8.0 Muonium in semiconductors

In semiconductors and insulators the positive muon can capture an electron and form stable muonium. This state corresponds to a non-ionized hydrogen atom in the solid. With muonium spin rotation it is possible to study electronic states and position of an isolated hydrogen atom (impurity) in the solid. Muonium states have been detected in various semiconductors and insulators. Muon spin rotation spectroscopy has played a pioneering role in the discovery and identification of intrinsic hydrogenlike states in semiconductors. Detailed investigations have been performed in SiO₂, in the pure semiconductors Si, Ge, in diamond, in the semiconductors of the group (III-V) and (II-VI) and in various oxides.

Contrary to the muon in magnetic substances or superconductors, the positive muon in a semiconductor is an active probe. With this we mean that we use μSR spectroscopy to investigate a state, which is created by the muon itself.

We consider in the following as examples Si and Ge. One can distinguish different states via the hyperfine interaction. In Si and Ge we find at low temperatures three states:
1) Normal muonium with a strong hyperfine interaction, 2) so called anomalous muonium with a weak anisotropic interaction and 3) to about 10% free or diamagnetic muon. (Ref. B. Patterson, Rev. Mod. Physics 60, 69 (1988) and S.F.J. Cox, Rep. Prog. Phys. 72, 116501 (2009)).

μ⁺-Spin precession in normal muonium (isotropic hf-interaction) in transverse field

The Hamilton function of the hyperfine interaction in muonium is given by eq. [3-34] (chapter 3), where we have determined the eigenstates and energy eigenvalues in a magnetic field (eq. [3-37] to [3-39], Breit-Rabi diagram).

Experimentally, we measure muon spin precession frequencies that correspond to transition frequencies between different muonium levels.

Consider the transverse field experiment. At t=0 the muon spin is parallel to the x-direction: $\mathbf{B}_{\text{ext}} \parallel z \perp \mathbf{I}(0) \parallel x$.

In this case we must calculate the expectation value of $\sigma_x = 2I_x ([I_x]=[1])$. The Pauli matrix $\sigma_x$ acts only on the muon part of the wave function.

The captured electrons forming muonium are unpolarized, so their spin is with 50% probability parallel or antiparallel to the muon spin.

This state can be represented by an incoherent superposition of two wave functions:

$$|\Psi_1(0)\rangle = \frac{1}{\sqrt{2}} \left[ |M_S = \frac{1}{2}, M_I = -\frac{1}{2} \rangle + |M_S = \frac{1}{2}, M_I = +\frac{1}{2} \rangle \right]$$

$$|\Psi_2(0)\rangle = \frac{1}{\sqrt{2}} \left[ |M_S = -\frac{1}{2}, M_I = -\frac{1}{2} \rangle + |M_S = -\frac{1}{2}, M_I = +\frac{1}{2} \rangle \right]$$
The wave functions at any time \( t \) are a superposition of eigenstates \( |i> \) (given in [3-39]) with their corresponding phase:

\[
|\Psi_{1,2}(t)> = \sum_{i=1}^{4} c_{i}^{1,2} |i> e^{-\frac{(E_{i}-E_{t})}{\hbar} t}
\]  

[8-1]

The constants have to be determined from the initial conditions and from the normalization.

Initial conditions:

\[
<\sigma_x> = 1, <\sigma_y> = 0, <\sigma_z> = 0
\]  

[8-2]

The (observed) polarization in x-direction is then given by following expression:

\[
P(t) = <\Psi_{1}(t)|\sigma_x|\Psi_{1}(t)> + <\Psi_{2}(t)|\sigma_x|\Psi_{2}(t)>
= \sum_{j,k=1}^{4} c_{k}^{1,2} c_{j}^{1,2} e^{-\frac{(E_{k}-E_{j})}{\hbar} t} <k|\frac{1}{2}(\sigma_{+} + \sigma_{-})|j> + \sum_{j,k=1}^{4} c_{k}^{2,3} c_{j}^{2,3} e^{-\frac{(E_{k}-E_{j})}{\hbar} t} <k|\frac{1}{2}(\sigma_{+} + \sigma_{-})|j> 
\]  

[8-3]

This expression can be evaluated using the explicit expression for the eigenstates (see [3-39]).

