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Shallow-level muonium centre in CdS

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Abstract

A new type of muonium defect centre has been observed in undoped CdS at low temperatures ($T < 20$ K). The hyperfine parameters are $A_{\parallel} = 335$ (7) kHz and $A_{\perp} = 199$ (6) kHz (approximately 10^{-4} of the vacuum value) with the symmetry axis along the Cd–S bond direction. The disappearance of the centre at around 20 K is in agreement with the binding energy of a shallow centre. The extremely weak hyperfine interaction implies that the electron is only weakly bound to the muon and is distributed over a large complex of atoms in the neighborhood of the muon resembling the dilated hydrogen-like wave functions of shallow centres in a dielectric medium. Comparing the hyperfine interaction with that of free muonium, a Bohr radius of $a_d = 26a_0 = 1.4$ nm is calculated for this defect, with a_0 being the Bohr radius for the free muonium.

Keywords: II–VI semiconductors; Hydrogen-like defects; Muonium states; μSR

1. Introduction

Muon spin rotation (μSR) spectroscopy has been used extensively to study intrinsic hydrogen-like states in semiconductors. A first overview over the field of muon states in semiconductors was given by Patterson [1]. A more recent report [2] gives an update of this field.

Usually, one finds a diamagnetic state with a muon Larmor frequency corresponding to the external magnetic field and one or two paramagnetic states distinguished by their hyperfine interaction. Experimental muon data on the II–VI compounds are rather scarce. In ZnS and ZnSe a spherical muonium 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. The large missing fractions usually encountered in these systems [1] are a sign that unobserved states are present.

In this paper we present the first observation of a paramagnetic state in CdS. The hyperfine interaction is extremely weak (of the order of 10^{-4} of the

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vacuum value) indicating that the unpaired electron is distributed over a large region and has only a small density at the muon site. This new muon state is observed only at low temperatures and in undoped material. We argue that the conversion of the paramagnetic to the diamagnetic state is due to ionisation.

2. Experimental details

For the experiments reported here, we used commercially available (from CrysTec, Berlin), undoped, hexagonal (wurtzite structure), single-crystalline CdS samples with an area of approximately 40 mm^2 and a thickness of 1.2 mm and the $\langle 0001 \rangle$ axis perpendicular to the plane. The resistivity of the n-type samples is about 3 Ωcm at room temperature. The muon spin rotation experiments were performed using the GPS instrument at the Paul-Scherrer Institute/Switzerland and at ISIS at the Rutherford Appleton Laboratory in England in perpendicular geometry [3].

3. Results and discussion

Fig. 1 shows the μSR spectrum and its Fourier transform at 100 G and 10 K. We observe three lines, the middle one corresponds to the external field, the two others are symmetrical around this line and are due to muonium. In the high field or Paschen-Back region, which is reached here already for fields above 100 μT, as used in these experiments, the following relation holds [1]:

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

where $\Delta\nu(\theta)$ is the separation of the 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 interactions parallel and perpendicular to the symmetry axis. Measurements at different angles (to be published elsewhere) reveal that the symmetry axis is along the Cd–S bonds and the hyperfine parameters are

$$A_{\parallel} = 335\,(7)\,\text{kHz} \quad \text{and} \quad A_{\perp} = 199\,(6)\,\text{kHz}.$$

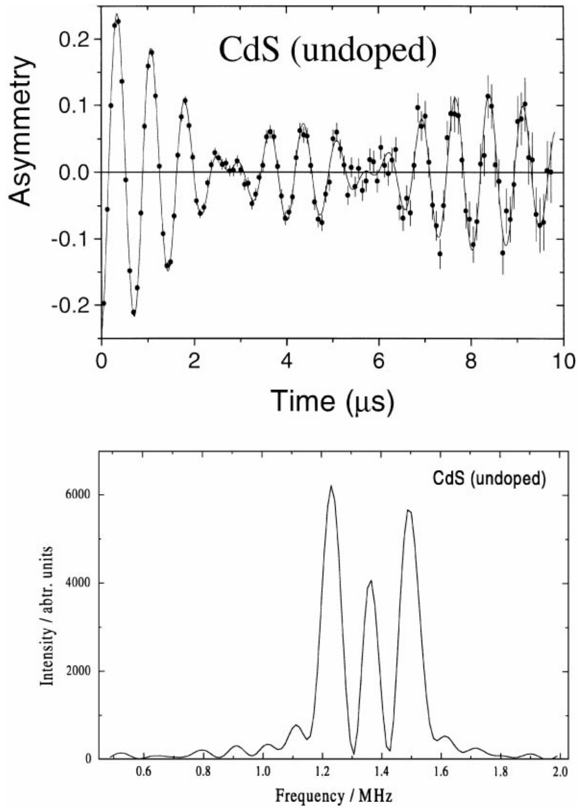

Fig. 1. μSR spectrum and its Fourier transform for undoped CdS at 10 K and transverse field of 0.01 T. The field was perpendicular to the c-axis.

