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Probing the magnetic ground state of the DX− center in Cd1−xMnxTe:In using muon spin relaxation

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Muon spin relaxation (μSR) measurements have been made on Cd0.85Mn0.15Te:In and Cd0.86Mn0.14Te:Al. The spin glass transition region has been studied using μSR and low-temperature magnetic susceptibility measurements. Persistent photoconductivity (PPC) has been shown to exist only in the In-doped sample, the effect of PPC on the spin glass transition temperature using bulk magnetic susceptibility has also been studied, indicating the presence of bound magnetic polarons. μSR on the Al-doped sample clearly shows the spin glass transition, however, the presence of the DX center, which causes PPC when doping with In donors, perturbs the muon response. Particular attention is paid to the possibility of the DX center trapping muonium, preventing the detection of the spin glass transition. PPC does not induce a change in the muon response, however, we find continuous illumination of the sample allows the observation of the spin glass transition. We suggest that these results can be explained by assuming the presence of multiple DX centers. The muon acting as a local magnetic probe of the DX center also suggests the ground state is diamagnetic.

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The nature of the DX center in GaAs:Si, under hydrostatic pressure, and in AlGaAs:Si has been the subject of intense investigation in the last 20 years. Perhaps the most dramatic consequence of the defect is persistent photoconductivity where illumination at low temperatures produces a change in conductivity that persists at low temperatures after the illumination is removed. It is generally accepted that the DX centers are an intrinsic property of the donor impurities that can be described by a “large lattice relaxation negative U model.” In this model the neutral donor state can reduce its energy by trapping an extra electron coupled with a large bond breaking displacement of the donor atom. The DX center can be described by the charge exchange reaction

$$2d^0 \rightarrow d^+ + DX^-,$$

where $d^0$ and $d^+$ represent neutral and ionized shallow donor states, respectively. DX-like centers have also been demonstrated to exist in the II-VI compound CdTe, doped with donors from groups III and VII, both under hydrostatic pressure and when alloyed with zinc. More recently, it was shown that donor-doped CdTe alloyed with manganese also exhibited the characteristic persistent photoconductivity of a DX-like system.

One issue relating to the DX center that is still largely unresolved is that concerning its magnetic state. Equation (1) suggests that the DX− state is a singlet while the $d^0$ donor is a doublet. ESR measurements support this picture with a signal being enhanced after illuminating at low temperatures. However, high sensitivity SQUID magnetometry measurements provide no convincing evidence for a moment change upon exciting the semiconductor into a persistent photoconducting state. DC-SQUID measurements made on Cd$_{1-x}$Mn$_{x}$Te$_{1-y}$Se$_y$:In were used to infer a singlet ground state of the DX-like center, following the observation of bound magnetic polarons only after illuminating into the persistently conducting state. However, such an observation cannot be taken as unambiguous proof of a singlet ground state of the DX-like center: electrons bound to such an energetically “deep” state would be expected to be strongly localized and hence unlikely to form large magnetic polarons, even if in a doublet state. Thus, a doublet state to doublet state transition after illumination would not be inconsistent with the results of Ref. 16. In light of this unresolved feature of DX centers, we have utilized muon spin relaxation (μSR), together with bulk dc SQUID magnetic measurements, to investigate the magnetic properties of a material containing DX-like centers. We have chosen to investigate the dilute magnetic semiconductor CdMnTe (CMT) that is known to exhibit a spin glass behavior at compositions $x \geq 0.01$, with a freezing temperature that increases with increasing manganese content. Muons have been found to be a useful probe of the spin glass behavior of CMT with $x > 0.2$. We investigate samples below the spin glass percolation limit ($x < 0.2$), moreover we observe the DX center perturbing the implanted muon environment. The CMT samples were doped with either indium or aluminum atoms as the former
dopant has been shown to form DX-like centers while the latter is expected to behave only as a shallow donor level. We show that the implantation of positively charged muons, which are local probes of magnetism, is affected by the presence of these deep centers. Moreover, the μSR data provide strong evidence for the diamagnetic nature of the ground state of the defect, and for the possible existence of multiple DX centers.