P(t) can be also evaluated within the density matrix formalism, which is useful in case of partial (or zero) polarization (as is the case here for the electrons) (see for instance E. Karlsson, Solid State Phenomena as seen by Muons, Protons and Excited nuclei, Oxford Science Publications 1995).

Some important properties of [8-3]:

- P(t) depends only on transition frequencies.
- Selection rules of the matrix elements: the terms in the sum with \( j=k \) are zero since \( \sigma_{+}, \sigma_{-} \) do not possess diagonal elements.
- From the explicit expression for \( |1>, |2>, |3> \) and \( |4> \) (eq. [3-39]) we note that the transitions \( 1 \rightarrow 2 \) and \( 3 \rightarrow 4 \) do not contribute to P(t).

The result of the calculation gives for [8-3]:

\[
P(t) = \frac{1}{2} \left[ \cos^2 \beta (\cos \omega_{13} t + \cos \omega_{24} t) + \sin^2 \beta (\cos \omega_{14} t + \cos \omega_{32} t) \right]
\]  

[8-4]

\[
\cos \beta = \frac{1}{\sqrt{2}} \left[ 1 + \frac{x}{(1+x^2)^{1/2}} \right]^{1/2}
\]  

[8-5]

\[
\sin \beta = \frac{1}{\sqrt{2}} \left[ 1 - \frac{x}{(1+x^2)^{1/2}} \right]^{1/2}
\]
where \[ x \equiv \frac{(g_e |\mu_B| + g_\mu |\mu_B^\mu|)B}{\hbar^2} = \frac{B}{B_0} \] 

(for vacuum muonium \( B_0 = 0.158 \) T).

Special cases:

A) The transition frequencies \( \omega_{24} \) and \( \omega_{14} \) are generally too large, to be resolved with conventional spectrometers with time resolution of about 0.5 ns (rms).

Therefore:

\[ < \cos \omega_{24} t > = < \cos \omega_{14} > = 0 \]

so that:

\[ P(t) = \frac{1}{2} \left[ \cos^2 \beta \cos \omega_{13} t + \sin^2 \beta \cos \omega_{32} t \right] \]  

This equation can be written in the following form:

\[ P(t) = \frac{1}{2} \cos \omega_+ t \cos \omega_- t + \frac{1}{2} \frac{x}{\sqrt{1 + x^2}} \sin \omega_+ t \sin \omega_- t \]

\[ \omega_\pm = \frac{\omega_{32} \pm \omega_{13}}{2} \]

which gives a beat frequency (see Fig. 8-1).
Fig. 8-1: TF-$\mu$SR spectrum in quartz at room temperature. Note the beating between frequency $\nu_{13}$ and $\nu_{32}$.

The corresponding frequency spectrum is:

Fig. 8-2: TF frequency spectrum in quartz (10 mT) at room temperature. Visible are the $\mu^+$ precession frequency and that of the isotropic muonium (frequency pair $\nu_{13}$ and $\nu_{32}$ centered around 140 MHz).
From the frequency splitting we can determine the hyperfine constant $A$. With the help of eq. [3-37] we find an expression for $A$ or the hyperfine frequency $\nu_{hf}$, which depends only on experimental quantities:

$$
h\nu_{hf} = \hbar^2 A = \frac{1}{2} \left[ \frac{(h\nu_{13} + h\nu_{32} + 2h\nu_{\mu})^2}{h\Delta\nu} - h\Delta\nu \right]
$$

$$
\Delta\nu = \nu_{32} - \nu_{13}
$$

B) If the applied field is very small ($x \ll 1$) one can further simplify [8-7] (see also Fig. 8-6a):

$$
\cos^2 \beta \approx \frac{1}{2}, \sin^2 \beta \approx \frac{1}{2}
$$

$$
\omega_{32} \approx \omega_{13} = \omega_{Mu} = \frac{T}{2} \gamma_{c} B = \frac{1}{2} (\gamma_{c} - \gamma_{\mu}) B
$$

$$
\omega_{=} \approx 0
$$

[8-7] becomes

$$
P(t) = \frac{1}{2} \cos \omega_{Mu} t
$$

This means that in very small TF fields ($< 0.5$ mT), muonium shows only half of the polarization amplitude (corresponding to the precession of the $M_F = \pm 1$ components in the triplet state). In this case the muon spin polarization precesses with a Larmor frequency $\omega_{Mu} \approx 103 \omega_\mu$ (with opposite sense of rotation of the precession of a “free” muon). This allows distinguishing the charged ($\mu^+$) from the uncharged state (Mu).
B) No applied field, isotropic hyperfine interaction.

