Experimental Confirmation of the Predicted Shallow Donor Hydrogen State in Zinc Oxide

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We confirm the recent prediction that interstitial protium may act as a shallow donor in zinc oxide, by direct spectroscopic observation of its muonium counterpart. On implantation into ZnO, positive muons — chemically analogous to protons in this context — form paramagnetic centers below about 40 K. The muon-electron contact hyperfine interaction, as well as the temperature and activation energy for ionization, imply a shallow level. Similar results for the cadmium chalcogenides suggest that such shallow donor states are generic to the II-VI compounds. The donor level depths should serve as a guide for the electrical activity of interstitial hydrogen.

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This Letter is in response to the very recent theoretical result by Van de Walle [1], that interstitial hydrogen can provide a donor level just below the conduction band in ZnO and therefore act as a source of n-type conductivity in this material.

We have detected and characterized the muonium counterpart of this state, adding to the theoretical predictions precise values of ionization temperature, donor level, and spin density at the donor site in the paramagnetic (undissociated) state. We also report the systematics of these parameters among the cadmium chalcogenides, further to our first observation of such a state in CdS [2]. This combination of experimental and theoretical evidence for a particular compound, together with data for three others, establishes the general importance of the shallow donor state in the II-VI compounds and raises the question of how widespread such behavior of hydrogen and its isotopes might be among other wide-gap semiconductors.

Isolated hydrogen atoms commonly form deep-level defects in semiconductors, with donor and acceptor states involving different interstitial locations. The paramagnetic neutral centers are especially difficult to study spectroscopically for two reasons. First, hydrogen defects typically constitute a negative-U system, so that the neutral states are only metastable. Calculations for another wide-gap semiconductor, GaN [3], illustrate this behavior and may be compared with those for ZnO [1]. Second, hydrogen is so mobile and reactive that it quickly pairs with and passivates other defects or dopants, removing their electrically active levels from the energy gap.

To obtain an atomistic picture of the behavior of the isolated centers, studies of the analogous states of muonium are at a considerable advantage [4,5]. In these experiments, muonium is treated as a light isotope of hydrogen: Mu $= [\mu^+ e^-]$, with $m_{\mathrm{Mu}}/m_{\mathrm{H}} \approx 1/9$. In their vacuum states, Mu and H have the same Bohr radius and binding energy to within a fraction of a percent. With due regard for differences in zero-point energy when constrained interstitially or chemically bound, muonium provides a good model for hydrogen, adopting the same sites and an essentially identical local electronic structure. It may be detected and characterized readily by the muon spin rotation (μSR) technique, thanks to the special properties of muon production and decay, which give this spectroscopy a particulary high sensitivity per spin. Following muon implantation in the sample, the evolution of spin polarization is displayed for up to 5–10 muon lifetimes ($\tau_\mu = 2.2\ \mu$s)—usually before the muonium encounters or reacts with other defects.

Prior to our own studies of CdS [2], muonium centers in semiconductors had all been found to have energy levels deep in the energy gap, with tightly localized electron wave functions. Thus in Si, for which the correspondence between Mu and H is best documented [6,7], muonium provides a donor level at about 200 meV below the conduction band, defined by its ionization energy at the bond-center site [6]. The negative-U issue is not fully resolved but the acceptor level, involving a change to the tetrahedral cage site, is believed to lie deeper still [7]. A similar metastability of neutral muonium and bistability of its charged states is seen in compound semiconductors such as GaAs [5]. According to Van de Walle's calculations for H in ZnO [1], interstitial protons could be sited either antibonding to oxygen in the wurtzite-type lattice or roughly midway between adjacent O and Zn atoms. The former may be imagined as the hydroxyl site which is common in oxides and the latter is analogous to the bond-center site which is established in the more covalent semiconductors with

the zinc blende (e.g., GaAs) or diamond-type (e.g., Si) lattices.

In experiments performed at the ISIS Pulsed Muon Facility we have implanted spin-polarized positive muons into ZnO (a powder sample of 99.999% purity from Alfa Aesar) to mimic the behavior of protons. At room temperature and down to about 50 K, the muon spin rotation signal shows precession at the muon Larmor frequency (in a magnetic field applied transverse to the initial polarization), suggesting that the muons thermalize as the positive ion. Below 40 K a distinctive beating appears in the μSR precession signal, as illustrated in Fig. 1(a). Such signals are equivalent to free induction decays in magnetic resonance. In the corresponding frequency spectra, satellite lines appear, symmetrically placed about the central Larmor line. These satellites are too intense and their frequency splitting too large to be explained by dipolar coupling between the muon and host nuclei, nuclear magnetism being particularly weak in ZnO. The splitting must therefore represent a hyperfine interaction with an unpaired electron spin, trapped and bound weakly by the muon at these temperatures.

