Mechanisms of electron polarization of shallow muonium in CdTe and CdS

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The low temperature electron polarization of the shallow muonium state in CdTe and CdS has been measured. We find a strong deviation of the polarization from that expected for paramagnetic muonium in thermodynamical equilibrium. In addition, in CdTe the observed polarization changes with the age of the sample and even an inversion of the polarization is observed upon annealing. An explanation of these findings is given in terms of two different routes for the formation of shallow muonium, i.e., formation by capture of an electron from the conduction band and formation via conversion from deep to shallow muonium. We conclude that the electron polarization is not due to the paramagnetism of the final shallow state but to the polarization buildup in the preceding stage immediately following muon implantation.

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I. INTRODUCTION

Muonium, consisting of a positive muon and an electron, is a pseudoisotope of hydrogen. Its behavior in semiconductors led to successful predictions with respect to the hydrogen impurity in the same materials, confirmed afterwards by techniques based on a direct observation of hydrogen.[1] In some II-VI semiconductor compounds like CdS, CdTe, CdSe, and ZnO a shallow muonium state is formed at low temperatures (below 40 K) with an unusually small hyperfine interaction (hundreds of kHz).[2–4] In a muon spin rotation experiment (μSR) under a transverse magnetic field, the presence of the shallow muonium state is identified by two precession frequencies, each one corresponding to a different electron spin state (up and down). The relative intensity of these lines is therefore a direct evidence of an electron spin polarization expected to build up at high magnetic fields and low temperatures. The observed polarization is also expected to reflect the electron Landé g-factor during the buildup of the polarization. Double-resonance experiments in these shallow muonium states[5] yielded absolute values of electron g-factors (1.86(2) for CdS and 1.675(25) for CdTe) which are consistent with results reported in the literature for conduction-band g-factors in these materials. The deviation from the electron g value in vacuum ($g=2.0023$) is due to the spin-orbit interaction and is particularly striking for free electrons in bulk CdTe, where the g-factor is known to be negative ($g=-1.65$).[6,7]

Muonium is a paramagnetic center and one might expect that the populations of the spin-up and spin-down electrons follow the equilibrium thermal occupation of the Zeeman levels as a function of temperature and magnetic field. For the shallow muonium state observed in GaN (Ref. 8) an imbalance in the hyperfine satellite amplitudes appeared consistent with a spin occupation probability given by a Maxwell-Boltzmann distribution of the spin-up and spin-down populations. This was interpreted as reflecting the paramagnetic equilibrium behavior of shallow muonium. Our early experiments showed that this is clearly not the case in CdTe. In particular the polarization does not reach the saturation value expected for high fields.[9] In the first measurements the saturation value was 0.3 instead of 1, and it had further decreased with the sample age.

In this work it is shown that the effect of annealing is even more drastic: a measurement on a CdTe sample, cut from the same original material but annealed at 823 K prior to the measurement, gave a negative polarization with a saturation value of -0.2. This astonishing result necessarily raises the question of whether the observed polarization reflects the paramagnetic behavior of shallow muonium. In fact, the polarization cannot have been built up in the final paramagnetic state since this would require spin-flips between spin-up and spin-down states and would consequently lead to the smearing out of the two hyperfine lines, in contrast with experiment. Thus the polarization must have been established before the formation of the final state. Very little is known about these epithermal and early thermal stages of the muon implantation, but in order to reach an inversion of the sign of the polarization, at least two different routes for the final muonium formation must exist.

In this work the electron polarization of the shallow muonium is studied in CdTe and CdS. The possible mechanisms for electron polarization are discussed and it is shown that the measured polarization reveals information on the properties of the preceding stages before the formation of the final state.

II. EXPERIMENTAL DETAILS

We used monocrystalline samples of CdTe and CdS, nominally undoped, commercially available. For CdS two different samples from different suppliers (Crystec and Eagle-Picher) were used. They were oriented with the c-axis perpendicular to the external field, which leads to the averaging of the anisotropic contributions of shallow muonium.

The CdTe samples were acquired from Crystec. The original p-type CdTe sample has been measured and cut in two pieces: one was annealed at 823 K in vacuum and the other was kept at or below room temperature. New μSR measure-

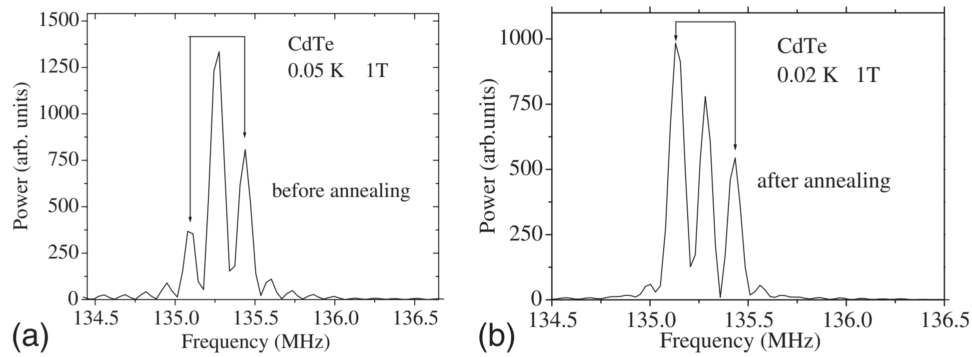

FIG. 1. Frequency distributions derived from CdTe μSR time spectra at an external magnetic field of 1 T (a) before and (b) after sample annealing at 823 K. The temperature measured at the sample position was 0.05 and 0.02 K, respectively. The arrows indicate the two muonium satellite lines. Note the inversion of the line intensities in the two spectra.