In this case there is only one hyperfine frequency, which in free muonium (corresponding to vacuum muonium) is very high ($\omega_0/2\pi = 4.46$ GHz). Generally it is observable only in systems with very good time resolution.

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**Fig. 8-3:** A zero-field $\mu$SR spectrum of quartz at room temperature. The Mu hyperfine frequency is close to the vacuum value (4.463 GHz). The FWHM time resolution of this experiment is 110 ps. From Holzschuh et al., Helvetica Physica Acta 54 552 (1981).
Example of muonium spectroscopy of synthetic quartz crystal in 8 T with a high resolution spectrometer. The High Field μSR instrument HAL-9500, which uses Avalanche Photo Diodes (APD’s) instead of the conventional Photomultipliers to transform and amplify the scintillator signal, has a very good time resolution (variance $\sigma=58$ or 80 ps, depending on the readout system). This allows spectroscopy of muonium in high fields.
Fig. 8-4: Breit-Rabi diagram and transitions in a synthetic quartz crystal measured with the HAL-9500 high resolution spectrometer at PSI in a 8T field (R. Scheuermann, private communication).
In inert non conducting substances muonium can exist in a state which is very similar to the atomic state. In this case it is localized in interstitial lattice positions. In alkali fluorides the hyperfine coupling is slightly higher than in vacuum muonium. This corresponds to a slightly compressed wave function with higher spin density at the muon site. Generally the hyperfine coupling is smaller. In some semiconductors it is even much smaller than in the free state. For instance in the elementary semiconductors of the group IV the electron spin density at the muon site is only 50% of the value in the free atom.

Fig. 8-5: Hyperfine constant for interstitial muonium in semiconductors and dielectrics. The graph shows the correlation between spin density at muon site and band-gap of host material (S.F.J. Cox J. Phys. C: Solid State Phys. 20, 3187 (1987)).

**Anomalous muonium**

In several semiconductors an additional muonium state has been found with a hyperfine constant which is axially symmetric around the [111] crystal axis. This state is called „anomalous muonium“ or „anisotropic muonium“ and indicated with Mu*. In general we can write the Hamilton function of the hyperfine interaction as follows:

\[ H = -\vec{\mu}_e \cdot \vec{B} - \vec{\mu}_\mu \cdot \vec{B} + \vec{I} \vec{A} \vec{S} \]  \[ [8-11] \]

(Compare with [3-34] chapter 3).
For anomalous muonium the assumption of an axial symmetric hyperfine tensor is justified. [8-11] can be written as:

$$H = -\vec{\mu}_e \cdot \vec{B} - \vec{\mu}_\mu \cdot \vec{B} + A_\perp (I_x S_x + I_y S_y) + A_\parallel I_z S_z$$  \hspace{1cm} [8-12]

In the special case $\vec{B} \parallel \hat{z}$ || [111] – axis (<111> symmetry axis)

$$H_{\text{Mu}} = -\mu_e^e \cdot B_z - \mu_\mu^e \cdot B_z + \frac{A_\perp}{2} (I_+ S_- + I_- S_+) + A_\parallel I_z S_z$$  \hspace{1cm} [8-13]

The eigenvalues of this Hamilton operator can be calculated as in the isotropic case. We obtain:

$$E_1 = \frac{A_\parallel \hbar^2}{4} + \frac{1}{2} (g_e \mu_B - g_\mu \mu_B^e) B$$

$$E_2 = \frac{A_\parallel \hbar^2}{4} - \frac{1}{2} (g_e \mu_B - g_\mu \mu_B^e) B$$  \hspace{1cm} [8-14]

$$E_3 = -\frac{A_\parallel \hbar^2}{4} + \frac{A_\perp \hbar^2}{2} \sqrt{1 + x^2}$$

$$E_4 = -\frac{A_\parallel \hbar^2}{4} - \frac{A_\perp \hbar^2}{2} \sqrt{1 + x^2}$$

with

$$x_\perp = \frac{(g_e \mu_B + g_\mu \mu_B^e) B}{A_\parallel \hbar^2}$$  \hspace{1cm} [8-15]
Fig. 8-6: Energy levels of muonium in low magnetic fields. a) Isotropic muonium. b) Anisotropic muonium with axial symmetry.