The μSR signals may be analyzed in either the time or frequency domain. We fit the time-domain signal with oscillatory components at three frequencies, each with Gaussian damping. Figure 1(a) is an example of such a fit and the amplitude data in Fig. 2 are obtained in this way. Analysis by the maximum entropy method [8], shown in Fig. 1(b), suggests that the actual frequency spectrum is somewhat more complex.

The μSR spectra being insensitive to any g-value anisotropy at the fields used (20 mT in Fig. 1), the asymmetric broadening of the satellite lines at the lowest temperatures undoubtedly represents a degree of anisotropy in the muon-electron hyperfine interaction. Assuming this to be axially symmetric with principal values $A_{\parallel}$ and $A_{\perp}$ corresponding to the extremal splittings, we obtain an isotropic component $A^{*} = (2A_{\perp} + A_{\parallel})/3 = 500 \pm 20$ kHz and a dipolar component $D = 2(A_{\parallel} - A_{\perp})/3 = 260 \pm 20$ kHz. The expected powder-pattern line shape, simulated with these values without additional broadening, is superimposed on the spectrum of Fig. 1(b). The isotropic component represents the contact interaction—a measure of electron spin density at the muon site. It remains roughly constant below 30 K at 500 ± 20 kHz, which is just 0.011% of the free muonium value ($A_0 =$ 4463 MHz). This is strongly suggestive of a shallow donor state with a highly dilated electron wave function,

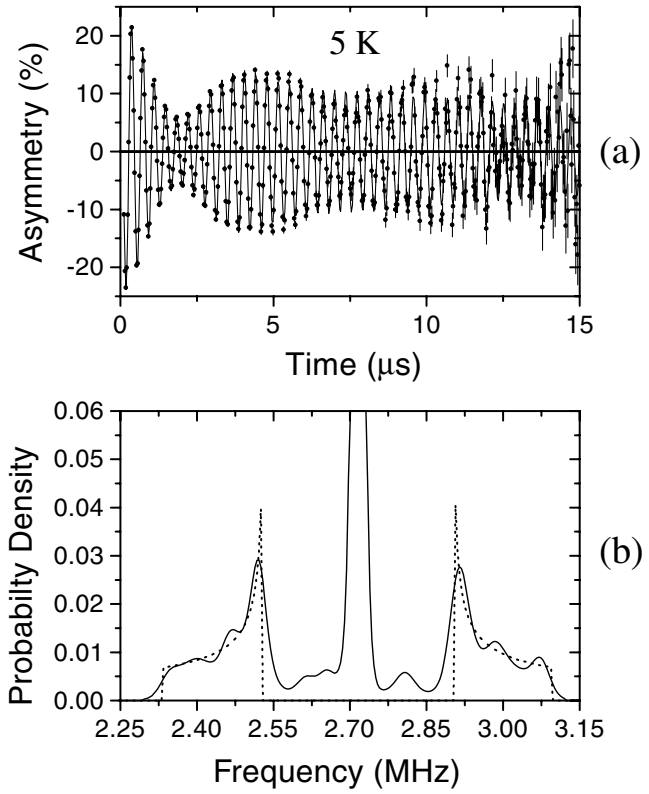

FIG. 1. (a) Muon spin rotation signal recorded for ZnO powder in 20 mT, below the ionization régime for the shallow donor state. (b) Maximum entropy frequency transform. The two broad distributions on either side correspond to the powder spectrum of the hyperfine-split lines. The dashed line is the expected frequency distribution for $A_{\mathrm{iso}} = 500$ kHz and $D = 260$ kHz.