ments were performed with the annealed sample. The effect of aging on the sample kept at room temperature was reported in a previous publication.[9]

Time-differential muon spin rotation (μSR) spectroscopy measurements were performed at low temperatures (0.02 to 4 K) at the LTF facility of the Swiss Muon Source, Paul Scherrer Institute, Switzerland. An external magnetic field was applied up to 2 T, perpendicularly to the muon spin initial polarization. The time evolution of the muon spin ensemble polarization is measured by detecting the asymmetric emission of decay positrons from muons implanted into the sample.[1,10]

The time-dependent experimental asymmetry was fitted to a sum of three cosine functions of the form $A\cos(2\pi\nu t+\phi)$ where A is the amplitude, ν the frequency and ϕ the initial phase. The Larmor precession frequency of diamagnetic muons was constrained to be at the center of the two shallow muonium frequencies, but the splitting of the muonium lines was set as a free parameter, as well as all the amplitudes and phases. No relaxation of the asymmetry was considered, due to the limited time window of the measurements. A silver calibration in the same field range of the experiments was used to correct for time resolution distortions at high fields. The frequency distributions were obtained from the corresponding spectra in the time domain using a transformation introduced by Lomb,[11] similar to Fourier analysis. These were used for better visualization purposes only, all quantitative information being extracted from fits to the time-domain spectra.

III. RESULTS

Figure 1(a) shows the frequency distribution for a CdTe μSR spectrum at a measured temperature of 0.02 K and an applied external magnetic field of 1 T. Due to the small hyperfine interaction (hundreds of kilohertz) of the shallow muonium states, the frequency distributions obtained for all samples, at all fields, show this typical high-field pattern: two muonium lines symmetrically placed on either side of a central diamagnetic line. In Fig. 1(a) the upper shallow muonium line is clearly more intense than the lower one. An imbalance of the lines may occur due to dephasing in a deep to shallow muonium conversion[12] and indications of this effect will be analyzed in detail below (page G). However, this effect is of importance only at low fields and cannot explain the observations in Fig. 1. Since each shallow muonium line corresponds to a different electron spin state (up or down) the observed imbalance indicates a higher population of one of the spin states of the electrons bound to the muon and thus the existence of electron spin polarization. If the two spin states were equally populated, the electron spin polarization being zero, the lines would be equally intense. Surprisingly, an inversion of the relative line intensity was observed in the frequency spectra of the annealed CdTe sample [Fig. 1(b)], the lower frequency muonium line being now the most intense one.

It should be noted that in CdS we also observe a frequency distribution of shallow muonium that is similar to the one observed in Fig. 1(a), i.e., the upper shallow muonium line is clearly more intense than the lower one. The same pattern was observed also in GaN.[8] In order to understand this frequency distribution, we recall that, if the electronic g-factor is positive, the population of the electron spin-down state is larger in an applied field. Moreover, if the hyperfine interaction A is also positive the higher frequency corresponds to transitions between the hyperfine spin states $|s_e,s_\mu\rangle=|-1/2,+1/2\rangle$ and $|-1/2,-1/2\rangle$, whereas the lower frequency corresponds to transitions between $|+1/2,+1/2\rangle$ and $|+1/2,-1/2\rangle$ states. Therefore in this scenario ($g>0, A>0$) the higher frequency is expected to be more intense since it corresponds to transitions between electron spin-down states. This is what we observe in Fig. 1(a) and that was actually the argument used to assign a positive sign to the $A_\parallel$ hyperfine constant in GaN.[8] However, if either the hyperfine interaction or the g-factor is negative the more intense frequency is expected to be the lower one, as observed in Fig. 1(b). The sign of the hyperfine interaction of shallow muonium in CdTe and CdS is not known, but at least for CdS a positive sign is suggested by the deep-to-shallow muonium conversion process investigated in the present experiment (see below, Sec. IV).

