Novel Muonium State in CdS

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A new type of muonium defect center has been observed in undoped CdS below 20 K. The hyperfine interaction amounts only to approximately 10^{-4} of the vacuum value, and is shown to have axial symmetry along the Cd-S bond direction. Results suggest that the muon is close to the sulfur antibonding site and the paramagnetic electron density is distributed over a large volume. In contrast to the behavior in other semiconductors, muonium forms a shallow center in CdS. By implication, analog isolated hydrogen impurity atoms act as electrically active shallow-level defect centers in CdS.

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Muon spin rotation (μSR) spectroscopy has played a pioneering role in the discovery and identification of intrinsic hydrogenlike states in semiconductors. A first overview of muon states in semiconductors was presented by Patterson [1]. Recent reports by Cox and Lichti [2] and by Chow, Hitti, and Kiefl [3] update the experimental data and summarize the present status of this field. Muonium behaves in solids similarly to a hydrogen atom in the sense that the muon models the intrinsic behavior of a proton. The muon is fairly insensitive to defects since it is implanted and comes to rest in most cases in an undisturbed lattice area. At least at low temperature, where diffusion to defects within the lifetime of the muon is unlikely, the properties of the intrinsic state can be detected. This contrasts with the time scale of most conventional spectroscopies, which observe hydrogen paired with other defects or impurities.

In the Group IV elemental semiconductors and III-V compounds, usually one finds [1–3] a diamagnetic state with a muon Larmor frequency corresponding to the external magnetic field, together with one or two paramagnetic states characterized by hyperfine splittings. Experimental muon data on the II-VI compounds are scarce. In ZnS and ZnSe a spherically symmetric muonium center with a rather large hyperfine interaction (80% and 77% of the vacuum value, respectively) is reported; for CdS only the diamagnetic state has been observed so far [1].

In this Letter we present the first observation of a paramagnetic state in CdS. This state has unusual properties, the most pronounced feature being that the hyperfine interaction is extremely small (in the order of 10^{-4} of the vacuum value) indicating that the unpaired electron is only weakly bound to the positive muon (the occupation probability at the muon site and consequently the contact interaction are very small). This new muonium state is observed only at low temperatures and in undoped materials. In a heavily doped CdS sample no muonium signal was found at 4 K.

For the experiments reported here, we used commercially available (from CrysTec, Berlin), undoped, hexagonal (Wurtzite structure), single crystalline CdS slabs with areas of approximately 40 mm^2 and thickness of 1.2 mm. The samples were oriented with the $\langle 0001 \rangle$ axis perpendicular to the plane. The muon spin rotation experiments were performed at the GPS instrument at the Paul-Scherrer Institute (PSI) in Switzerland and at the EMU line at the ISIS facility of the Rutherford Appleton Laboratory in England. A perpendicular geometry was used [1–3]. Part of the PSI data was recorded with the recently installed option MORE (Muons On Request) which allows measurements of time spectra encompassing wide time windows.

Figure 1 shows the μSR MORE spectrum and its Fourier transform, obtained with an external applied field of $B = 0.01$ T parallel to the c axis and at 2.1 K. In addition to the Larmor precession signal at 1.38 MHz, the Fourier spectrum shows two pairs of lines positioned symmetrically around this central line. The outer pair [$\Delta\nu =$ 335(7) kHz] and the inner pair [$\Delta\nu = 214(5)$ kHz] together with their intensity ratios can be assigned to two orientations of the muonium defect center. The new muonium center is therefore described by a hyperfine tensor which can be oriented along definite crystallographically equivalent directions (specific bond directions) which are differentiated by the applied magnetic field.

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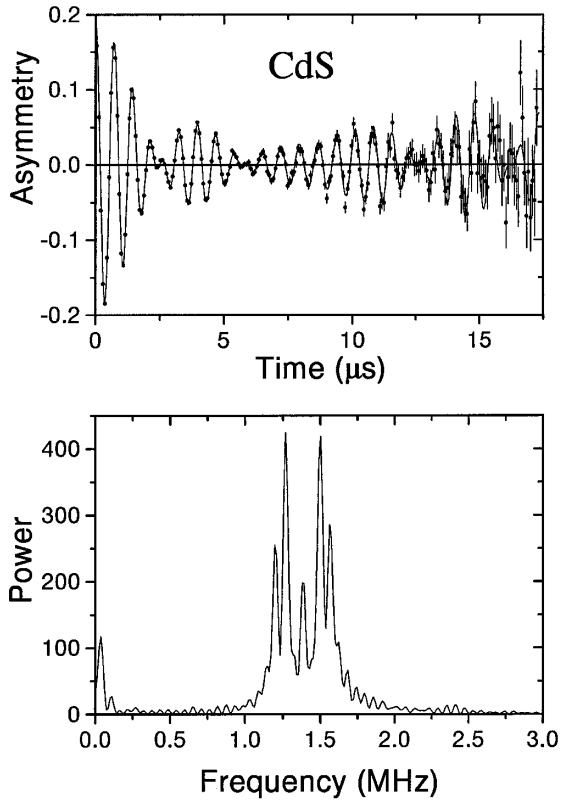

