



# Probing the shallow-donor muonium wave function in ZnO and CdS via transferred hyperfine interactions

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## Abstract

The assignment of muon spin rotation spectra to muonium counterparts of hydrogen shallow-donor states is reviewed in four II–VI widegap semiconductors, CdS, CdSe, CdTe and ZnO. The existence of extended electronic orbitals is argued from the muon–electron hyperfine parameters and supported by the new muon spin repolarization data for CdS and ZnO, characterizing the superhyperfine parameters on the sparse Cd and Zn dipolar nuclei. The possibility of a more tightly bound electron occupying a compact orbital is reasonably excluded in these materials, contrasting with the muonium state in HgO. © 2001 Elsevier Science B.V. All rights reserved.

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Muonium, the light pseudo-isotope of hydrogen, provides an experimentally accessible model for interstitial hydrogen in the II–VI compounds, as in other semiconductors. In these experiments, positive muons are implanted in the materials, where they are expected to adopt the same crystallographic sites as protons. In the Cd chalcogenides, and in ZnO, the implanted muons bind electrons weakly into a muonium state which has all the characteristics of a hydrogenic shallow donor [1–3]. The ZnO result is especially significant in that it confirms the theoretical prediction for protium [4]. Parameters characterizing the defect centres are given in Table 1. The muon–electron hyperfine parameters in these materials are exceedingly low, suggestive of an extended electron wave function. They were measured directly from the frequency splittings of the muon spin

rotation ( $\mu$ SR) spectra in the Paschen–Back régime, i.e. in a magnetic field (applied transverse to the initial muon polarization) sufficient to decouple the muon and electron spins. The temperature dependences of the  $\mu$ SR signals are also suggestive of ionization or dissociation of shallow-donor states: the activation energies deduced from the detailed temperature dependences of the signal amplitudes are fully consistent with estimates of these quantities in the effective-mass model.

Despite the overall consistency of this picture, the shallow-donor interpretation should be distinguished from a possible alternative model in which the electron wave function is more compact, but in which the spin density on the proton or muon is small due to some symmetry of the singly occupied orbital or special feature of the local bonding. Such a molecular–radical species would be tightly bound and unlikely to dissociate at cryogenic temperatures, but the disappearance of its

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**Table 1**  
Experimental hyperfine parameters and donor-level depths for the four shallow muonium states so far identified<sup>a</sup>

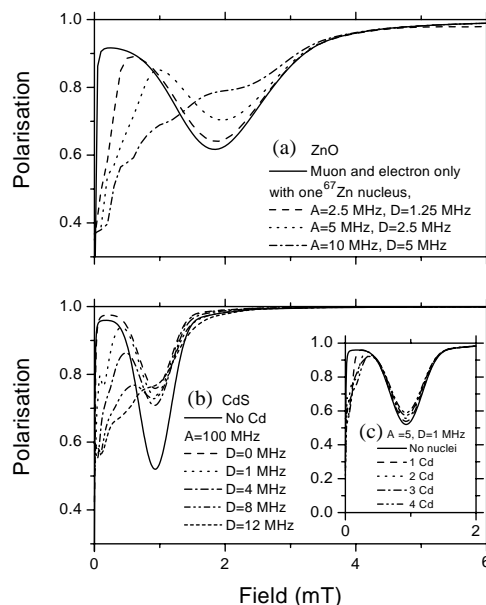
|      | $A_\mu$<br>(kHz) | $D_\mu$<br>(kHz) | $T_i$<br>(K) | $E_d^{\text{exp}}$<br>(meV) | $E_d^{\text{theo}}$<br>(meV) |
|------|------------------|------------------|--------------|-----------------------------|------------------------------|
| CdS  | $244 \pm 5$      | $91 \pm 6$       | $22 \pm 2$   | $26 \pm 6$                  | 33                           |
| CdSe | $87 \pm 4$       | $< 40$           | $12 \pm 2$   | $20 \pm 4$                  | 19                           |
| CdTe | $261 \pm 4$      | $< 50$           | $13 \pm 2$   | $16 \pm 4$                  | 11                           |
| ZnO  | $500 \pm 20$     | $260 \pm 20$     | $38 \pm 2$   | $58 \pm 6$                  | 52                           |

<sup>a</sup> The slightly anisotropic hyperfine interactions are expressed as isotropic (contact) and traceless (dipolar) components. The contact terms  $A_\mu$  are four orders of magnitude smaller than the free-muonium hyperfine constant, which is isotropic and equal to 4.5 GHz. Donor depths are derived assuming equilibrium statistics; if the process involved is, in fact, direct ionization to the conduction band, the corresponding activation energies are about half these values. Shown for comparison are the shallow-donor depths calculated in the simple effective-mass model.

hyperfine signature might be attributed to spin-exchange depolarization, when extrinsic carriers are released by the ionization of other defects or impurities.