In this work the electron spin polarization was evaluated as $P=(A_3-A_1)/(A_1+A_3)$, where A_3 and A_1 are the amplitudes of the upper and lower shallow muonium lines, respectively, as obtained from fitting to the time-dependent asymmetry signals. This polarization sign convention was used

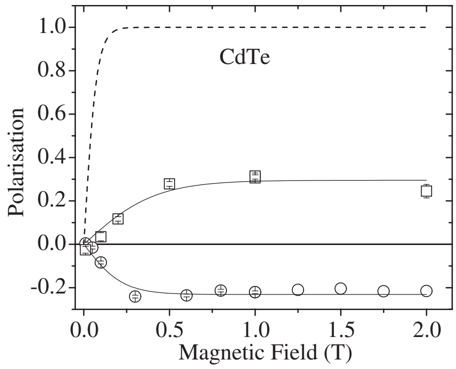

FIG. 2. Electron spin polarization of shallow muonium in CdTe at 0.05 K, for the original sample (squares) and at 0.02 K, after sample annealing at 823 K (circles). The dashed line is the Brillouin function predicted for a paramagnetic center with $S=1/2$ and $g=2$, at 0.05 K. The solid lines are fits with the modified Brillouin function $P=\alpha\tanh[\gamma\mu_B/(2k_B)]$ as detailed in the text.

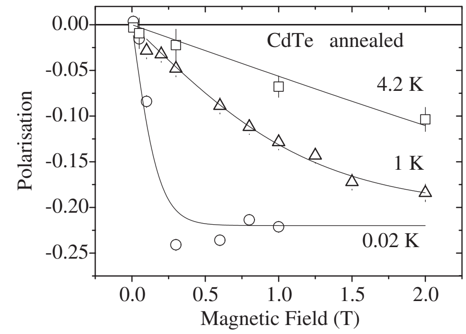

FIG. 3. Electron polarization of shallow muonium in the CdTe annealed sample, for different temperatures: 0.02 K (circles), 1 K (triangles), and 4.2 K (squares). The solid lines are fits with a modified Brillouin function as detailed in the text.

throughout the present work and was chosen to be consistent with a positive hyperfine interaction of shallow muonium, giving the polarization the same sign as the electron g-factor. The essence of the discussion in this work is not affected by this convention but the relative importance of the different routes for shallow muonium formation, as discussed below, would have to be reversed if a negative hyperfine interaction was the case.

The magnetic field dependence of the electron spin polarization of muonium at low temperatures (0.05 and 0.02 K) is presented in Fig. 2 for CdTe, before and after sample annealing. In addition to the sign change, the polarization is seen to saturate at relatively low values [0.30(2) and −0.22(4) for the original and annealed sample, respectively]. Similar measurements at different temperatures for the annealed sample show that the absolute values of the polarization decreases with increasing temperature, as expected for a Brillouin-like dependence (Fig. 3).

In CdS the field dependence of the electron spin polarization follows the same general trends observed in CdTe [Fig. 4(a)] and its magnitude is also found to be sample dependent. One should note the polarization is considerably smaller for the CdS (Eagle-Picher), measured at 0.05 K, than for the CdS (Crystec) sample, measured at 0.2 K. If only the measured temperature, and not the sample dependence, determined the polarization, the opposite effect would be expected. The polarization is generally positive for both samples, except at low fields (below 0.05 T) where a small but clearly negative and varying polarization is observed [Fig. 4(b)]. In the original CdTe sample the data also suggest a small polarization undershoot at the lowest fields but the information is sparse.

IV. DATA ANALYSIS AND DISCUSSION

A. Modified Brillouin function

In thermodynamical equilibrium, the polarization of a paramagnetic center with $S=1/2$ is given by the Brillouin function,

$$P = \tanh\left(\frac{g\mu_B B}{2k_B T}\right), \tag{1}$$

where g is the g-factor of the state, μ_B the Bohr magneton, k_B the Boltzmann constant, B the external applied magnetic

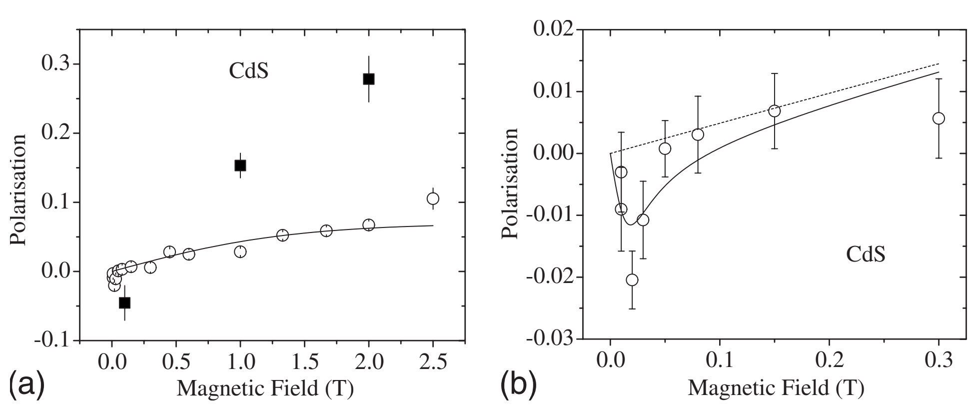

FIG. 4. (a) Electron spin polarization for two different nominally undoped CdS samples from different suppliers, Crystec (full squares) and Eagle-Picher (open circles), at the temperatures 0.2 and 0.05 K, respectively. The solid line is a fit with the modified Brillouin function (see text). (b) Detail of Fig. 4(a) showing the negative values of electron spin polarization in CdS (Eagle-Picher) at low fields. The dotted line shows the Brillouin-like behavior. The solid line shows this contribution together with the effect of the deep-to-shallow muonium conversion (see text). The fitted parameters (hyperfine interaction and mean lifetime) for the deep muonium precursor are: $A=500\pm300$ MHz and $\tau=0.3\pm0.2$ ns.