The hyperfine interaction of Mu$^*$ is generally smaller than that of Mu

$$\frac{A_{\perp}(\text{Mu}^*)}{A(\text{Mu})} \approx 0.05 \text{ in Si. Furthermore it is anisotropic } \frac{A_{\parallel}}{A_{\perp}} \approx 0.2 \text{ in Si. The precession frequencies depend not only on the B-field strength but also on its direction (see Fig. 8-7, and Fig. 8-8 bottom).}$$
Fig. 8-7: The field-dependent $\mu^+$ and Mu* precession frequencies in silicon. The field was directed along the [111] axis. The solid line shows the expected dependence of the diamagnetic $\mu^+$ signal, and the finely and coarsely dashed curves are fits to the axially symmetric spin Hamiltonian (2.9) for angles between the field and Mu* symmetry axis of 0 and 70.5°, respectively. From Patterson, Hintermann et al. (1978).

Fig. 8-8: Transverse-field $\mu$SR frequency spectra taken at 10 mT in quartz at room temperature and [111] Si at 77 K showing the precession components from diamagnetic $\mu^+$ ($\nu_{\mu^+} = 1.36$ MHz) and isotropic Mu (the pair $\nu_{12}$ and $\nu_{23}$ centered on 140 MHz). Note the larger Mu splitting in Si, indicating a weaker hyperfine interaction and the presence in Si but not in quartz of Mu* precession lines ($\nu_{12}$ and $\nu_{14}$, $\theta = 70.5^\circ$, at 41 and 46 MHz). From Brewer et al. (1973).
A $\mu$SR frequency spectra taken with the high-field, high-time-resolution apparatus in high-resistivity GaAs at 10 K with a 1.15-T field applied along the [110] axis. Note the two Mu lines $\nu_{12}$ and $\nu_{34}$, the Mu* lines $\nu^*_i(\theta)$ ($\theta$ is the angle between the [111] Mu* symmetry axis and the applied field), and the diamagnetic muon line $\nu_{\mu^+}$. From Kiefl et al. (1985).