FIG. 1. μSR spectrum and its Fourier transform for undoped CdS at 2.1 K. The magnetic field of $B = 10$ mT was parallel to the hexagonal $\langle 0001 \rangle$ axis which was also normal to the plane of the disklike sample. In this geometry, one Cd-S bond direction (suggested to be the symmetry axis of the hyperfine tensor) is at 0° and three are at 70.6° to the field direction.

Further angular and field dependence measurements show that all spectra can be explained by assuming an axially symmetric hyperfine interaction with symmetry axis along the Cd-S bond direction. It is noteworthy that neither the intensity ratio of the spectral lines nor their orientation dependence can be attributed to dipole-dipole interactions with the dipolar nuclei in CdS. One should bear in mind that in the hexagonal structure the bond along the c axis and the three other bonds are not exactly equivalent, and therefore the hyperfine parameters as well as the formation probabilities of the muonium complex could be different for these two configurations. On the other hand, the local environment of muonium associated with the various Cd-S bonds is not significantly different, and therefore the local properties (e.g., the hyperfine parameters) are expected to be similar. The available data are consistent with a unique hyperfine interaction for all configurations although more refined measurements may reveal slight deviations. The formation probabilities seem to depend slightly on the bond configuration.

In the geometry where the magnetic field is along the $\langle 0001 \rangle$ axis, there is a Cd-S bond with $\theta = 0°$ (θ being the angle between the bond direction and the external field) and three bonds with $\theta = 70.6°$. The intensity ratio in Fig. 1 suggests that the outer pair of lines corresponds to $\theta = 0°$ and the inner pair to $\theta = 70.6°$. In the high field limit ($A \ll \gamma_e B/2 = 140$ MHz for $B = 10$ mT) and axial symmetry the following relation holds:

$$\Delta\nu(\theta) = A(\theta) = |A_{\parallel} \cos^2\theta + A_{\perp} \sin^2\theta| , \qquad (1)$$

where $\Delta\nu(\theta)$ is the separation of two lines symmetrical around the central line, $A(\theta)$ is the hyperfine interaction for a given angle θ, and $A_{\parallel}$ and $A_{\perp}$ are the hyperfine interaction parallel and perpendicular to the symmetry axis, which we assign to the Cd-S bond direction. The analysis of the spectrum of Fig. 1 yields $A_{\parallel} = 335(7)$ kHz and $A_{\perp} = 199(6)$ kHz.

Measurements at different angles confirm that $A_{\parallel}$ and $A_{\perp}$ have the same sign, but both could be either positive or negative. In what follows we quote the absolute value.

A useful choice of a different geometry is—in analogy to the magic angle geometry in the cubic structure—a rotation of the c axis by an angle of 54.7°. In this way, five of the eight bonds of the unit cell have a θ close to that value and the predicted hyperfine value is 244(5) kHz ($A_{\parallel}$ and $A_{\perp}$ as given above). For the three remaining bond directions, somewhat different hyperfine values are predicted but their center of gravity is again 244 kHz. Thus, in this geometry and with a moderate resolution a single pair of hyperfine lines is expected. Figure 2 shows the Fourier transforms of time spectra obtained for this specific field orientation and different temperatures. Only a single pair of lines shows up as expected. The experimental value of the hyperfine interaction at this angle at 2.1 K is 243(4) kHz, in excellent agreement with the predicted value of 244(5) kHz for $\theta = 54.7°$ obtained using Eq. (1).

Figure 2 shows that the three lines, which are well separated at 2.1 K, do merge when temperature increases and that the intensity of the middle line increases. This behavior is more clearly seen in the contour plot in Fig. 3. The separation of the outer lines, corresponding to the hyperfine interaction, gradually decreases, and spectral weight is transferred to the middle line with increasing temperature. In a second sample, of different origin but also nominally undoped, this variation with temperature was similar but not identical. Above about 20 K only the central single line is observed.