TABLE I. Fit parameters obtained from the analysis of CdTe data. T is the temperature measured with the temperature sensor at the sample position whereas T_{eff} and α are the two fitting parameters. A value $|g|=1.8$ was used in all fits (see text).

Sample treatment	T (K)	T_{eff} (K)	α
Original sample	0.05	0.2(1)	0.3(1)
Aged one year	0.02		0.11(5)
Aged three years	0.02	0.06(5)	0.04(2)
Annealed at 823 K	0.02	0.11(5)	−0.22(4)
Annealed at 823 K	1	0.8(3)	−0.20(4)
Annealed at 823 K	4.2	4.2(fixed)	−0.4(2)

field and T the temperature. The Brillouin function is plotted in Fig. 2 as a dashed line, for a paramagnetic center with $S=1/2$ and $g=2$, at 0.05 K. Clearly, it does not describe the data. In particular the measured polarization saturates at a value below 1, in contrast with the prediction of Eq. (1). Nonetheless the data can be described with a modified Brillouin function given by

$$P = \alpha \tanh\left(\frac{\gamma \mu_B B}{2k_B}\right), \qquad (2)$$

with two adjustable parameters α and γ. The parameter α represents the saturation value and γ is related to the rate of increase of the polarization with field, which is dependent on both the electron g-factor and the effective temperature, i.e., $\gamma = g/T_{\mathrm{eff}}$. In the final analysis, the g-factor was fixed ($|g|=1.84$ in CdTe and $|g|=2$ in CdS, see discussion below on sections E and F) and only α and T_{eff} were adjusted. Results for the fitted parameters are presented in Table I for CdTe, including a reanalysis of previous results obtained in aged samples.[9] The errors in the parameters include the uncertainties both from the fitting and the estimated g-factor. The analysis of CdS (Eagle-Picher) data [Fig. 4(a)] at a measured sample temperature $T=0.05$ K, yields $\alpha=0.08(5)$ and $T_{\mathrm{eff}}=1.1(5)$ K. The scarcity of data for the CdS (Crystec) sample does not allow an unambiguous fit.

B. Effective temperature T_{eff}

For both CdTe and CdS at low temperatures (below 1 K) the effective temperature T_{eff} is considerably larger than the temperature measured with the temperature sensor at the sample position. Two possible causes can be envisaged to explain this discrepancy: (i) The samples may not have reached thermal equilibrium at measurements below 1 K. The samples were allowed several hours to equilibrate at low temperatures, prior to data acquisition, but it might not have been enough due to their low thermal conductivity. (ii) The electron spin system is at a higher temperature than the sample, due to muon implantation. In this latter hypothesis T_{eff} would be a measure of the local spin temperature. Both effects should become less important at higher temperatures. We cannot distinguish between the two effects here.

C. Incomplete buildup of polarization

In order to address the incomplete buildup of polarization we must first identify the possible time window where the polarization of the electron spin might have taken place. The muonium lines are well resolved, thus the observed phenomena cannot be due to a transfer of intensity between the two lines after the formation of the shallow muonium state. Nonetheless, some electron spin exchange may occur in shallow muonium at a low spin flip rate, as suggested by Gil *et al.*[13] based on a model presented by Senba.[14] Using this model a spin-flip rate of $\lambda_{\mathrm{sf}}=0.08$ μs^{-1} may be estimated for shallow muonium in CdS at 4 K. A corresponding spin-lattice relaxation time $T_1=(2\lambda_{\mathrm{sf}})^{-1}\approx 6$ μs may be inferred but would not yield a significant polarization during the time window of the experiments. Furthermore, electron spin flips during a measurement cause an increase in the relaxation rates of the hyperfine lines, without affecting their relative intensity. In a polarized medium, the increase of relaxation rates may be slightly different for the two muonium lines[15] but the effect is too small to be observed in these spectra. Thus the line imbalance must be due to phenomena preceding the formation of the shallow muonium state.

Additionally, the samples used in this work are essentially diamagnetic and the vast majority of electrons are not polarized. The concentration of paramagnetic impurity or paramagnetic defect centers is very low and an electron capture from these centers is extremely unlikely. Thus the electrons which are finally captured by the muon in order to form the shallow muonium are not polarized before the muon implantation.