$A_{\parallel}$ and $A_{\perp}$ have the same sign, but both could be either positive or negative.

With increasing temperature, the separation of the muonium lines decreases and the spectral weight is transferred to the middle line. Assigning the sharp middle line with $\sigma = 0.025\,\mu s^{-1}$ to the diamagnetic state and all broad lines, in particular the split lines, to muonium, we observe a steep increase of the diamagnetic fraction at around 20 K (Fig. 2). The Arrhenius plot of this fraction gives an activation energy of approximately 9 meV. Assuming that the conversion is due to ionisation, 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 the muonium forms a shallow level.

The crucial point in our reasoning is the assumption that the conversion is due to ionisation. An

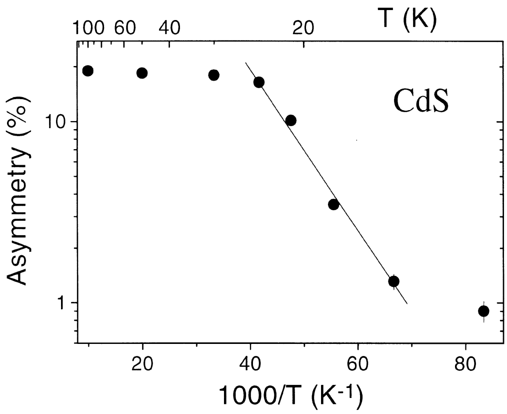

Fig. 2. Arrhenius plot of the diamagnetic fraction of the muons in CdS in the temperature range around 20 K.

alternative process would be the thermally activated spin exchange with conduction electrons. However, the experimental findings speak against this possibility. Firstly, spin dynamics effects (line shift and broadening) observed on the paramagnetic state below 20 K vary with temperature much more slowly than the fairly abrupt transition from the para- to the diamagnetic state around 20 K. Thus, a smooth extrapolation of the spin dynamics from low temperatures does not describe the rapid change observed around 20 K. Secondly, measurements on two different samples (both nominally undoped) showed deviations in the spin dynamics at low temperatures but the transition to the diamagnetic state was very similar in both cases as expected for ionisation, and thirdly, the assumption of a strongly bound state with the electron localised at nearby atoms (e.g. at the Cd atom of the Cd–S–Mu radical molecule) would hardly be reconciled with the small dipolar field observed at the muon.

4. Conclusion

Thus, the present data provide convincing evidence that the muonium in CdS is a shallow centre (donor or acceptor) with a binding energy of approximately 18 meV. The electron distribution of a shallow centre may be roughly described by a dilated hydrogen-like wave function in a dielectric medium. In this picture, the hyperfine interaction scales inversely with the cube of the Bohr radii of the corresponding 1s 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 centre 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 $\varepsilon = 9.6$ [4] and effective electron mass of approximately $m_e = 0.2m_0$ [5], i.e. $E_d = (m_e/m_0/\varepsilon^2)$, $E_0 = 29$ meV and $a_d = (\varepsilon/m_e/m_0)a_0 = 48a_0$. A closer agreement is not expected with the rough models considered.

Acknowledgements

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Comments

Kiefl:
The observed anisotropy in the hyperfine interaction seems reasonable even for a shallow center. For example if the muon is bondcenter and $\sim 1\%$ *of the electronic spin density is a non bonding* Cd–S *orbital, one would obtain anisotropy as observed.*

Gil:
We have considered the anti-bonding site by analogy to the assignments made for the muon in the chalcopyrites $CuInSe_2$ *and* $CuInS_2$, *which have a similar local bonding structure.*

Percival:
I do not understand why you assume that the unpaired electron is centered on the muon. This results in a very expanded Mu atom. Why not assume a different nuclear centre for the atom and simply have transfer of a small part of the electron density to the muon?

Gil:
We agree that a molecular-radical model is an appealing solution. The question is what species might be consistent with our hyperfine parameters. We have been prompted to consider the model Cd-S-Mu, *where the muon is antibonding to sulphur and the major spin density is on the beta-cadmium. While it is difficult to estimate the muon contact interaction, we have calculated the dipolar interaction for this geometry to be* 1500 kHz, *which is much higher than our experimental value of* $(2/3)(A_{\parallel}\text{-}A_{\perp}) = 90$ kHz. *To explain our data, the unpaired electron would have to be localized at the distance of about* 8 Å *from the muon site. We would welcome suggestions of alternative structures. Furthermore, we expect the molecular-radical to be stable up to much higher temperatures.*