(Note that in our notation of eq. [3-37] $\nu_{12}, \nu_{23}$ and $\nu_{34}$ in Fig 8-8 and 8-9 are designed as $\nu_{13}, \nu_{32}$ and $\nu_{24}$)
### TABLE VIII. Fractions of incoming muons forming the various muon states in undoped diamond and zincblende semiconductors at low temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$f_{\mu^+}$ (%)</th>
<th>$f_{\text{Mu}^*}$ (%)</th>
<th>$f_{\text{Mu}}$ (%)</th>
<th>$f_{\text{mixing}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>8.1 (3.0)</td>
<td>22.7 (8)</td>
<td>68.9 (1.0)</td>
<td>0.3 (3.3)</td>
</tr>
<tr>
<td>Si</td>
<td>7.5 (4)</td>
<td>36.8 (1.8)</td>
<td>61.0 (7.6)</td>
<td>-5.3 (7.8)</td>
</tr>
<tr>
<td>Ge</td>
<td>10 (2)</td>
<td>8 (4)</td>
<td>72 (10)</td>
<td>10 (11)</td>
</tr>
<tr>
<td>$\beta$-SiC</td>
<td>65 (12)</td>
<td>30 (5)</td>
<td>5 (19)</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Sn</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaP</td>
<td>11 (1)</td>
<td>18 (3)</td>
<td>72 (10)</td>
<td>-1 (11)</td>
</tr>
<tr>
<td>GaAs</td>
<td>9 (1)</td>
<td>35 (5)</td>
<td>63 (6)</td>
<td>-7 (8)</td>
</tr>
<tr>
<td>GaSb</td>
<td>56 (1)</td>
<td>19 (3)</td>
<td>72 (10)</td>
<td>-1 (11)</td>
</tr>
<tr>
<td>InP</td>
<td>75 (3)</td>
<td>25 (3)</td>
<td>44 (1)</td>
<td></td>
</tr>
<tr>
<td>InAs</td>
<td>106 (2)</td>
<td></td>
<td>-6 (2)</td>
<td></td>
</tr>
<tr>
<td>InSb</td>
<td>72 (2)</td>
<td>28 (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnS</td>
<td>20 (1)</td>
<td>19 (3)</td>
<td>61 (3)</td>
<td></td>
</tr>
<tr>
<td>ZnSe</td>
<td>36 (1)</td>
<td>11 (2)</td>
<td>53 (2)</td>
<td></td>
</tr>
<tr>
<td>CdS</td>
<td>92 (3)</td>
<td>8 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CdTe</td>
<td>69 (2)</td>
<td>36 (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuCl</td>
<td>16 (4)</td>
<td>66 (3)$^j$</td>
<td>9.9 (8)$^{11}$</td>
<td>8 (5)</td>
</tr>
<tr>
<td>CuBr</td>
<td>23 (4)</td>
<td>66 (5)$^j$</td>
<td>5.8 (8)$^{11}$</td>
<td>5 (6)</td>
</tr>
<tr>
<td>CuI</td>
<td>18 (8)</td>
<td>72 (3)</td>
<td>10 (9)</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE IX. Low-temperature hyperfine parameters for anisotropic Mu$^+$ ($A_\parallel, A_\perp$) and isotropic Mu ($A$) in diamond and zincblende semiconductors, the maximum temperatures of their observation, and observed transitions among the muon states. The hyperfine parameters for the III-V and II-VI compounds refer to 10 K, and the other values are extrapolations to 0 K. The hyperfine frequency of Mu in vacuum is 4463.30288 (16) MHz (Marlan et al., 1982).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_{\parallel}$ (MHz)$^a$</th>
<th>$A_\perp$ (MHz)$^a$</th>
<th>$A$ (MHz)</th>
<th>$T_{\text{mix}}$ (K)</th>
<th>$T_{\text{Mu}}$ (K)</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>+167.983 (57)$^b$</td>
<td>-392.586 (55)$^b$</td>
<td>3711 (21)$^b$</td>
<td>$\geq$ 1000$^p$</td>
<td>405$^p$</td>
<td>Mu$^-$Mu$^{\ast}$</td>
</tr>
<tr>
<td>Si</td>
<td>16.819 (11)$^d$</td>
<td>92.59 (5)$^d$</td>
<td>2006.3 (2.0)$^d$</td>
<td>165</td>
<td>300$^j$</td>
<td>Mu$^*$-Mu$^{\ast}$</td>
</tr>
<tr>
<td>Ge</td>
<td>27.269 (13)$^d$</td>
<td>131.037 (34)$^d$</td>
<td>2359.5 (2)$^d$</td>
<td>$\geq$ 22$^p$</td>
<td>$\geq$ 22$^p$</td>
<td>Mu$^*$-Mu$^{\ast}$</td>
</tr>
<tr>
<td>$\beta$-SiC</td>
<td>219.0 (2)$^j$</td>
<td>79.48 (7)$^j$</td>
<td>2914 (5)$^j$</td>
<td>100</td>
<td>240</td>
<td>(Mu,Mu$^*$)→Mu$^{\ast}$</td>
</tr>
<tr>
<td>GaP</td>
<td>217.8 (2)$^j$</td>
<td>87.74 (6)$^j$</td>
<td>2883.6 (3)$^j$</td>
<td>100</td>
<td>300</td>
<td>Mu$^*$-Mu$^{\ast}$</td>
</tr>
<tr>
<td>ZnS</td>
<td>3547.8 (3)</td>
<td></td>
<td></td>
<td>$\geq$ 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnSe</td>
<td>3456.7 (3)</td>
<td></td>
<td></td>
<td>$\geq$ 13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuCl</td>
<td>1334.23 (8)$^{11}$</td>
<td>1212.3 (1)$^{11}$</td>
<td>$\geq$ 300$^{11}$</td>
<td>$\geq$ 300$^{11}$</td>
<td>$\geq$ 300$^{11}$</td>
<td></td>
</tr>
<tr>
<td>CuBr</td>
<td>1403.66 (6)$^{11}$</td>
<td>1250.9 (2)$^{11}$</td>
<td>$\geq$ 300$^{11}$</td>
<td>$\geq$ 300$^{11}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuI</td>
<td>1670.9 (2)$^{11}$</td>
<td></td>
<td></td>
<td></td>
<td>102$^{11}$</td>
<td></td>
</tr>
</tbody>
</table>
Muonium states in elemental and III-V compound semiconductors have been found and studied to a great extent. Charged states \( \text{Mu}^+ \) and \( \text{Mu}^- \) and two forms of the neutral state \( \text{Mu}^0 \) have been identified and the interplay of site and charge states is understood. \( \text{Mu}^0 \) can either be isotropic, when in a symmetric interstitial site such as the tetrahedral site in diamond or zincblende structures (\( \text{Mu}^0_{\text{T}} \)), or anisotropic when situated at the bond-centre site (\( \text{Mu}^0_{\text{BC}} \)). In these semiconductors, isolated H and Mu are known to form deep-level centers.