These two limitations imply that the time window available for the buildup of the polarization is the time between the muon implantation into the sample and the subsequent time of formation of shallow muonium. It thus corresponds to the lifetime τ of the precursor stage, which is in the picoseconds to nanoseconds range. This being a short time interval, the polarization may not fully develop to its equilibrium value P_∞ [as given by the Brillouin function, Eq. (1)] but can be quenched at a lower value. The final polarization which is observed experimentally is

$$P = P_\infty \int_0^\infty (1-\exp^{-t/T_1})\left(\frac{1}{\tau}\exp^{-t/\tau}\right)dt = \frac{\tau}{\tau+T_1}P_\infty, \qquad (3)$$

where the first factor under the integral describes the buildup of the polarization with the spin-lattice relaxation time T_1 and the second factor corresponds to the probability of interruption of this process due to the formation of the final shallow muonium state. This probability is governed by the mean life time τ of the precursor stage. The result is a reduction of the amplitude of the polarization [expressed by the α factor in Eq. (2)], the functional dependence of the polarization P_∞ on temperature T and field B (given by a Brillouin function) remaining unchanged. It should be emphasized that this incomplete buildup of the polarization may possibly explain the reduction of the amplitude seen experimentally but not the inversion of the sign.

D. Two-routes model

The most intriguing result of this experiment is that the polarization changes sign in CdTe upon annealing of the sample. This change cannot be due to a sign inversion of the hyperfine interaction of the observed shallow muonium since the absolute values of the hyperfine interaction are the same on both samples within rather small experimental errors, indicating that the same state is formed in the original and in the annealed sample. Thus the only explanation for the sign change is that muonium is formed via two different routes, one with a positive and one with a negative polarization in the precursor stage. We identify these two routes with deep-to-shallow muonium conversion (route 1, positive g-factor) and electron capture from the conduction band (route 2, negative g-factor in CdTe).

In route 1, epithermal deep muonium diffuses in the lattice until it stops and converts to shallow muonium. Deep muonium is a hydrogenlike atom and its g-factor is known to be positive and similar to the vacuum value,[16] $g=2$. Thus a positive contribution to the polarization is expected from this formation route. The time delay for the conversion [τ in Eq. (3)] is expected to be in the nanosecond to picosecond region (otherwise dephasing would inhibit the observation of shallow muonium in transverse field) and therefore a highly efficient polarization mechanism is required in the precursor state. In the epithermal and early thermal state after muon implantation, muonium is still diffusing and as it changes site spin flips may occur. Muonium diffusion measurements in GaAs (Ref. 17) and in KCl (Ref. 18) indicate muonium hopping rates are about 10^{10} to 10^{11} s^{-1} at low temperatures. These fast site changes, together with the interaction of the muonium electron with the host electrons during the transitions, may provide an efficient polarization mechanism in this stage.

In route 2 shallow muonium is formed through the capture of an electron from the conduction band. At low temperatures, practically no electrons are available in the conduction band in these materials. However, such electrons are generated due to ionization processes when the muon enters the sample. These radiolytic electrons are initially not polarized but due to spin-lattice interaction a polarization may build up in the presence of the applied field. Different spin relaxation processes have been identified as relevant for conduction electrons, with different orders of magnitude and temperature dependencies for T_1.[19,20] The lack of inversion symmetry and the spin-orbit coupling mechanisms were found to dominate in CdTe at room temperature, with T_1 values of the order of a few picoseconds.[21] At temperatures near 1 K, however, T_1 is expected to be significantly larger and it is possible that a different mechanism of spin-lattice interaction dominates at these low temperatures.[22] The exchange interaction between electrons and holes is known to be important at low temperatures in p-doped semiconductors[20] and it has been identified as the dominant process in p-type GaAs, where T_1 is of the order of hundreds of picoseconds at 1 K.[19] This order of magnitude of T_1 would give rise to a polarization build up of radiolytic electrons prior to muon capture.

E. CdTe

Within this model the sign change observed in CdTe can be explained: Route 1 (deep-to-shallow conversion) dominates in the original sample and results in a positive polarization. In the annealed sample, route 2 (electron capture from the conduction band) becomes predominant and a negative polarization occurs. A more quantitative analysis is given below. If the two routes contribute with amplitudes a_1 and a_2 and g-factors g_1 and g_2, respectively, the total polarization of shallow muonium is given by

$$P = a_1 \tanh\left(\frac{g_1}{2}\frac{\mu_B B}{k_B T_{\mathrm{eff}}}\right) + a_2 \tanh\left(\frac{g_2}{2}\frac{\mu_B B}{k_B T_{\mathrm{eff}}}\right). \tag{4}$$

An effective temperature T_{eff} was considered in the expression, allowing for a possible deviation of the actual temperature from the temperature measured with the sensor. For simplicity, we take T_{eff} to be identical for the two routes, since we are unable to distinguish possible differences within the experimental errors. The g-factor of route 1 is that of the precursor muonium and was set to $g_1=2$. For the conduction electrons in CdTe, g_2 is known to be negative, given by $g_2 = -1.65$.[6,7] With these g-values, the previous expression becomes

$$\begin{aligned} P &= a_1 \tanh\left(\frac{2}{2}\frac{\mu_B B}{k_B T_{\mathrm{eff}}}\right) + a_2 \tanh\left(-\frac{1.65}{2}\frac{\mu_B B}{k_B T_{\mathrm{eff}}}\right) \\ &\approx (a_1 - a_2)\tanh\left(\frac{1.8}{2}\frac{\mu_B B}{k_B T_{\mathrm{eff}}}\right). \end{aligned} \tag{5}$$