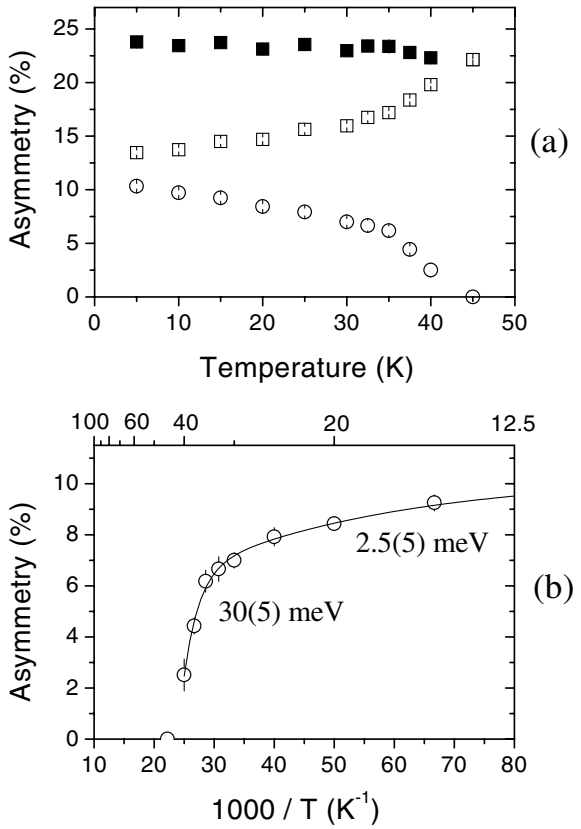

FIG. 2. (a) Amplitudes of the Larmor precession signal (open squares) and satellite lines (open circles), corresponding, respectively, to diamagnetic and paramagnetic states. The sum of these is approximately constant (filled squares). (b) Arrhenius plot for disappearance of the paramagnetic signal.

as we have also argued for CdS [2]. In ZnO we envisage the unpaired electron wave function as made up largely of $4s$(Zn) atomic orbitals: a rough estimate of the effective hydrogenic radius which describes the envelope of the wave function is the Bohr radius scaled by the inverse cube of the contact hyperfine constants, $a^* = a_0(A_0/A^*)^{1/3}$, which gives 1.1 nm. This may be compared with the simple prediction for a shallow-donor state, $a^* = a_0\epsilon/(m^*/m) = 1.7$ nm, based on literature values for the static relative permittivity ϵ and electron effective mass ratio m^*/m [9]. (In both these estimates we ignore the anisotropy in the wurtzite structure and electronic parameters.)

The temperature dependences of the amplitudes of the paramagnetic and diamagnetic signals are shown in Fig. 2. The activation energy with which the paramagnetic component disappears, obtained from the combined amplitude of the satellite lines, is $E_a = 30 \pm 5$ meV; an Arrhenius plot for the corresponding growth of the central diamagnetic line gives a similar value. Assuming the muonium centers to be isolated, the donor energy level is $E_D = 2E_a = 60 \pm 10$ meV below the conduction band edge. The result may be compared with a simple estimate for shallow donors, $Ry(m^*/m)/\epsilon^2$, of about 50 meV and similar values inferred from early electrical measurements [10,11]. ($Ry = 13.6$ eV is the Rydberg constant for hydrogen.)

Throughout the region of ionization, the diamagnetic central line grows at the expense of the paramagnetic satellites. Expressed as muon decay asymmetry, the sum of these amplitudes remains close to the instrument maximum, accounting for the full incoming muon polarization. This observation excludes the coexistence of a deep state with a much higher contact interaction, whose signal might otherwise go unnoticed at a pulsed muon source. (At the lowest temperatures, about half the incoming muons evidently fail to pick up electrons, or else reach some other electronically diamagnetic state.) Some process other than simple ionization is apparent in the results of Fig. 2, with the amplitudes showing a weaker temperature dependence at low temperatures. This could be spin exchange with other centers. In experiments in longitudinal and null external field, the muon response also shows evidence for spin dynamics at temperatures well in excess of the ionization temperature. It seems likely that this is charge exchange, i.e., the repeated trapping and detrapping of electrons causing muon depolarization via intermittent hyperfine coupling. This is well known for muonium in silicon and other semiconductors at much higher temperatures [12]. In the undissociated state at low temperatures, zero-field μSR experiments display the muon response to all the local interactions, including superhyperfine couplings to host nuclei. Although nuclear magnetism in ZnO is weak—the dipolar ^{67}Zn nuclei are 4% abundant only—the shallow donor model implies superhyperfine interactions with a large number of these nuclei; we expect to exploit these in future experiments to map the hydrogenic distribution of spin density away from the muon site.

In the present work, following our observation in CdS [2], we have found that shallow muonium states are also present in CdSe and CdTe.