**Muonium Centers in Si/Ge**

![Diagram of muonium centers in Si and Ge](image)

Fig. 8-10: Two different muonium states in Si and Ge. „Bond Centered Muonium“ \( \text{Mu}_{\text{BC}} \) (\( \text{Mu}^* \)) and “tetrahedral Muonium“ \( \text{Mu}_{\text{T}} \).

**Weakly bound muonium (shallow muonium)**

More recently, studies of Mu in II-VI semiconductors revealed the existence of a third form of neutral anisotropic \( \text{Mu}^0 \) in CdS, CdSe, CdTe and ZnO. This state has binding energies characteristic of shallow-level donor centers and is believed to be at the interstitial site antibonding to S (Se, Te, or O). Its hyperfine interaction is very weak, amounting to approximately \( 10^{-4} \) of the free-atom value. Figure 8-9 shows the \( \mu \text{SR} \) signal in CdS, taken over a period of eight muon lifetimes. The Fourier transform of the signal shows five distinct frequencies, indicating an extremely shallow muonium state and providing the first information on this hydrogen-like impurity in the compound (J. M. Gil et al., Phys. Rev. Lett. 83, 5294 (1999)). In addition to the Larmor precession signal at 1.38 MHz, the Fourier spectrum shows two pairs of lines symmetric around the central line. The outer pair \( (\Delta\nu = 335.7 \text{ kHz}) \) and the inner pair \( (\Delta\nu = 214.5 \text{ kHz}) \) together with their intensity ratios can be assigned to two orientations of the muonium defect center. The shallow muonium state is described by a hyperfine tensor which can be oriented along definite crystallographically
equivalent directions (specific bond directions) which have different orientation with respect to the applied magnetic field.

Fig. 8-11: µSR spectrum and its Fourier transform for undoped CdS at 2.1 K (From J.M. Gil et al, Phys. Rev. Lett. 1999). The magnetic field of B =10 mT was parallel to the hexagonal <0001> axis which was also normal to the plane of the disc-like 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.

In the high field limit (\( A \ll \gamma_e B/2 = 140 \text{ MHz} \) for \( B = 10 \text{ mT} \)) and axial symmetry a simple relation between measured frequencies and hyperfine tensor holds:

\[
\Delta \nu = A(\theta) = \left| A_\parallel \cos^2 \theta + A_\perp \sin^2 \theta \right| \quad [8-16]
\]

where \( \Delta \nu \) is the separation of two lines symmetrical around the central line, \( A(\theta) \) is the hyperfine interaction for a given angle \( \theta \) (angle between magnetic field and symmetry axis), and \( A_\parallel \) and \( A_\perp \) are the hyperfine interaction couplings parallel and perpendicular to the
symmetry axis, given by the Cd-S bond direction. The analysis of the spectrum of Fig. 8-11 yields $A_{||} = 335(7)$ kHz and $A_{\perp} = 199(6)$ kHz.

![Graph showing asymmetry as a function of temperature](image)

Fig. 8-12: Paramagnetic (Mu) 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 asymmetry as a function of temperature shows that the diamagnetic line grows at the expense of the paramagnetic lines (Fig. 8-12). This is taken as evidence that the muonium center becomes ionized, i.e., that the electron is no longer bound to the muon. The binding energy of the electron obtained from the activation energy is $E_d = 18$ meV indicating that muonium forms a shallow level with a widely distributed electron wave function as already suggested by the low hyperfine interaction.

![Diagram of CdS with muonium state](image)

Fig. 8-13: Shallow muonium state in CdS (green circle) and energy level.