In this paper we present new information on the local electronic structure of the muonium states in ZnO and CdS, namely estimates of the transferred hyperfine interactions on surrounding nuclei. We refer to these as superhyperfine interactions, reserving the term hyperfine for the central muon, and probe them in these experiments by examining the muon response in low longitudinal fields, i.e. in magnetic fields applied parallel to the initial muon polarization. Host nuclei carrying a dipole moment are sparse in these materials but a measurement of how electron spin density is distributed over them would, in principle, allow a mapping of the wavefunction. In CdS, the relevant isotopes are <sup>111</sup>Cd and <sup>113</sup>Cd, both with spin  $\frac{1}{2}$  and a combined natural abundance of 25%. At below 1% abundance, <sup>33</sup>S can reasonably be neglected even though the muon may bond or antibond to S atoms. In ZnO, <sup>67</sup>Zn has spin  $\frac{5}{2}$  and 4.1% abundance; no feature is likely to be observable in  $\mu$ SR spectra from <sup>17</sup>O in natural abundance although a study of samples enriched in this isotope would be worthwhile.

In Fig. 1, we show examples of the expectations of longitudinal-field measurements. The simulated quantity is muon polarization averaged over certain time windows and the field dependences are variously known as repolarization, decoupling or quenching curves. Fig. 1(a) is for ZnO and includes a simulation for muon-electron coupling alone (using the parameters of Table 1 from the transverse-field experiments). In this particular case, i.e. in the absence of nuclear superhyperfine couplings, it may be seen that the contact interaction is rapidly decoupled, in fields of order  $A_\mu(2\pi/\gamma_e) = 0.02$  mT, and that the main feature is a level crossing resonance at a field close to  $A_\mu(\pi/\gamma_\mu) = 1.8$  mT. The resonance occurs where the applied field “tunes out” the parallel hyperfine field, leaving the muon spin precessing around transverse components: an



**Fig. 1.** Simulated muon spin repolarization curves for (a) ZnO and (b) CdS. The solid lines are in each case for the two-spin system of muon and electron only, using the hyperfine parameters as determined experimentally (Table 1). The broken lines are simulations including couplings to a third spin—<sup>67</sup>Zn in (a) and <sup>111</sup>Cd in (b)—for various combinations of contact (A) and dipolar (D) superhyperfine couplings. The evolution of polarization is averaged over the time interval 0.8–8  $\mu$ s in (a) and 8–16  $\mu$ s in (b) for comparison with the experimental data of Fig. 2, where the level-crossing resonance is more prominent in the later time window. The inset to (b) shows an approximately  $\sqrt{N}$  dependence when more than one nuclear spin with identical coupling parameters are included.

oscillatory signal at the dipolar frequency is indeed visible in the time-domain signal at this field, confirming the parameters. Addition of superhyperfine interaction with, to begin with, a single <sup>67</sup>Zn nucleus, modifies both the strength of the resonance and the form the initial

repolarization. Simulations are shown for CdS in Fig. 1(b) and (c), where the corresponding level-crossing resonance falls around 0.9 mT. Varying the parameters independently, the strength of the resonance is found to be most sensitive to the nuclear contact interaction, up to a certain value beyond which there is no further suppression (roughly 100 MHz for CdS); the initial repolarization, on the other hand, is sensitive to both the dipolar component of nuclear coupling and to the number  $N$  of coupled nuclei, the decoupling field varying roughly as  $\sqrt{N}$ .

Experimental repolarization curves for comparison with these simulations are shown in Fig. 2. Here polarization is measured as usual via the muon decay asymmetry (a summary account is given in an accompanying paper [5]; these signals were recorded using the  $\mu$ SR instrument at ISIS. Data for two different time windows are shown, indicating that the cross relaxation occurs on the timescale of several microseconds and that the hyperfine level-crossing resonance is more or less obscured by superhyperfine decoupling according to the time window and the relative strengths of the interactions in the two materials. Cross relaxation to the host nuclei is certainly mediated by the paramagnetic

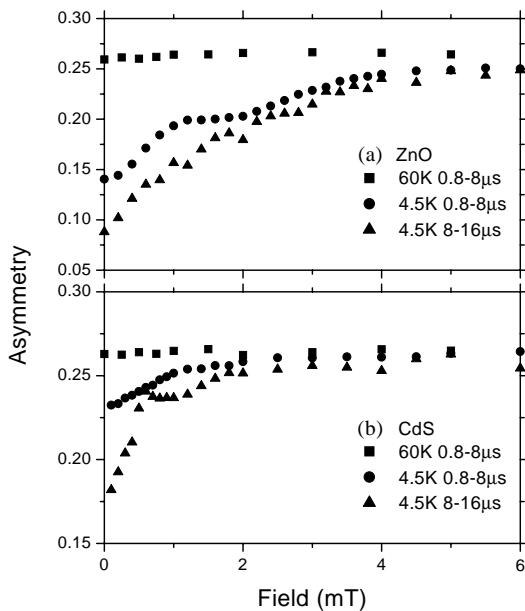


Fig. 2. Muon spin repolarization data for (a) ZnO and (b) CdS, for the temperatures and time windows indicated. The time evolution of muon polarization or relaxation function in response to Zeeman, hyperfine and superhyperfine interactions, is averaged over these time windows and expressed as muon decay asymmetry. According to the relative strengths of the various parameters, the level-crossing resonance due to the muon hyperfine interactions alone is more prominent in the early or late windows.