The hyperfine parameters and ionization characteristics of these compounds are displayed in Table I alongside those for ZnO. The very weak contact interaction, indicative of an extended wave function with low electron density at the muon center, is observed in all four cases. The ionization of the muonium states occurs at similar temperatures, implying that the donor levels are also similar. The slight variations are broadly consistent with the different values of ϵ and m^* for each material, within the simple hydrogenic model. It appears that the shallow state could be common in II-VI semiconductors.

These hyperfine and ionization parameters are not explicitly predicted by *ab initio* methods: for ZnO (the only compound in this class for which hydrogen centers have been tackled theoretically so far) the calculations demonstrate instead the stability of the H^+ ion over localized H^0 or H^- states. The electronic orbitals associated with these latter are found to be resonant with the conduction band, so Van de Walle notes that electrons placed here will relax to the conduction band minimum—conditions favorable for formation of the weakly bound hydrogenic state [1]. Our μSR data add to as well as confirm the theoretical prediction, therefore, with two separate demonstrations of the weak binding. The hyperfine parameters quantify the low electron density at the donor site and the temperature dependence of signal amplitudes gives the ionization temperature and donor level directly. We expect that our values will carry over as a guide to the corresponding parameters for protium, since neither hyperfine parameters nor energy level *differences* are greatly sensitive to the different zero-point energies of muon and proton. Thus, for protons, the hyperfine parameters will be reduced in the approximate ratio of the muon and proton magnetic moments, $\mu_\mu/\mu_p = 3.18$; e.g., the contact interaction will be $500/3.18 \approx 160$ kHz. The corresponding splitting in an ESR spectrum may be too small to resolve, but ESR should be able to measure the electronic g-value of the undissociated donor.

The *ab initio* calculations are more specific on the question of the location of the interstitial atom: in ZnO, Van

TABLE I. Hyperfine parameters and ionization temperatures for three tetrahedrally bonded Cd compounds and ZnO. A^* is the isotropic component of the hyperfine interaction and D the dipolar component, as defined in the text. T_{ionizn} is the temperature at which the paramagnetic signal is halved in amplitude.

	CdS	CdSe	CdTe	ZnO
A^* (kHz)	244(5)	87(4)	261(4)	500(20)
D (kHz)	91(6)	<40	<50	260(20)
T_{ionizn} (K)	22(2)	12(2)	13(2)	38(2)

de Walle finds candidate sites near the center of a Zn—O bond and antibonding to the oxygen atom, with the binding eneries marginally favoring the bond center [1]. He gives vibrational frequencies to aid identification of the state via IR spectroscopy. For muons in place of protons, these will be increased in the approximate ratio $\sqrt{m_{\mathrm{H}}/m_{\mathrm{Mu}}} = 3$; IR spectroscopy has not previously been used in conjunction with μSR, but the muon response could undoubtedly serve as trigger detection of vibrational excitation. Site information in μSR is more normally obtained from the linewidth of the Larmor signal, as may be done in this case *above* the ionization temperature. The small number of dipolar nuclei in these materials makes the measurements rather imprecise but our data so far favor the antibonding site over the bond center—in this respect contradicting the calculations. It may be that, pending more specific predictions of the local bonding, i.e., of the core states superposed with a hydrogenic envelope, our hyperfine anisotropy data can be used for a definitive site determination in the undissociated state.

In conclusion, muonium in ZnO shows a hyperfine interaction and an ionization energy that are characteristic of a shallow donor state. Observation of such a state in several other II-VI compounds establishes its general importance within this family. Here muonium offers an accessible experimental model for hydrogen behavior and gives results that carry over, *mutatis mutandis,* as a guide to its electrical activity. In particular, the agreement and complementarity of theoretical and experimental results in a particular compound—ZnO—opens a new chapter in the understanding of the electrical activity of hydrogen impurities.

Evidently the hexagonal structure is not essential for formation of the shallow state since this is now known for muonium in CdS, CdSe, and ZnO (wurtzite structures) and in CdTe (zinc blende structure). Neither is the bond center site essential, if our own experimental assignment in CdS [2] and Van de Walle's calculation for ZnO [1] are both correct. Elucidation of the properties responsible for the switch from deep to shallow behavior—perhaps by studies of mixed crystals—now becomes a high priority, as does the search for similar shallow states of muonium and protium in other classes of wide-gap semiconductors.

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