

Muonium states in $\text{Cu}_2\text{ZnSnS}_4$ solar cell material

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Abstract. We investigated bulk and thin-film samples of the quaternary p-type semiconductor $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) by μSR , in order to characterize the existing muonium signals. We find that the majority of the implanted muons form a diamagnetic state broadened by an interaction with the Cu nuclear moments, which we interpret as Mu^+ bound to sulphur. A paramagnetic fraction is also present at low temperatures and the ratio between the two muon charge states, Mu^+ and Mu^0 , varies between 20 and 40% prior to the onset of muon diffusion, which occurs at around 150 K. The fraction of Mu^0 is found to be sensitive to the defect content of the sample. The paramagnetic fraction has two different contributions and their origin is discussed and related with the muon role as a probe for charge carriers in the material.

1. Introduction

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a p-type semiconductor based on earth-abundant elements and with a band gap energy of 1.5 eV, which is near the optimum value for application in solar cells. The low cost and low environment impact of its component elements make it an advantageous solution for solar cells. Power conversion efficiency of solar cells based on CZTS has reached 8.4% [1] and was observed to surpass 12% when incorporating Se [2], but these values are still significantly below the aimed 15-20% efficiency range needed to be a serious competitor in thin film solar cell technology. Further progress depends on a deeper understanding of the electrical properties of the devices p-n junctions. The non-stoichiometric compositions required for the increase of the solar cell efficiency have a huge influence on the density of defects. The edges of both valence and conduction bands are affected by these changes and, consequently, also the radiative and non-radiative channels [3]. This research effort would greatly benefit from additional information on the local charge carrier dynamics.

Structurally similar I-III-VI₂ solar cell materials such as CuInSe_2 and CuInS_2 were studied by μSR by our group [4, 5, 6, 7] and it was found that the major fraction of the muons are



in a diamagnetic state, most likely Mu^+ , bound to anion S or Se. At low temperatures, a small portion of the signal (5 to 10%) is missing. Repolarization experiments showed that this missing fraction is due to a paramagnetic center Mu^0 with a hyperfine interaction consistent with neutral muonium in a interstitial position [8, 9]. Linewidth analysis suggested that Mu^+ is at an anti-bonding position close to S (or Se) [4]. Muonium is a pseudo-isotope of hydrogen and μSR results should be compared with theoretical calculations for the isolated hydrogen. First-principles total-energy calculation for hydrogen impurities in CuInSe_2 [10, 11] concluded that H^+ takes up the Cu-Se bond center position, whereas H^0 and H^- take up the tetrahedral interstitial site next to In. Hydrogen creates a negative-U center in these compounds, i.e., the neutral state is never stable and in a p-type material it is expected to be in H^+ charge state.

Our goal in this work is to characterize and compare the muonium states formed in CZTS both in bulk and in film and discuss the information provided by the muon probe in the material. We aim not only to provide information on the hydrogen impurity in these material, but also to test the sensitivity of the muon to the properties of this new solar cell material that might be used in future studies of solar cell junctions.

2. Experimental Details

We have investigated bulk CZTS and two CZTS thin-film samples, named SF and RTP24. Photoluminescence measurements have shown a broader emission, with a much lower relative intensity, for sample SF when compared to the RTP24. This result suggests the presence of a higher number of different types of defects and also a higher total concentration of defects in sample SF.

Transverse field μSR experiments at a field of $B = 0.01$ T were performed at the Paul-Scherrer Institute, in Switzerland, at GPS and LEM[13, 12] facilities, for, respectively, bulk and thin films.

Figure 1 shows a typical time spectrum for the bulk CZTS material at low temperatures, indicating the presence of a small, fast relaxing component in addition to the main diamagnetic signal. The same general features were also observed in the time spectra for the CZTS thin films.

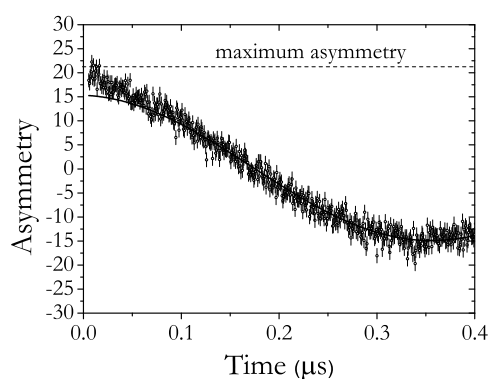


Figure 1. Time spectrum of bulk CZTS at $T = 5$ K, in transverse geometry ($B = 0.01$ T). The solid line is a one-component fit with a Gaussian-damped cosine function. The deviation at initial times indicates the presence of a fast relaxing component. A missing fraction is also apparent.

