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Low-energy muon [LEM] study of Zn-phthalocyanine and ZnO thin films

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ABSTRACT

Implantation of low-energy muons in zinc-phthalocyanine (ZnPc) thin-films leads to the formation of muoniated radical states, the fast decaying of the μSR signal at low fields being a clear indication of muonium formation. The formation probability of these paramagnetic states is independent of the implantation depth and amounts, as in the bulk, to approximately 100% of all muons. In these molecular crystals the formation of muonium is a highly local effect and is fairly independent of crystalline structure and defects in the sample. In contrast to that, in vapour-grown ZnO films the paramagnetic signal known from bulk experiments is not observed, even for the deeper implantations. We suggest that in this case muonium is not formed due to the low concentration of free electrons. In these strongly distorted films, electrons are captured at defects and are not available for muonium formation.

1. Introduction

Organic semiconductors are promising candidates for applications in spintronics, i.e. for the integration of spin-transport based-devices with the current electronics technology [1]. They exhibit long spin diffusion lengths when compared to their inorganic counterparts, and have been recently shown to be able to possess giant magnetoresistance at room temperature [2] and to be well suited for use in spin-valves [3].

Phthalocyanines are an example of non-polymeric organic semiconductors used in electronic devices and can occur in many forms which differ by the central atom (Zn, Cu, Mg, and Co) [4]. The inorganic semiconductor ZnO is used as a transparent electrode for solar cells and is also discussed in connection with spin injection devices.

All these devices are layered structures built up of thin films with thickness in the order of 10 to some 100 nm. From this point of view it is clear that they can be studied with muons only with the recently developed low-energy muon (LEM) beams [5,6]. The depth resolution provided by LEM offers an ideal method to investigate these structures [13]. Before the complex layer structures of these devices can be investigated, knowledge of the μSR signal of the individual layer is required. The purpose of the present investigation is acquiring that information.

Previous studies have been performed in bulk, both for ZnPc [7–9] and for ZnO [10,11] using the μSR technique. In bulk ZnPc the positive muon was found to react with the molecule, forming three muoniated radical states of paramagnetic origin (two states with hyperfine interactions in the range 110–150 MHz and a third state with about 25 MHz). In bulk ZnO, the implanted muon forms a shallow donor state with a weakly bound electron and a reduced hyperfine constant (few hundreds of kHz).

2. Experimental details

A zinc-phthalocyanine (ZnPc) thin film with 300 nm thickness and a ZnO thin film with 200 nm thickness were investigated. The samples were nominally undoped and were grown on a Si substrate with an area of $5 \times 5\,cm^2$. The μSR measurements were performed at the Swiss Muon Source, Paul Scherrer Institut, Switzerland, using the LEM instrument. Positive muons were implanted with initial spin polarization parallel to the plane of the film. The implantation energy of the muons was varied between 2.5 and 15 keV for the ZnPc film and 2.5–20 keV for the ZnO film. TRIM simulations (version SRIM-2003.26) [12] show that the muon implantation depth in ZnPc covers a region between around 40 and 250 nm in ZnPc. The μSR measurements were performed in transverse field (TF) geometry, with the field perpendicular to the plane of the film. For ZnO the measurements were performed in a temperature range between 5 and 50 K, whereas in ZnPc the temperature was fixed at 200 K.

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3. Results

3.1. ZnPc thin film

The investigation of the ZnPc thin film was performed using an applied TF of 10 G. At this low field, the Zeeman splitting of the triplet muonium state corresponds to a precession frequency of 14 MHz and is approximately the same for all muonium states with hyperfine interaction much larger than this splitting (low field limit). The amplitude of this frequency corresponds to one half of the full amplitude. The remaining transitions have frequencies close to the hyperfine splitting and are not observable in this low statistic runs because of the large broadening due to the anisotropic hyperfine interaction and due to disturbances. For the same reason zero field measurements are not suitable. Note that the 14 MHz muonium signal is clearly distinguishable from the 0.14 MHz signal of the diamagnetic muon and thus allows the determination of muonium formation.