Bulk single crystals of CMT doped with indium and aluminium were grown using the vertical Bridgman technique. The crystals were annealed in a cadmium atmosphere to reduce cadmium vacancies that act as compensating centers. Two n-type samples were produced for this study, one of each dopant type with the indium-doped sample (I1) having a Mn fraction of 0.15, determined by EDAX measurements, and the aluminium (A1) sample with a Mn composition of 0.14. Standard four terminal dc resistivity measurements were performed on each sample from 4–290 K to determine if the samples exhibit the PPC effect. The bulk magnetic measurements were carried out upon an Oxford Instruments (Oxford) helium 3 system modified to include a Quantum Design DC SQUID with a first-order gradiometer pickup coil configuration. This setup allowed dc susceptibility measurements to be made in the temperature range 0.350–2.5 K in a field of 10 μT, with a magnetic field of up to 0.01 T being applied upon cooling. The He^3 system also included an infrared LED operating at 940 nm, to allow for in situ illumination of the sample. μSR was carried out at the ISIS laboratory, Oxford, UK upon the beamline EMU. We operated in the “fly-past” mode due to the relatively small sample sizes. A bottom-loading OI helium 3 cryostat with a silver sample holder was modified to enable direct illumination with a LED that has a peak output of 940 nm. In particular, the LED was heat sunk to the 1 K pot to enable continuous irradiation of the sample while at low temperatures. The LED was shielded from the muon beam by a silver plate. All measurements were performed upon samples cut from the same crystal ingots that have been used for electrical and magnetic characterization.

The electrical transport data are shown in Fig. 1 for both samples, before and after illumination. Sample I1 was illuminated at 4.2 K until the PPC was saturated. The same illumination method was applied to A1, but no evidence of PPC was observed, even after an extended period of irradiation. It is obvious under the given experimental conditions that only I1 was excited into a PPC state, indicating the presence of DX centers. No centers form in A1 due to the small distortion in the lattice when doping with Al. Room temperature Hall measurements were performed, giving carrier densities of 1.1 × 10^16 cm^-3 and 2.3 × 10^16 cm^-3 for I1 and A1, respectively. Resistivity measurements indicate that the shallow donor binding energy for I1 is ~220 K and ~150 K for A1. We observe only one quenching temperature at 100 K, however, other investigations into Cd_{1-x}Mn_xTe:In^{22} and Cd_{1-x}Zn_xTe:Cl^{24} have recorded another higher quenching temperature proving the existence of more than one possible deep center, which have been theoretically predicted. It is believed that heavy doping levels of the crystals could also contribute to multiple DX states.

Figure 2 shows the bulk magnetic data of sample A1. The sample was field cooled (FC) from above the spin glass transition temperature (T_g) in 4 and 10 mT and then measured in the remnant field. The remnant field was determined to be 10 μT, by a calibration of the same sample in the temperature range 2 to 5 K in a commercial Quantum Design MPMS magnetometer. The data indicate a spin glass, with a T_g of 0.95 K consistent with a Mn fraction of x=0.14, which is in good agreement with the EDAX characterization. Our data show that the sample behaves in a similar manner to many of the wide band gap dilute magnetic semiconductors.

Figure 3 shows the results of the bulk magnetic susceptibility measurements of sample I1. The main figure shows the derivative of the susceptibility with respect to the temperature before and after illumination. The inset demonstrates the mass susceptibility of the sample before illumination. The sample was field cooled and measured in 50 μT. The inset clearly shows the spin glass transition before illumination,
FIG. 3. (Color online) Magnetic susceptibility as a function of temperature for CdMnTe:In. The main figure shows the derivative of the susceptibility with respect to the temperature before and after illumination. The inset shows the mass susceptibility before illumination.

with $T_g$ of 1.06 K, which is in agreement with the literature for a Mn fraction of $x=0.15$, confirming that I1 has a slightly higher Mn concentration than A1. The derivative of the susceptibility shows that the effect of inducing PPC appears to shift $T_g$ to 1.10 K. Previous measurements have indicated that photoinduced magnetism can make a significant contribution to the magnetic susceptibility in dilute magnetic semiconductors.\textsuperscript{16,27} The enhancement has been attributed to an increase in the number of bound magnetic polarons that are localized around donor atoms. For the case of I1 it is possible that the electrons can become localized at shallow donor impurity sites after they are photoexcited from the deep DX center. If the DX center is near Mn atoms that are part of the spin glass cluster, it is feasible that these small bound magnetic polarons will have an effect upon the spin glass freezing temperature.