All the asymmetry data were analysed with Wimda software [14] considering a two-component fit, where the main component is assumed to have a Gaussian depolarization function and the second component is described with a Lorentzian envelop:

$$A(t) = A_{dia} e^{-\frac{1}{2}\sigma^2 t^2} \cos(\omega t + \phi) + A_{fast} e^{-\lambda t} \cos(\omega t + \phi) \quad (1)$$

where σ and λ are the Gaussian and Lorentzian depolarization rates, respectively. The frequency ω and the phase ϕ were assumed to be the same in both components.

In dynamic situations where the muon is diffusing, the Gaussian envelope was substituted by a Abragam depolarization function given by

$$P(t) = \exp \left\{ -\sigma^2 \tau_c^2 \left[\exp \left(-\frac{t}{\tau_c} \right) - 1 + \frac{t}{\tau_c} \right] \right\} , \quad (2)$$

where τ_c is the correlation time.

In thin films, a sample size correction was used in addition to silver calibration for an accurate determination of muonium fractions.

3. Results and Analysis

The dominant feature of the spectrum of bulk CZTS is a diamagnetic signal (Fig.1). At low temperatures, it accounts to about 60 % of the total μ SR signal. The depolarization rate σ of this signal is constant below 150 K with an average value $\sigma = 0.12 \mu\text{s}^{-1}$. This value is similar to the value $\sigma = 0.14 \mu\text{s}^{-1}$ found in $\text{CuInS}(\text{Se})_2$ chalcopyrites [4] and is consistent with nuclear dipolar broadening caused by Cu nuclear moments when the muon is at the Cu-S bond axis, close to the anion. We therefore assign this component to diamagnetic muons bound to the anion S and call it Mu_S^+ .

The depolarization rate σ of the diamagnetic signal is seen to decrease above 150 K, which is interpreted as motional narrowing due to the onset of muon diffusion. The motional narrowing region was analysed using the Abragam depolarization function, fixing σ at the low temperature value. An Arrhenius plot of the hop rate $\nu = 1/\tau_c$ obtained from this analysis is displayed in Fig.2, yielding an attempt frequency $\nu_0 = 1.1 \times 10^7 \text{ s}^{-1}$ and an activation energy of 60 meV. Comparing with the $\text{CuInS}(\text{Se})_2$ data [4], the onset of muon diffusion occurs at a lower temperature and with a lower activation energy in this family of compounds. The attempt frequency is also smaller. The reason for these differences is unclear. In $\text{Cu}_2\text{ZnSnS}_4$ the cations are, in average, lighter than in $\text{CuInS}(\text{Se})_2$ and it is possible that the lattice is less rigid and the muon potential well at low temperatures is wider and less profound. However, additional studies are needed to identify the parameters affecting muon mobility in CZTS samples.

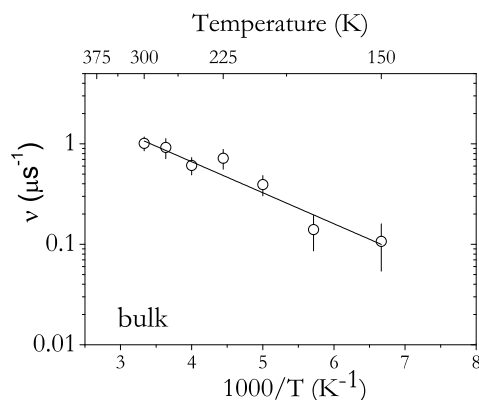


Figure 2. Arrhenius plot of the hop rate ν in the region of motional narrowing for bulk CZTS in transverse field. The straight line is a fitting to an activated hop rate and yields a pre-exponential factor $\nu_0 = 1.1 \times 10^7 \text{ s}^{-1}$ and an activation energy of 60 meV.