The approximation in the lower line of the equation was made in order to arrive at the two-parameter fit function used in the analysis which describes the data. The errors made by this simplification are almost negligible for the extracted value of $\alpha = (a_1 - a_2)$ since this quantity is determined by the saturation value of the polarization at high fields (see Fig. 2) where both tanh functions approach 1. The errors in T_{eff} are in the order of 10%, given by the deviation of the average g_{av} from the actual absolute g-factors (1.65 and 2). Due to positive and negative contributions in Eq. (5), the polarization can assume values between +1 and −1, in particular the inversion of the polarization is possible if the relative contributions from the routes with positive and negative g-factors change by the sample treatment. For the further analysis of the measured amplitudes $(a_1 - a_2)$ we will discuss two extreme cases:

(1) Assuming that the polarization in the original sample is completely due to route 1 and in the annealed sample completely to route 2, α yields an estimate of the ratio T_1/τ, the spin-lattice relaxation time divided by the mean lifetime of the respective state. For the original sample, the amplitude is about 0.3 (see Table I) which, if attributed to incomplete polarization buildup [see Eq. (3)], yields $T_1/\tau \approx 2.3$, i.e., the polarization buildup, here in the deep muonium precursor state, is about 2.3 times slower than the decay of this state. For the annealed sample the observed amplitude is about −0.2 (see Table I). If the polarization is attributed completely to route 2, the same analysis as above yields $T_1/\tau \approx 4$. These are extreme cases and the polarization buildup may be simi-

lar or faster than the decay. The duration of the precursor stage is in the ns to ps range and thus the T_1 times ought to have similar values (see discussion in the two-routes model above). It should be noted that in route 1, τ represents the average time for deep to shallow muonium conversion, whereas in route 2 it corresponds to the mean time for electron capture by an implanted positive muon.

(2) Assuming that in both routes full polarization is reached, the measured amplitude yields the mixture of the two routes contributing to the polarization. The α value of +0.3 for the original sample implies, within this model, that 65% of shallow muonium is formed via route 1 and 35% via route 2. For the annealed sample, with experimental amplitude of about −0.2, the probabilities are 40% for route 1 and 60% for route 2. These are limiting values for the dominant routes, i.e., for the original sample, at least 65% of shallow muonium is formed via deep-to-shallow muonium conversion whereas in the annealed sample the dominant route is electron capture from the conduction band and at least 60% of shallow muonium proceeds via this route.

F. CdS

In CdS, the g-factor of conduction-band electrons is positive and in the range 1.8–1.9.[5,23] The g-factor of the two routes is therefore similar and a simplified form of Eq. (4) may be written for CdS,

$$P = (a_1 + a_2)\tanh\left(\frac{2}{2}\frac{\mu_B B}{k_B T_{\text{eff}}}\right), \tag{6}$$

where the two fitting parameters α and γ in Eq. (2) are now given by $\alpha = a_1 + a_2$ and $\gamma = 1/T_{\text{eff}}$. It should be noted that the observation that the electron polarization (as defined in this work) and the g-factor are both positive in CdS is an indication that the shallow muonium hyperfine interaction is positive in this material.

If full polarization is reached in the two channels, $a_1 + a_2$ should be 1. That is clearly not the case in CdS [Fig. 4(a)]. Within the two-routes model, $a_1 + a_2$ should be given by

$$a_1 + a_2 = \frac{x_1}{\left(\frac{T_1}{\tau}\right)_1 + 1} + \frac{x_2}{\left(\frac{T_1}{\tau}\right)_2 + 1}. \tag{7}$$

where x stands for the fraction of shallow muonium formed by each route ($x_1 + x_2 = 1$) and the subscripts in x and T_1/τ refer to routes 1 and 2. It should be noted that x_1 represents the fraction of the final shallow polarization that has been formed by the deep precursor route, not the yield of deep muonium formed promptly. Here the reduction of the amplitude ($a_1 + a_2 \approx 0.08$) is entirely due to incomplete polarization buildup. μSR experiments conducted in CdS show that 85% of the shallow muonium signal is lost if electron capture is suppressed due to the presence of an electric field.[24] This indicates that electron capture from the conduction band is the dominant route in CdS. For the main channel the rather low amplitude indicates that the polarization buildup takes about ten times longer than the time the system exists in the precursor stage, i.e., T_1 is around ten times larger than τ, the average time for shallow muonium formation.

G. Evidence for the precursor state

Besides an electron polarization buildup, for CdS we must include an explanation of how the polarization undershoots at low fields [Fig. 4(b)]. We attribute it to the dephasing that occurs when a deep muonium precursor converts to shallow muonium with some time delay. In this case, the two shallow muonium lines have different intensities because the dephasing, which depends on the frequency change by the conversion, is different for the two lines. In the high-field limit the frequency change in the conversion is the same for the two lines and therefore no imbalance occurs. Thus the dephasing is seen at low fields only and can be separated from the polarization effect due to spin-lattice relaxation.

