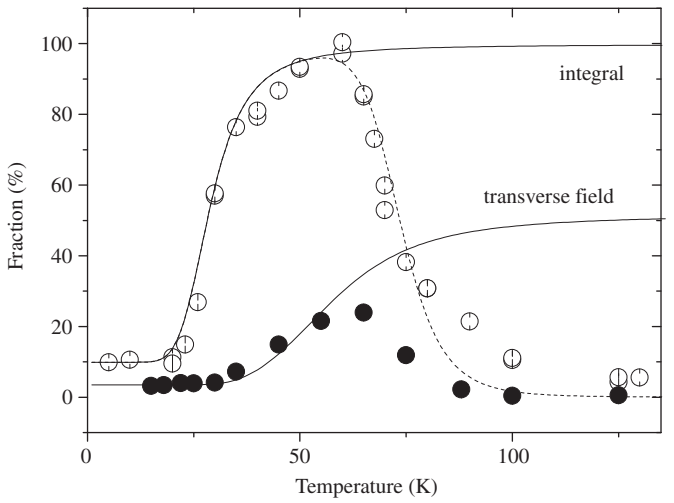

Fig. 1. Temperature dependence of the diamagnetic fraction in ZnSe, as seen by integral rf-μSR measurements (open circles) and by transverse-field ($B = 1$ mT) measurements (closed circles). The solid lines are fits assuming delayed electron capture at muonium to form Mu^- (for details of the model, see text). The strong reduction of the fraction due to dephasing in the transverse field measurement is clearly seen. The thin dotted line indicates the onset of Mu^- ionization (loss of the second electron at the muon). Without the ionization the fraction would continue as indicated by the solid lines.

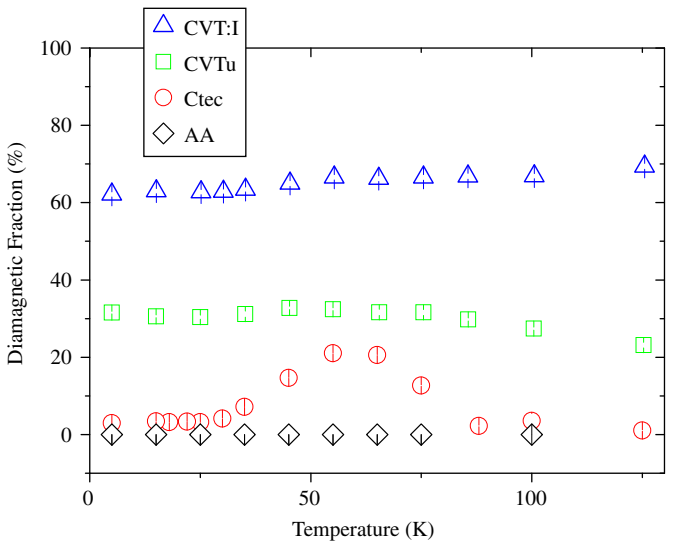

Fig. 2. Temperature dependence of the diamagnetic fraction at TF = 0.001 T, for various ZnSe samples with different free-carrier concentrations (cf. Table 1). A wide variation is observed from the nominally undoped samples (diamonds and circles) up to the iodine-doped sample (triangles).

2.3. Capture of second electron

Now, we argue that this diamagnetic state arises from the paramagnetic Mu^0 by (delayed) capture of a second electron, according to the reaction

$$Mu^0 + e^- \underset{\nu_c}{\rightarrow} Mu^- \quad (1)$$

with a capture rate $\nu_c = \sigma_c \nu_e n$, where σ_c is the capture cross section, $\nu_e = \sqrt{(3kT/m_e^*)}$ is the thermal velocity (m_e^* is the effective electron mass), and n is the density of conduction electrons. The main temperature dependence of the capture rate arises from the activation of the donors and we have kept only this Arrhenius part in the formula summarizing everything else in a constant prefactor ν_c^0. We set

$$\nu_c = \nu_c^0 \exp(-E_a/k_B T) \quad (2)$$

where E_a represents the activation energy of the donors.

We have observed a pronounced sample dependence of the diamagnetic fraction observed in TF-μSR at $B = 0.001$ T (Fig. 2). Table 1 summarizes as well the results of basic transport (resistivity and Hall-effect) and μSR measurements on three other samples: a nominally undoped sample used in previous experiments [11], obtained commercially from Alfa Aesar (AA), and two samples grown by the chemical-vapor-transport (CVT) method, which were kindly provided by the Leibniz-Institut für Kristallzüchtung, Berlin. The chemical agent used in the CVT growth was iodine (a donor in ZnSe). Iodine is known to be incorporated in these samples, either deliberately (CVT:I sample) or not (CVT sample) [12].

From Fig. 2 and Table 1, a clear correlation of the diamagnetic fraction with the (net) concentration n of free electrons is apparent: the diamagnetic fraction gets larger for the samples with larger n.