At early times in the spectrum (Fig.1), a fast relaxing component is seen. The value of the relaxation at low temperatures, $\lambda \sim 3 \mu\text{s}^{-1}$ is about 20 times larger than the nuclear dipolar broadening and clearly indicates an interaction of the muon with an electron to form muonium. This relaxation shows a rapid increase above 200 K (Fig.3).

A missing fraction is also apparent in the spectrum which is attributed to the dephasing caused by a muonium precursor [15, 22]. The temperature dependence of the various fractions is presented in Fig.4 for the bulk sample. At room temperature only the diamagnetic fraction survives.

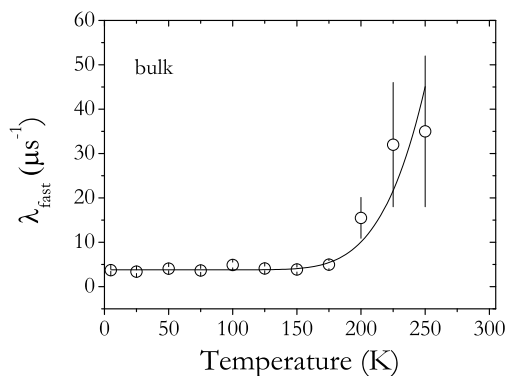


Figure 3. Temperature dependence of the relaxation rate of the paramagnetic component, in a transverse field of $B = 0.01$ T. The line is a fit with an Arrhenius activated function, yielding an activation energy of $0.16(3)$ eV.

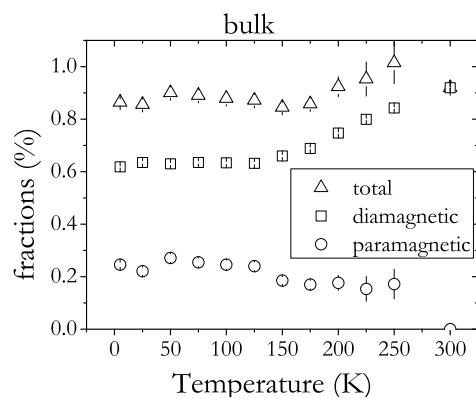


Figure 4. Temperature dependence of muonium fractions in bulk CZTS, in transverse geometry ($B = 0.01$ T).

The results in the CZTS thin films follow the same general trends described above for bulk, namely concerning the values of σ and λ at low temperatures and their temperature behaviour. The main difference is the relative fraction of the various components below 150 K. A separation of the two non-diamagnetic components is difficult due to fitting uncertainties and therefore we will represent these two paramagnetic fractions together and call it the muonium fraction f_{Mu} . However, we have to keep in mind the possibility that they play different roles in the behaviour of f_{Mu} .

Figure 5 shows the muonium formation probability f_{Mu} as a function of temperature for bulk and for the two thin films, SF and RTP24. Above 150 K, f_{Mu} follows a similar trend for the three samples: f_{Mu} decreases until it disappears at around room temperature, indicating that muonium becomes unstable. However, below 150 K f_{Mu} is clearly different for the various samples. In both thin films f_{Mu} is lower than the bulk value, being smaller for SF, the film with higher defect concentration. The muonium formation probability is therefore sample dependent and is smaller in samples with higher defect content. Interestingly, the same observation was reported in CdS and Si single crystal samples[15] with very different final muonium states. In a ZnO thin film, no muonium signal was observed[16], in contrast with bulk behaviour [17] and this was also attributed to a higher defect/impurity concentration in the thin film as compared to bulk.

4. Discussion and Conclusions

The observation that the formation probability of the muon bound state is sensitive to the defect content of the sample indicates that this quantity is sensitive to interactions occurring during the muonium formation process. In order to interpret the information conveyed by this quantity

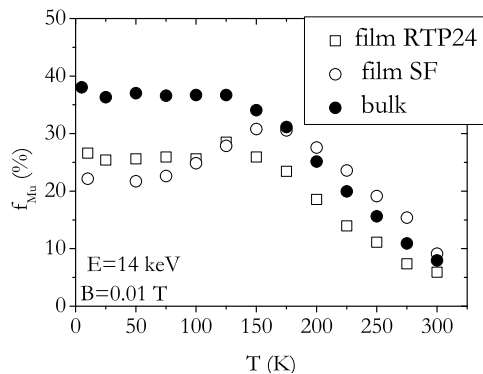


Figure 5. Temperature dependence of the Mu fraction in CZTS at $B = 0.01$ T for bulk and for two different thin films. The implantation energy was $E = 14$ keV for the thin films.

it is important to discuss the origin of the two contributions for the paramagnetic fraction: the missing fraction and the fast relaxing component.