The analytical expressions for the deep-to-shallow muonium conversion are known from the literature[12] and were used to analyze the effect. In this model both the deep precursor and the final shallow state are assumed to have isotropic hyperfine interactions. The hyperfine interaction of the final shallow muonium state was fixed to the experimental value of $A_s = 220$ kHz. For this very low interaction strength the high-field limit applies for the external fields used here and only two shallow muonium frequencies, ω_{12s} and ω_{43s}, are present. In contrast, the hyperfine interaction of the deep muonium precursor is large (in the 500 MHz region) and the full Hamiltonian has to be used in the calculation. The precursor hyperfine interaction, A_p and lifetime, τ, were used as fitting parameters in Fig. 4(b). Within this model, assuming no electron polarization buildup during the precursor lifetime, the normalized intensities of the two shallow muonium lines P_{12} and P_{43} are given by[12]

$$P_{12} = \frac{f}{2}\left(\frac{c^2}{1 + \Delta_{1212}^2} + \frac{s^2}{1 + \Delta_{1412}^2}\right), \tag{8}$$

$$P_{43} = \frac{f}{2}\left(\frac{c^2}{1 + \Delta_{4343}^2} + \frac{s^2}{1 + \Delta_{2343}^2}\right), \tag{9}$$

where f is the paramagnetic fraction and $\Delta_{1212} = \tau(\omega_{12p} - \omega_{12s})$, $\Delta_{1412} = \tau(\omega_{14p} - \omega_{12s})$, $\Delta_{2343} = \tau(\omega_{23p} - \omega_{43s})$, $\Delta_{4343} = \tau(\omega_{43p} - \omega_{43s})$,

$$c^2 = 0.5\left(1 + \frac{\omega_e + \omega_\mu}{\sqrt{\omega_0^2 + (\omega_e + \omega_\mu)^2}}\right),$$

$$s^2 = 0.5\left(1 - \frac{\omega_e + \omega_\mu}{\sqrt{\omega_0^2 + (\omega_e + \omega_\mu)^2}}\right),$$

ω_0 being the coupling constant of the precursor state, and ω_μ and ω_e the Larmor angular frequencies of the muon and of the electron, respectively. The subscripts p and s in the frequencies refer to the precursor and shallow muonium states, respectively. The fact that the imbalance is negative implies that the hyperfine interactions before and after the conversion have the same sign.

It should be stressed that the polarization due to dephasing goes to zero for high fields and therefore cannot explain the main effect observed in the present experiment where the polarization increases with the strength of the external field. A complete description of the data in Fig. 4(b) requires a fit including two contributions: the deep to shallow conversion (significant only at very low fields) and a real electron polarization buildup, described by a modified Brillouin function. The analysis of the high-field data [Fig. 4(a)] yielded the value of $T_{\mathrm{eff}}=1.1(5)$ K and an estimate of the value of $(1+T_1/\tau)^{-1}\approx 0.08$ for the main route (electron capture). Using these values in the analysis of the low field region we obtain a precursor hyperfine interaction of the order of 500 MHz and a precursor lifetime of the order of 0.3 ns. Note that the hyperfine interaction, though not very well defined, is definitely smaller than the hyperfine interaction of 2000–4000 MHz observed for deep muonium in other systems.[25] This suggests that the deep muonium in CdS is not in its final configuration but rather that it is a transient situation. The conversion model was also used to predict the missing fraction due to dephasing in the deep to shallow conversion. If the precursor state has an hyperfine interaction of the order of $A_p\approx 500$ MHz and a lifetime of the order of 0.3 ns, the predicted missing fraction is negligible. This result is consistent with the observations, namely the absence of a missing fraction in CdS μSR data.

Evidence of the presence of a deep muonium state in CdTe have been reported[3,26] with an hyperfine interaction A_p of the order of 2000 MHz. It should be noted that a missing fraction of about 30% is expected for a deep state with $A_p\approx 2000$ MHz and a lifetime of the order of 0.1 ns, in agreement with the findings in CdTe μSR spectra. However, we have no direct evidence that this state is the precursor of shallow muonium. In fact, in CdTe no polarization data is available in the low field range where the effect of a precursor could be observed.

H. Changes for muonium formation route

The remaining question to be answered is what caused the change in the relative importance of the two shallow muonium formation routes. Aging and annealing is usually associated with changes in the impurity/defect system of the semiconductor.

It has been suggested that the cadmium vacancy (V_{Cd}), which is an acceptor, is responsible for p-type conductivity of as-grown CdTe material.[27] Annealing at 823 K in vacuum, followed by slow cooling leads to a significant increase of Cd vacancies[28] further enhancing the p-type character of the sample. The alteration of CdTe properties as a result of natural aging is also known from the literature[29–33] and has been attributed to changes in the defect system involving Cd vacancies.[29,32,33] We used photoluminescence measurements to characterize both the original and the modified CdTe samples. The spectra obtained are similar to those published in the literature for as-grown and annealed CdTe samples [see Figs. 1(a) and 1(b) in Song *et al.*[34]]. In the spectrum of the as-grown sample the $(A^0\text{-}X)$ emission at 1.589 eV is dominant in the bound exciton region; the extremely low intensity of the defect band at 1.4 eV is indicative of the good sample quality. In contrast, the defect band at 1.4 eV (together with its phonon replicas) is very intense in the modified sample. This band is ascribed[34] to the recombination of substitutional donors and complex defects involving Cd vacancies (V_{Cd}-D). We therefore suggest that the Cd vacancies are responsible for the increase of the amplitude of route 2, involving polarization of conduction electrons, both in the vacuum annealed and the aged samples. The role of V_{Cd} in the polarization mechanism is however unclear.