We chose $\mu$SR to complement these measurements, as it is a sensitive local magnetic probe with which to investigate the spin glass transition. The muon beam is spin polarized with each muon carrying a positive charge. The pulsed nature of the ISIS facility means that approximately 500 muons enter the sample every 20 ms, all of which decay before the next pulse arrives. Electronic dipole calculations suggest the muons will sit at an interstitial site in CdMnTe, in agreement with previous work.\textsuperscript{18} Figure 4 shows a typical relaxation above $T_g$ ($T=1.5$ K) in both samples along with the fit, details of which will be described later in the paper. The first observation is that the relaxation functions required to fit the data will be different, immediately suggesting that the muon site is different in the two samples. Thus, the nature of the donor clearly has a major impact upon the muon relaxation. The specific form of relaxation for each sample did not change over the entire temperature range studied. The observed relaxation is from muonium; transverse field measurements indicate a diamagnetic muon fraction consistent with the background levels obtained for each sample, as identified in Fig. 4. The application of a 10 mT longitudinal field above the spin glass transition temperature produces starkly different results. For A1 the relaxation is partially decoupled, indicating a possible dynamic relaxation, as is expected for a material just above $T_g$. However, for I1 the sample is fully decoupled at the same temperature in the same field, indicating the importance of the In doping on the relaxation. This further suggests that the muon sites are different for both samples, indicating the importance of the DX center. The measurements described below were carried out in the zero-field configuration.

For sample A1 the data were fitted over the entire temperature range with a relaxation function $G_z(t)$ of the form

$$G_z(t) = A_{\text{Lor}} \exp(-\lambda t) + A_{\text{bg}},$$

representing a Lorentzian relaxation plus a background term. $A_{\text{Lor}}$ and $A_{\text{bg}}$ represent the initial asymmetry of the Lorentzian exponential and the background term, respectively. $\lambda$ represents the muon spin depolarization rate and the fluctuation rate that is proportional to the magnetic field distribution around the implanted muon and $t$ represents time. Figure 5 shows the depolarization rate in sample (A1) with respect to temperature, and it is clear from this that there is a subtle change in relaxation above 0.95 K, coincident with the observed spin glass transition in the bulk magnetic susceptibility shown in Fig. 2. The temperature dependence of the depolarization rate shows no change within the experimental error from 2 to 10 K. $A_{\text{Lor}}$ and $A_{\text{bg}}$ remained constant through the transition region. Much work has been carried out using $\mu$SR to examine spin glass transitions, but the work has tended to concentrate upon canonical systems. Although the Lorentzian relaxation tends to indicate dilute spin systems, none of the other expected properties were observed.\textsuperscript{28} Measurements were also carried out under constant illumination at 0.9 K, but no change in the relaxation was observed. This measurement was essential to confirm the fact that the sample A1 was not affected by subband gap radiation, it also doubled as a test, to ensure that under constant illumination, the temperature did not change. Although
magnetic measurements is shown through the spin glass transition region identified via bulk magnetic measurements (Fig. 2). This exact nature of relaxation is not normally observed for a spin glass, an unpublished study upon the dilute magnetic semiconductor Cd$_{0.95}$Mn$_{0.05}$Te has observed a similar small change in the relaxation at $T_g$. This indicates that the $T_g$ for our samples can be used as a marker for the observed magnetic properties induced by optical excitation.

The ZF data of sample II was fitted with a relaxation function of the form

$$G_z(t) = A_{Gauss} \exp\left(-\frac{t^2}{\tau}\right) + A_{BG},$$

where $A_{Gauss}$ represents the initial asymmetry of the Gaussian squared relaxation with $\sigma$ representing the depolarization rate of the decay. Initial measurements were made without illumination and the results are presented in Fig. 6 (hollow squares). The results indicate that there is no clear change in the relaxation at $T_g$ (1.05 K), and therefore suggest that the implanted muon is coupled to the DX center, which is thought to be diamagnetic. The diamagnetic nature of the DX center could mean that the coupled muonium is insensitive to the Mn clusters undergoing the spin glass transition.

We have already shown that the sample undergoes a subtle change in the bulk magnetization (Fig. 3) after illuminating until the PPC is saturated. Therefore we tried to investigate this phenomenon using $\mu$SR. The sample II was illuminated at 4 K and subsequently cooled to the base temperature in the dark. The ZF relaxation was measured in the dark; no change in the depolarization rate ($\sigma$) was detected between 300 mK and 5 K, indicating that the muons could still not observe the known contribution to the magnetic susceptibility of the photoinduced carriers. This cannot be explained by the binding of the muon to a shallow state, as no evidence was detected upon the application of a transverse field. If the muon couples to the diamagnetic negative $U$ center to form muonium, it could be insensitive to the Mn clusters and cannot be photoexcited under any conditions. Here the implanted muon is perturbing the normally well characterized behavior of a persistent photoconductor. However, there is another possible explanation based on the premise that there is more than one type of DX center, including a center that does not contribute to the PPC state. For this particular scenario it is reasonable to assume that there is a relaxation back into the ground state after an initial excitation.