Fig. 1 shows the μSR spectrum of ZnPc with the fast decay of the asymmetry, for an implantation energy of 2.5 keV. The involved μSR frequencies (see also the maximum entropy spectrum in Fig. 2) are much higher than expected for the diamagnetic muon thus indicating muonium formation. The solid lines in Fig. 1 are fits with a frequency of 14 MHz and a Gaussian relaxation of about 40 μs^{-1}. Similar LEM time spectra and maximum entropy distributions as those of Figs. 1 and 2 were obtained at muon implantation energies of 7.5 and 15 keV, i.e., no change in the muonium fraction was observed as a function of the implantation energy. These results suggest that the muon capture in ZnPc follows the same behaviour in thin films as in bulk and is independent of the muon implantation depth.

3.2. ZnO thin film

Fig. 3 shows the μSR time spectrum of the ZnO thin film at 5 K and a TF of 100 G, for a muon implantation energy of 20 keV. The signal is purely diamagnetic, corresponding to the μ^+ Larmor precession frequency at this field, with a (Gaussian) relaxation rate of the order of 0.096 μs^{-1}. No shallow muonium signal is observed, in contrast with bulk measurements in nominally undoped samples [10,11], and with recent LEM studies on 0.33-mm thick single crystals of undoped ZnO [13]. Similar results were obtained at 10 K with different implantation energies, ranging from 2.5 to 20 keV. The results are consistent with a purely diamagnetic signal, except perhaps at the lowest implantation energies.

The measured depolarization rates of the diamagnetic signal (Fig. 4) are larger than that expected for purely nuclear dipolar broadening ($\approx 0.01\ \mu s^{-1}$) and vary slightly with implantation energy (depth) and temperature. The depolarization is larger for implantations close to the film surface than deeper inside, and increases with decreasing temperature. The somewhat high depolarization rates probably indicate a weak interaction of the muon with distant or fluctuating electron spins. In addition, the electrons from the muon track may play a role. Also, at the lowest

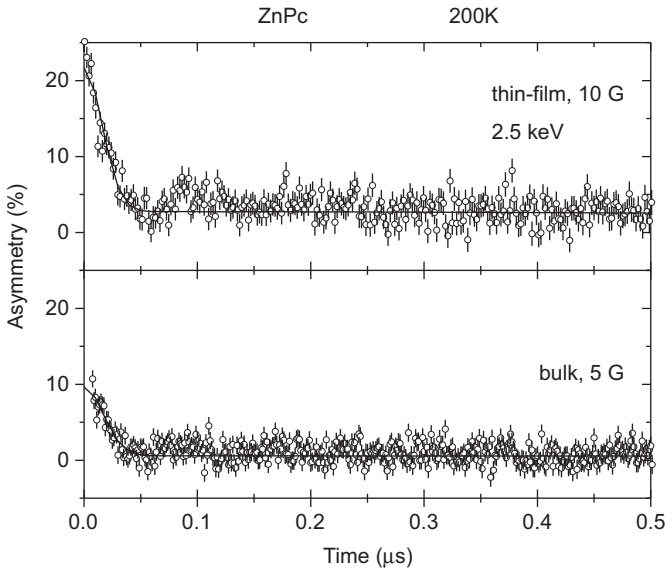

Fig. 1. Low transverse field μSR spectrum of the ZnPc thin film at 200 K with a muon implantation energy of 2.5 keV, and of bulk ZnPc at the same temperature.

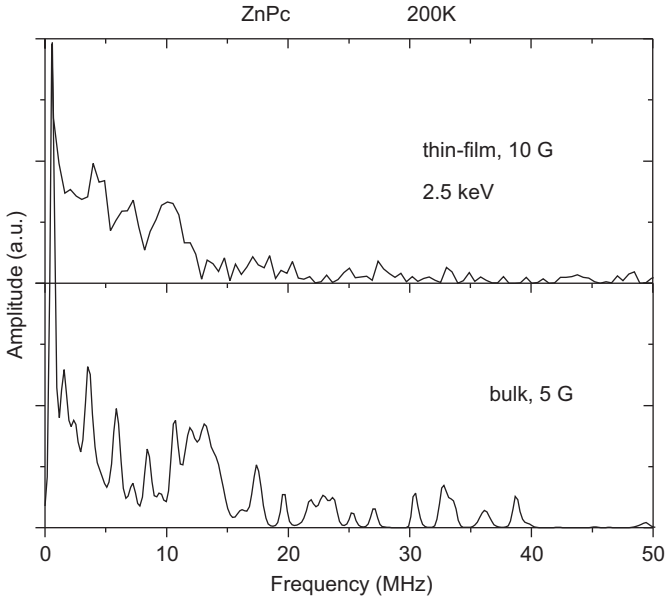

Fig. 2. Maximum entropy plot of the ZnPc data presented in Fig. 1. The spectral weight is concentrated below 20 MHz.