In the temperature behavior, two regimes can be distinguished: below 20 K the lines are very broad and consist of the two hyperfine lines discussed above and a broad background under the line spectrum. Above 20 K, a single, very sharp line with a depolarization rate of $\sigma = 0.025(5)\ \mu s^{-1}$ shows up. This line is clearly identified as the diamagnetic muon precession in the external field. The depolarization rate has a value as expected considering the dipole-dipole interaction with nuclei of the odd Cd isotopes (abundance 25%). The broad lines below 20 K definitely

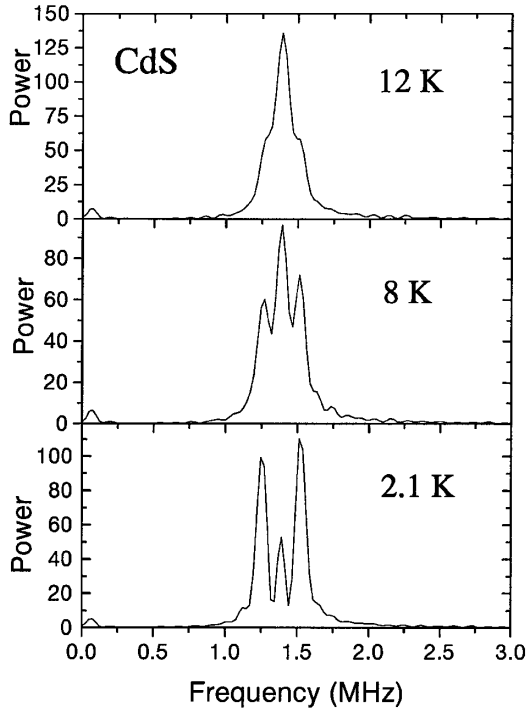

FIG. 2. Fourier transforms of μSR spectra for undoped CdS at $B = 10$ mT, $\theta = 54.7°$ (see text), and three different temperatures.

require the interaction of the muon with an electron moment and are therefore indicative of muonium formation. The transition between the two regimes occurs in a narrow temperature range around 20 K as shown in Fig. 4 where the summed amplitude of all broad lines and the amplitude of the narrow diamagnetic line are plotted as a function of temperature. An activation energy of 9 meV is obtained from the slopes of these curves.

We suggest that two different mechanisms are active: the spectral changes observed below 20 K are attributed to spin exchange dynamics and will be discussed below, whereas the rather abrupt transition to the diamagnetic state is assigned to ionization. A continuous extrapolation of the spin dynamics towards higher temperatures would imply a gradual decrease of the hyperfine splitting leading to a broad central line which finally should narrow with further increasing temperature. The observed behavior was found to be quite different. In the transition region, the lines remain broad but their intensity decreases and a sharp diamagnetic line grows at the expense of the broad lines (Fig. 4). This is taken as evidence that the center becomes ionized, i.e., that the electron is no longer bound to the muon, above the transition region. The binding energy of the electron derived from the observed activation energy via the relation $E_d = 2E_a$ (where E_d is the defect level energy and E_a the activation energy) yields for the present case $E_d = 18$ meV, suggesting that muonium forms a shallow level with a widely distributed electron wave function as already suggested by the low hyperfine interaction.

Further evidence for the ionization hypothesis comes from a comparison of the spin dynamics and the transition to the diamagnetic state of the two different investigated samples, both nominally undoped. The spin dynamics behavior below 20 K is different (as expected for slightly different carrier concentrations). On the other hand, the transition to the diamagnetic state, which is a property of the center, is the same. In addition, the assumption of a strongly bound electron localized at surrounding atoms (e.g., at the Cd atom of the Cd-S-Mu radical molecule), in order to be consistent with the low contact interaction, would hardly be reconciled with the small dipolar field observed at the muon.

Thus the present data provide convincing evidence that the muonium in CdS is a shallow center (donor or acceptor) with a binding energy of approximately 18 meV.

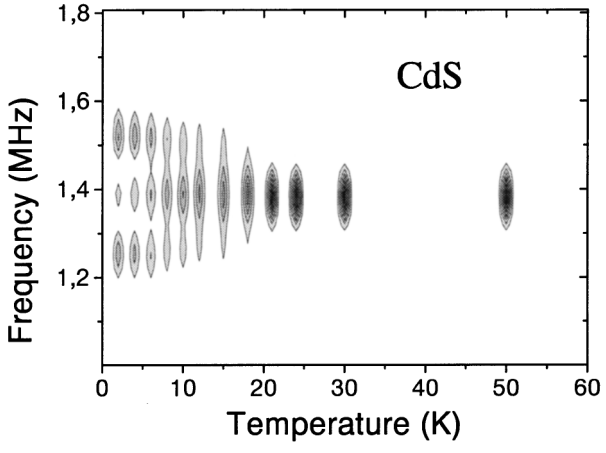

FIG. 3. Contour plot of the μSR data Fourier transforms at different temperatures for CdS at $\theta = 54.7°$ and $B = 10$ mT. The widths of the contours in the temperature axis direction were chosen for purposes of presentation only.