As mentioned in the introduction, a missing fraction is observed in similar systems [4] and is known to correspond to a deep muonium state in an atomic-like configuration. We therefore assign the missing fraction to a neutral state thermalizing at an interstitial position, Mu_I^0 .

The origin of the fast relaxing component is less clear and can be attributed to different mechanisms. One possibility is that it corresponds to unresolved lines [18, 19, 20] due to muonium formed at a donor configuration, bound to the anion S, which ionizes to form Mu_S^+ :



In this hypothesis, the observed relaxation $\lambda \sim 3 \mu s^{-1}$ at low temperatures (Fig 3) corresponds to the hyperfine interaction of the paramagnetic state. It should be noted that in p-type $CuInSe_2$ a frequency shift of the diamagnetic line was observed in high transverse magnetic field and interpreted as a neutral state with a hyperfine interaction of 3 MHz [7].

An alternative scenario is that the fast relaxing component corresponds to a delayed muonium formation at an acceptor configuration, i.e., in an interstitial position. If the average time τ for muonium formation is large compared with the period of muonium precession, i.e., if $\omega_{Mu}\tau \gg 1$ there is a coherence loss. In this case, the relaxation rate could be interpreted as a muonium formation rate $1/\tau$ [21], which would yield a muonium formation time of the order of $\tau = 0.3 \mu s$. Two different mechanisms can be envisaged for delayed muonium formation, an electron capture or an electron loss, depending on whether we interpret the diamagnetic component as Mu^+ or Mu^- , respectively :



Muonium is expected to create a negative-U center in this family of compounds [11] and since the sample is p-type, the Mu^+ state is predicted to be more stable than Mu^- . The diamagnetic component is therefore interpreted as being mainly Mu_S^+ but it cannot be ruled out that it includes a contribution of Mu_I^- . None of processes 3, 4 or 5 can be excluded based on the existing information. Thus, the fast relaxing component of the μSR signal may be assigned either to a hyperfine interaction of the muon at the stable anion-bound position, Mu_S^0 , or to a delayed muonium formation at the metastable interstitial position Mu_I^0 .

All these observations are consistent with a picture similar to one presented before [15, 22] for muonium formation in semiconductors. In this picture, the muon comes to rest at an interstitial position in the unrelaxed lattice, either as Mu_I^+ , Mu_I^0 or even Mu_I^- . The initial formation probabilities of these different charge states are strongly sample- and temperature dependent.

The interstitial bare muon, Mu_I^+ , will move to the more stable Mu_S^+ site or eventually converts to Mu_I^0 (process 4). The Mu_I^- , if formed, is unstable. In order to convert to Mu_S^+ it has to undergo an intermediate step (process 5) and this is likely to be a delayed process. The neutral Mu_I^0 is not stable either, but lives long enough to leave a signature in the μSR signal. The general behaviour of the neutral state may be described as follows: the lattice reacts to the presence of the impurity and starts to relax. The muonium tends to migrate, but along its path its energy level may come close to the conduction band and interact with electrons. The final result of this interaction may be either a drift to the more stable bonded position, as Mu_S^0 or Mu_S^+ , or a return to the metastable interstitial position as Mu_I^0 . At this intermediate stage, the fate of the muon is likely to be very sensitive to the presence of defects. On one side, the muon interaction with electrons depend on the number of electrons available in the conduction band and on the competition with electron-hole recombination processes. On the other end, defects may affect the muon transition path, favoring the transition to the donor configuration, close to S. The diamagnetic fraction, assigned to muons at the more stable site, is found to be larger in a sample with higher defect content, in agreement with findings in systems like CdS and Si [15], with very different final muonium states. The sensitivity of the muon probe on the local electronic properties of the material depends on the details of the processes occurring during the muonium formation stage. In particular, the dependence of the muonium formation probability on the local charge carrier density and dynamics, opens the possibility to use it as a probe in future studies of CZTS-based solar cell junctions.

Acknowledgments

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