One possibility is that defects enhance the polarization buildup in the conduction band (route 2) via a more effective spin-lattice relaxation (shorter T_1) and/or via more delay for the capture of the electron to shallow muonium (larger τ). By these effects the prefactor $\tau/(\tau+T_1)$ in Eq. (3) becomes larger giving more weight for the negative polarization formation via route 2. In fact, some of the relevant spin relaxation mechanisms involve interactions with the impurity/defect system. The spin-orbit coupling mechanism, suggested to play an important role in CdTe at room temperature,[21] becomes more effective if scattering on impurities comes into play.[20] The other effective T_1 process, based on an exchange interaction of electrons and holes, is known to be very efficient in p-type semiconductors at low temperatures.[19] An enhancement of the p-type character in the annealed CdTe sample may thus shorten the spin-lattice relaxation time T_1 and therefore increase the relative importance of the electron capture route [see Eq. (4)]. A longer delay time τ may occur if, due to defects, electron-hole recombination decreases the number of electrons available for capture.

On the other hand, the deep-to-shallow muonium route (route 1) may become less important if the defects shorten the lifetime of the precursor state. Thus both the more effective buildup of polarization in route 2 due to defects and the reduction of the importance of route 1 go in the same direction and could possibly cause the reduction of the polarization in the aged samples and the reversion of the polarization in the annealed sample.

A decrease of the spin-lattice relaxation time of conduction-band electrons with the increase of impurity/defect concentration would also explain the different behavior of the two CdS samples, i.e., the observation that the less pure sample shows a higher degree of electron polarization.

Another possibility for the change of the dominant route for the polarization formation is a modification of the fractions x_1 and x_2 of shallow muonium formed by the two routes. It seems unlikely that the defect/impurity system affects the yield of deep muonium and Mu^+ formed promptly. The subsequent fate of these two species may however be influenced by defects and/or impurities. At present no distinction can be made between these different explanations.

V. CONCLUSIONS

We show in this experiment that the polarization of shallow muonium in CdTe and CdS at low temperatures is not due to the paramagnetism of these final states but rather to the polarization buildup in the preceding stage immediately following muon implantation. The observed inversion of the polarization in the CdTe sample after annealing is particularly interesting since it shows that there are two different routes for the formation of the final state, one with a positive and one with a negative g-factor in the precursor state. The fact that the g-factor of the conduction electrons in CdTe is negative led us to the final interpretation of our data: in the annealed sample the dominant route for shallow muonium formation proceeds via delayed electron capture from the conduction band, the electrons being polarized while in the conduction band. The other route involves a deep muonium precursor state which converts with some time delay (in the 100 ps range) to shallow muonium. In this case the electron polarization is created during the lifetime of the deep muonium precursor state which is assumed to have a positive g-factor. This deep-to-shallow muonium conversion route is dominant in the original (not annealed) CdTe sample. In the unlikely case that the hyperfine interaction of shallow muonium in CdTe is negative, the assignment of the two routes would have to be inverted.

The polarization buildup in the short-lived deep muonium precursor state requires a very efficient polarization mechanism. We assume (in agreement with literature results on similar systems) that muonium in this epithermal and early thermal stage is still highly mobile and experiences spin-flips during site changes. This early muon-electron configuration probably involves a strong mixing of the muonium electron with the host electrons resulting in a high spin-flip probability during motion. The rather low hyperfine value ($\approx$500 MHz) inferred in CdS indicates that the electron is in this case less localized at the muon than in the usual quasi-atomic muonium.

It should be noted that the arguments used on the CdTe and CdS data also apply to the electron polarization observed earlier in shallow muonium in GaN.[8] GaN is a diamagnetic material and the hyperfine lines of shallow muonium are well resolved. Thus the observed electron polarization cannot have been built up in the final paramagnetic state because that would cause the smearing out of the hyperfine-split spectral lines. In GaN the electron g-factor is positive and close to 2 (Ref. 35) and no negative polarization is expected. The data was acquired at 2.5 K which is probably high enough to get an effective temperature T_{eff} similar to the measured sample temperature. On the other hand, the author's observation that the electron polarization is consistent with the equilibrium value, suggests that the spin-lattice relaxation mechanisms are extremely efficient in GaN.

In this paper, the routes for shallow muonium formation in CdTe and CdS are specified and information on the spin dynamics of transient states en route to the final state is presented. The polarization measurement is a very sensitive tool to obtain this information.

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