To elucidate the interaction mechanism between the muon and the DX center we continually illuminated the sample while varying the temperature through the spin glass transition region. The results of this measurement are shown in Fig. 6 (solid squares), where the relaxation rates were fitted with Eq. (3). The data show a major change in the depolarization rate between 1.05 and 1.1 K, in agreement with the $T_g$ obtained from the bulk magnetic measurements as demonstrated in the inset of Fig. 3. We did not see any change in $A_{Gauss}$ and $A_{BG}$ over the temperature range investigated (0.350 mK–7 K). The experimental procedure of constant illumination from the LED that was heat sunk to the 1 K pot meant we had a much shorter stability time for the cryostat, leading to reduced statistics, hence the increase in the error bar size. However, there is a discernible difference in the muon depolarization above and below the spin glass transition.

It is clear from the measured relaxation rate ($\sigma$) that the muonium coupling is intrinsic to the observation of the spin glass transition, and we suggest that the positively charged muon coupled directly to the DX$^-$ center. This leads to the conclusion that both before and after excitation into the PPC state the muons are still relaxing close to a deep center that does not detect the magnetic transition. Such a model indicates that not all the DX centers are being photoexcited into the shallow donor state and only under continuous illumination are all electrons excited out of their deeply bound state and experience the host magnetism. The muon results also suggest that some electrons are recaptured, indicating there are some centers that do not contribute to the PPC state. This recombination rate is clearly of the order of microseconds, as the muons can detect a subtle change in the local magnetic structure, as under constant illumination they are not bound to the deep state.

Park and Chadi have predicted that multiple DX centers in CdTe, ZnTe, and Cd$_{1-x}$Zn$_x$Te when doped with group VII
donors. However, the same model predicts that only one DX center will exist when doped with a group III element such as In. Leighton et al.\textsuperscript{22} have noted that the very high quenching temperature (190 K) of the PPC, they see for Cd_{1-x}Mn$_x$Te:In suggests the existence of another DX center. Indeed, much work on Al$_{1-x}$Ga$_x$As\textsuperscript{31} has suggested that centers with different binding energies can arise because of the sensitivity of the impurity center of its local atomic environment. The number of Mn ions surrounding a donor will affect the actual binding energy ($E^r$) of the DX center, which should be labeled according to the number of Mn ($i$) ions surrounding the impurity center, where $i=0, 1, 2, 3$. Using a similar statistical argument as other work,\textsuperscript{22} and assuming no Mn clustering, we find that, for $x=0.14$, the probability of obtaining a center with $i=0, 1, 2, 3$ Mn atoms as 55%, 37%, 5.7%, and 2.3%, respectively. So far the experimental evidence has only pointed to two possible deep centers, this has been predicted only a concentration of 10$^{18}$ cm$^{-3}$ DX centers can be transformed because the substitutional concentration all the electrons from all the deep centers are excited into the conduction band, however, a certain proportion of the electrons recombine to form a DX$^-$ center (in a time of approximately 10 $\mu$s), leading to a situation where constant illumination has to be applied to detect the spin glass transition. We suggest that the electrons will recombine with previously unobserved DX centers.

The large negative $U$ model also predicts that the DX$^-$ center is diamagnetic; this is a direct consequence of Eq. (1), as two electrons will pair with opposite spin. When the implanted muon is tightly bound to the DX$^-$ center, no magnetic transition is visible, however under photoexcitation we observe $T_m^e$ as the muons are no longer tightly bound. Previous work has concentrated on the influence of the deep center on the bulk magnetic properties,\textsuperscript{14,15,33,34} however, we have used a local probe (~2 nm) concentrated around the deep center to detect its magnetic properties and provide strong evidence for the diamagnetic nature of the DX center ground state. Again, it is essential to note that we have also carried out work on a sample (A1) without a DX center with nominally the same Mn concentration, indicating the importance of the deep center upon the implantation site.

In conclusion, we have evidence to suggest that muons are attracted to DX$^-$ centers and the muon becomes a local magnetic probe of the deep center. We have carried out the first local measurements, indicating the diamagnetic nature of the ground state of the DX$^-$ center. We have also proved that there is more than one possible DX$^-$ center that has before been experimentally observed and theoretically predicted, however, the previous measurements have only been able to distinguish centers that participate in PPC. From our measurements it has been possible to prove that there are more DX$^-$ centers that do not participate in the PPC effect, leading to the situation where this could possibly explain the lack of the expected photoinduced carriers.\textsuperscript{35}

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29 A. Golnik (private communication, 2005).