electron, since measurements above the ionization temperature show close to maximum asymmetry throughout this field range. (That is, cross-relaxation due to purely nuclear-dipolar couplings in the diamagnetic or dissociated state is weak.) Below the ionization temperature it is apparent that the initial repolarization is more gradual than can be accounted for by the muon hyperfine parameters alone and that the form and strength of the level-crossing resonances, though visible, are greatly modified. The following conclusions can be drawn.

From the muon dipolar parameters  $D_\mu$  in Table 1, we can state that major spin density (1 Bohr magneton) must either be localized at a distance greater than 1.5 nm from the muon in ZnO (and at even larger distances in the other materials) or else it must be distributed so that the dipolar term almost vanishes by symmetry. This already argues against a compact molecular radical comparable with bond-centred hydrogen or muonium in Si or GaAs, for which the (muonium) dipolar parameters are 51 and 86 MHz, respectively [6]. Such a compact state may well be formed in HgO, for which the hyperfine and ionization parameters are all quite large ( $A_\mu = 15$  MHz,  $D_\mu = 5$  MHz,  $T_i = 150$  K,  $E_d^{\text{exp}} = 300$  meV [7,8]) but we can reasonably exclude it for the materials of Table 1. For ZnO and CdS we can also state that all the muons which form paramagnetic centres are subject to the same superhyperfine interactions: there are not different components to the  $\mu$ SR signals according to the isotopic abundance of near neighbours.

Pending simulations for a large number of coupled nuclei, with a distribution of coupling strengths, the following estimate of characteristic superhyperfine parameters may be made. We treat the electron spin density as distributed equally over  $N$  cations (spin density on the muon itself being so small). If the free-atom coupling for the cation in question is  $A_0$  in frequency units and the isotopic abundance of the dipolar nuclei is  $c$ , there are  $cN$  interactions to be decoupled, each of  $A_0/N$ . The characteristic contact interaction to be decoupled may therefore be estimated as  $\sqrt{cN}(A_0/N) = \sqrt{c/N}A_0$ , and likewise for the dipolar parameter. We use the values of the atomic couplings given by Moreton and Preston [9]:  $A_0 = 2087$  MHz for  $4s(^{67}\text{Zn})$ , 13650 MHz for  $5s(^{111}\text{Cd})$ . (The value for  $^{113}\text{Cd}$  is not given by these authors, so we take it equal to that for  $^{111}\text{Cd}$ ; dipolar parameters corresponding to occupation of the atomic p orbitals are not given for these elements.) Setting  $N$  equal to the number of cations contained within the effective Bohr radius of a hydrogenic shallow donor, we obtain parameters as in Table 2.

These values of  $A_0\sqrt{c/N}$ , the effective contact superhyperfine interactions to be decoupled, are not inconsistent with the repolarization curves of Fig. 2 if the accompanying dipolar parameters are about 5 MHz in ZnO and 10 MHz in CdS. The present model of

Table 2  
Decoupling parameters as described in the text<sup>a</sup>

|     | $A_0$<br>(MHz) | $c$   | $a^*$<br>(nm) | $N$  | $cN$ | $A_0/N$<br>(MHz) | $A_0\sqrt{c/N}$<br>(MHz) |
|-----|----------------|-------|---------------|------|------|------------------|--------------------------|
| ZnO | 2087           | 0.041 | 1.7           | 2000 | 80   | 1                | 10                       |
| CdS | 13650          | 0.25  | 3.4           | 3000 | 750  | 5                | 100                      |

<sup>a</sup>  $a^*$  is the effective Bohr radius of hydrogenic shallow donors in these materials, calculated from electron effective mass and dielectric constant.

equivalent nuclear couplings is crude and these values may only indicate orders of magnitude. A more sophisticated treatment of the shallow-donor model would evidently involve simulating the muon response to a distribution of superhyperfine interactions. With individual couplings varying with radius according to a hydrogenic spin–density function  $\rho(r) = \rho_0 \exp(-2r/a^*)$ , the expected distribution has the form  $P(\rho) \propto (\ln \rho)^2 / \rho$  (with limits  $0 < \rho < \rho_0$ ). Our estimates of the typical couplings do suggest, however, that resonant cross-relaxation with the nearer nuclei (at fields given approximately by  $(A_\mu - A_n)(\pi/(\gamma_{\text{mu}} - \gamma_n))$  [10]) may be accessible—the low isotopic abundance making these resolvable, if weak. Pending this more sophisticated treatment, and a search for these resonances, we can at least reasonably exclude a tightly bound and compact electronic orbital interacting with a small number of cation nuclei. The present data are more compatible with an extended electronic orbital.

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