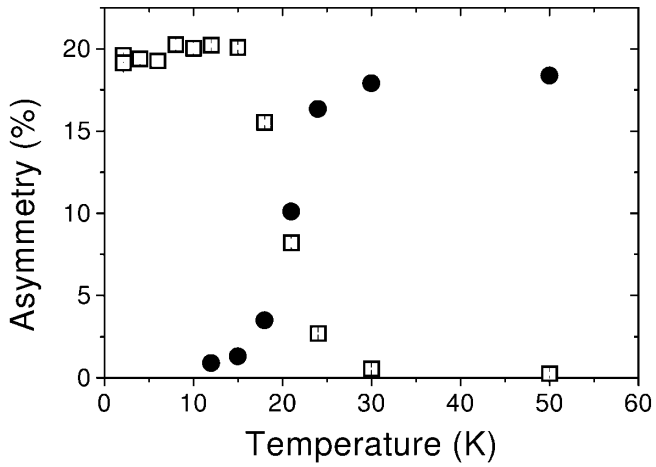

FIG. 4. Paramagnetic fraction (open squares) and diamagnetic fraction (closed circles) as a function of temperature for CdS at $B = 10$ mT and an angle of 54.7°.

The electron distribution of such a center may be roughly described by a dilated hydrogenlike wave function in a dielectric medium. In this picture the hyperfine interaction scales inversely with the cube of the Bohr radii of the corresponding 1*s* wave functions. In the present case the isotropic part of the hyperfine interaction is $A_d = (A_\parallel + 2A_\perp)/3 = 244$ kHz which has to be compared with $A_0 = 4463$ MHz for the free muonium, i.e., $A_0/A_d = 1.8 \times 10^4$. This leads to $a_d = 26a_0 = 1.4$ nm, where a_d is the Bohr radius for the defect center and a_0 the Bohr radius for the free muonium.

This finding is in qualitative agreement with the estimated value calculated with the CdS dielectric constant $\varepsilon = 9$ [4], and effective electron mass of approximately $m_e = 0.2m_0$ [5], i.e., $a_d = (\varepsilon/m_e/m_0)a_0 = 45a_0$. A closer agreement is not expected within the rough models considered.

We also considered the possibility that the observed muonium corresponds to a metastable excited state, the formation of the ground state being hindered by a barrier at low temperature. However, this interpretation seems unlikely since in this case we would expect the formation of the ground state at higher temperatures, where the barrier could be overcome. Experimentally, we find no evidence for a paramagnetic state, neither static nor fluctuating, between 30 and 300 K. Thus, the existence of a paramagnetic deep level seems unlikely.

The present shallow muonium center may be compared to the phosphorus defect center in silicon, for which case extensive EPR studies are available [6]. There, the low temperature changes of the spectrum are attributed to the excitation of a bound excited state which has a zero hyperfine interaction. The fluctuation between these two states leads to a shift of the hyperfine splitting as the temperature is increased, since the probability of the electron being in the excited state increases. In the present case, a bound excited state seems unlikely, but it seems possible that an electron fluctuates between the bound and the unbound states without a spin change due to the extremely low electrical conductivity of undoped CdS at low temperatures [7,8]. This process preserves the structure of the separated lines, but the hyperfine interaction decreases. At somewhat higher temperatures, but still below the 20 K transition, spin exchange processes will come in and lead to spectral changes due to spin dynamics until, at around 20 K, the center is ionized and the electron disappears permanently.

A possible scenario is that the muon is covalently bound to sulfur near the antibonding site. Such a position has been proposed for the muon in the chalcopyrites $CuInSe_2$ and $CuInS_2$ on the basis of nuclear dipolar broadening measurements [9]. Since the local bonding structure in CdS is similar to the structure in chalcopyrites and since the observed hyperfine parameters have the symmetry corresponding to the bond direction, such an assignment seems reasonable also for the present system. The observed dipolar width of the diamagnetic state ($\sigma = 0.025\ \mu s^{-1}$) is consistent with this assignment if we assume that this is caused by the Cd nuclear moments of the odd Cd isotopes. The bond-center position would give a much larger dipolar width and therefore can be discarded on the basis of the experiment.

The extremely weak hyperfine interaction and the disappearance of the center at around 20 K by ionization strongly suggest that muonium in CdS forms a shallow center. It appears to be the first example of a muonium center with such an electronic structure. By implication, hydrogen atoms form an electrically active shallow center in CdS, in contrast to the deep-level centers formed in other semiconductors and dielectrics [1–3].

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