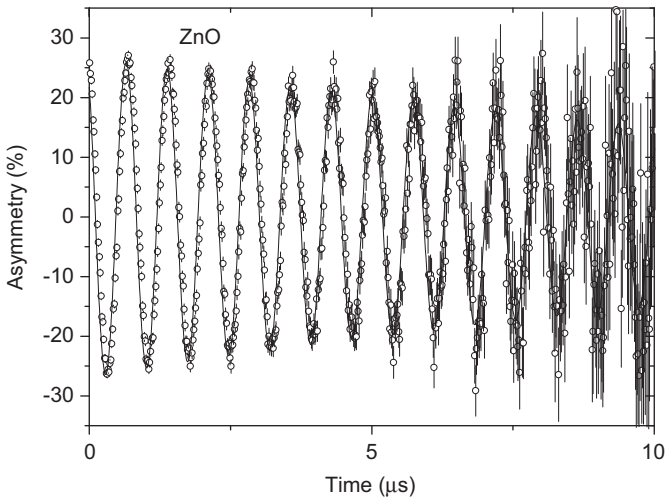

Fig. 3. μSR time spectrum of ZnO thin film at 5 K at a transverse field of 100 G (muon implantation energy is 20 keV). The solid line is a fit with a Gaussian-damped single frequency, corresponding to the Larmor muon precession frequency at the applied field, with a relaxation rate of 0.096 μs^{-1}.

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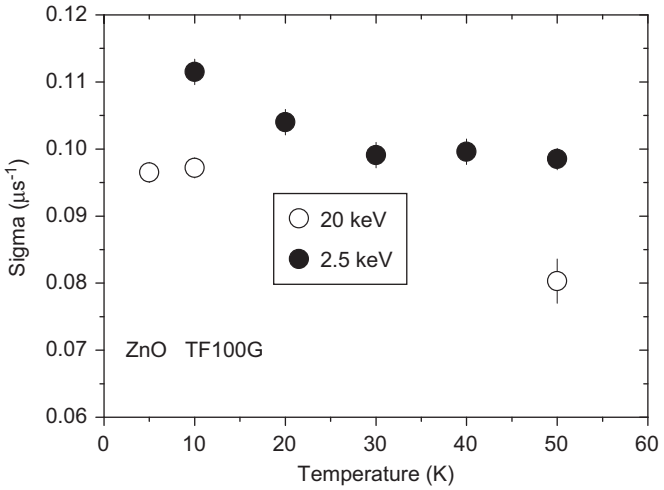

Fig. 4. Transverse field relaxation rate of the diamagnetic signal in ZnO thin film as a function of temperature, for a muon implantation energy of 2.5 and 20 keV.

implantation energies, part of the relaxation arises from back-scattering from the sample surface. Most importantly, no stable muonium is formed.

The striking differences between thin-film and bulk behaviour observed in ZnO are possibly due to the role of defects in the formation of paramagnetic states in a inorganic semiconductor. Defects are present at larger concentrations in thin-films as compared with those found in bulk, reducing the concentration of free electrons available for capture. Notwithstanding, in organic semiconductors muons form radical states by reacting with the molecule, leading to similar results both for thin films and bulk.

4. Conclusions

In this experiment, the μSR signals in vapour-deposited thin films were determined. For the organic semiconductor ZnPc the signal is the same as in bulk, originating presumably from the same radical states as in the bulk. For ZnO the situation is different, since only a diamagnetic signal is observed, the paramagnetic muonium signal known from bulk experiments being absent. We suggest that muonium is not formed in these highly distorted thin films due to reduced concentration of free electrons for capture.

Acknowledgements

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