We have also measured two other pieces of the Ctec sample subject to different treatments: (i) one piece was annealed for 100 h at 900 °C in a zinc atmosphere, thereby reducing the concentration of compensating zinc vacancies [9]—the tf-μSR diamagnetic fraction here was observed to be 26% at 75 K, increasing as expected from the reduced compensation; (ii) another piece of the Ctec sample was annealed in a 16 atm H_2 atmosphere at 500 °C for 22 h, leading to the incorporation of hydrogen, which is expected to compensate and most possibly passivate existing donors. The tf-μSR diamagnetic fraction was observed to drop below 6% at 55 K.

Table 1
Room temperature resistivity ρ, free-carrier concentration n, and diamagnetic fraction f_d at 55 K, 1 mT, for the ZnSe samples investigated.

Sample	ρ (Ω cm)	n (cm^{-3})	f_d
AA	$\geqslant 10^{11}$	Below 10^{10}	1.6(1)%
Ctec	7×10^9	Below 10^{10}	21(1)
CVT	1×10^5	3×10^{12}	32(1)
CVT:I	1×10^4	1×10^{13}	62(1)

These evidences strongly support the formation of negatively charged Mu^- state from the paramagnetic state as the best candidate process justifying the growth of the diamagnetic fraction in the temperature region 25–50 K, according to reaction (1).

2.4. Analysis

In Ref. [3] we have analyzed the integral rf-data in Fig. 1 assuming process (1) (Eq. (2) in that reference) and have obtained for the capture rate the following parameters: $\nu_c^0 = 400 \times 10^6\ \mu s^{-1}$ and $E_a = 17$ meV. In transverse field measurements, the time distribution of the conversion from one state to another state with a different precession leads to a dephasing and the amplitude of the second state is reduced by the factor

$$f_d = \frac{1}{\sqrt{1 + (\Delta\omega/\nu_c)^2}} \quad (3)$$

where $\Delta\omega$ is the difference in (angular) frequencies of the converting states and ν_c is the capture rate. In the present case we consider the conversion from isotropic muonium to diamagnetic muon and therefore four frequency differences have to be

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taken into account. In the present low field case one has

$$\Delta\omega_{12} \approx \Delta\omega_{23} \approx \tfrac{1}{2}\gamma_e B$$
$$\Delta\omega_{14} \approx \Delta\omega_{34} \approx 2\pi A \quad (4)$$

each with an amplitude $\approx \frac{1}{4}$. γ_e is the electron gyromagnetic ratio, B the applied field, and A the muonium hyperfine constant. The contributions to the diamagnetic fraction from 1–4 and 3–4 transitions are rather small because of the large frequency difference. We have fitted the transverse field diamagnetic fraction (Fig. 1) with this conversion model. There are no extra parameters in this fit in addition to those of the capture rate for which we have already values from the fit to the integral rf data. With exactly these parameters, the fits to the transverse field data were not completely satisfactory. A reasonable fit (see Fig. 1, transverse field curve) was obtained by changing the pre-exponential factor of the capture rate from 400 to 1600 μs^{-1} but keeping the activation energy to its value of $E_a = 17$ meV.

We relate this change of the pre-exponential factor to the lifetime of the radiolytic electrons created during the passage of the muon to its stopping site. The importance of the radiolytic electrons has been discussed already in Ref. [3], in order to explain the rather large capture rates observed experimentally. In the integral rf measurements, the presence of the radiolytic electrons is integrated over the muon life time (2.2 μs^{-1}), whereas in the tf measurements the relevant time is $1/\Delta\omega$ (≈ 11 ns for $B = 1$ mT). Thus, if the radiolytic electrons recombine on an intermediate time scale, their concentration will be larger for the tf than for the rf (integral) experiments. Electron–hole recombination lifetimes in the order of 100 ns are not unreasonable for the present sample and temperature conditions (Ref. [13]).

From Eqs. (3) and (4), the diamagnetic fraction is thus expected to present an approximate inverse dependence with applied field. In Fig. 3, we present two such transverse-field dependence curves, for two different temperatures, together with the simulations using Eq. (3) with the parameters obtained from the tf-μSR measurements ($E_a = 17$ meV and $\nu_c^0 = 1600\,\mu s^{-1}$). The 75 K curve was divided by a factor 4 since at this temperature there is already a big loss of the diamagnetic Mu^- fraction due to ionization. This is an over-simplification, particularly for the smallest fields. But the sensitive field dependence as expected from the dephasing is clearly seen.

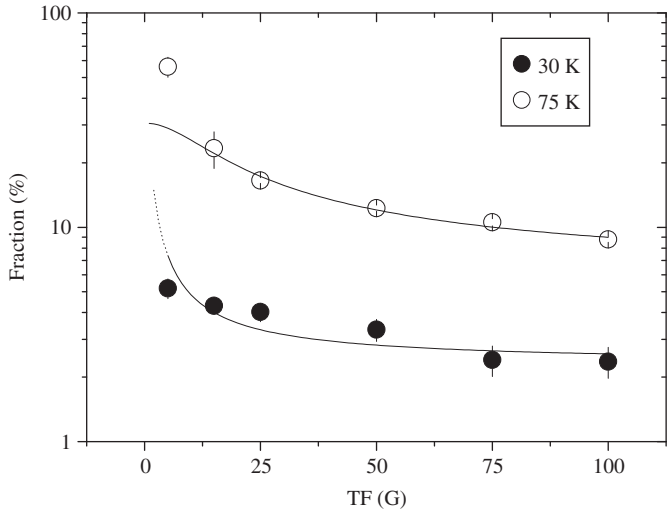

Fig. 3. Dependence of the diamagnetic fraction in ZnSe with applied transverse field, for two different temperatures. The line is a simulation with a delayed capture model, as described in the text.

3. Discussion and conclusions

As mentioned in the Introduction, the observation of negatively charged muonium is by itself an uncommon feature, particularly in highly resistive samples such as those used in this work. However, this finding bears much significance from the view point of the influence of hydrogen in the electrical properties of ZnSe. In particular, the ionization of Mu^- is bound to provide the position of the acceptor level 0/− in the bandgap. The difficulty from an experimental viewpoint is accurately identifying the transition process.

In Fig. 1, it is clear that the diamagnetic state we identify with Mu^- becomes thermally unstable above 60 K, which is visible by a drastic reduction of the diamagnetic fraction above this temperature. The simplest interpretation of this thermal instability, assuming that the hole concentration is negligible in this n-type material, relates it to the thermal ionization of the second electron to the conduction band. This was analyzed in detail in Ref. [3], and the obtained fitting curve with Eq. (4) in that reference is included in Fig. 1 as reference. The acceptor level of hydrogen in ZnSe was thereby proposed to be at 0.1 eV below the bottom of the conduction band in ZnSe. However, at the present stage of this research, other dynamical hypothesis such as hole capture and/or site change cannot be excluded.

In Fig. 4 we represent the known +/0 donor levels from the literature [14] and the ZnSe and ZnS 0/− levels proposed in Ref. [3], in a band diagram for a group of Zn and Cd semiconductor compounds. This band diagram was built, following Ref. [15], by addition of the experimental band gaps taken from Ref. [16] to the valence band offsets calculated in Ref. [17] placed in an absolute scale using the position of the valence band of ZnO with respect to vacuum calculated in Ref. [18]. This diagram allowed us to propose that the electron affinity of interstitial muonium (i.e. the ionization energy measured here plus the conduction band edge energy) be placed at about 3.1 eV in the vacuum scale (dashed line in Fig. 4). This was discussed at length in Ref. [3]. In an accompanying paper [19], we discuss the problematics associated

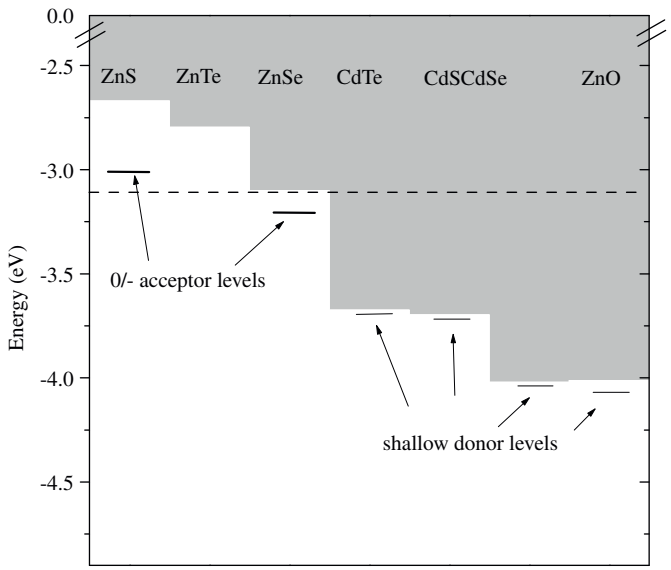

Fig. 4. Conduction band alignments for the cadmium chalcogenides and the zinc chalcogenides and oxide (adapted from Ref. [15], see text) together with proposed 0/− acceptor levels for ZnSe and ZnS (Ref. [3]) and the shallow donor levels from the literature (Ref. [14]). The dashed horizontal line indicates the proposed approximately constant value of the muonium electron affinity ($E_A \approx 3.1$ eV) in these materials.

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with this interpretation, when confronted both with high-temperature rf-μSR data on the Mu_{II} state, and with the theoretical considerations arising from the $+/-$ pinning model [1,20].

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