HTML ABSTRACT + LINKS

Hydrogen In Oxides, Modelled By Muonium

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Abstract. The nature of the neutral, monatomic states of interstitial hydrogen in a wide range of oxides, both semiconducting and dielectric, has been surveyed experimentally via μSR spectroscopy of their muonium counterparts. The states fall into three categories: shallow donor, deep donor and trapped atom – these latter probably the neutral state of deep acceptors. New examples are found in all three categories, giving an emerging picture of the systematics, for comparison with current theoretical models of the electrical activity of hydrogen impurity.

Following the prediction [1] and confirmation [2,3] that hydrogen impurity forms shallow-donor defect centres in ZnO, we have screened a selection of oxides in which the possibility of hydrogen-induced electronic conduction is at issue [4], namely Ag_2O, CdO, HgO, PtO, PbO, Bi_2O_3, ZrO_2, HfO_2, SnO_2, TiO_2, Ta_2O_5, Sb_2O_5, Nb_2O_5, PbO_2 and WO_3. Given the difficulty of translating purely electrical measurements in terms of atomistic pictures of proton site and local electronic structures, as well as the relative sparsity of ESR data, we use muonium as an experimentally accessible model for hydrogen in our a systematic survey. This is the pseudo-isotope of hydrogen formed when positive muons are implanted from an accelerator source to play the rôle of interstitial protons, usually remote from other defects or impurities. The spectroscopy does not rely on favourable hydrogen solubility: it is in essence a combination of ion implantation and a highly sensitive form of magnetic resonance. A hyperfine splitting of several hundred kHz in the μSR spectrum provides the simplest signature of electrons captured into neutral shallow-donor states of muonium, as in ZnO [2]. This contrasts with the very much larger hyperfine constants of several GHz which have long been known for quasi-atomic or deep-level muonium centres in oxides such as MgO and SiO_2 [5]. In our new survey, all the samples were polycrystalline powders from Alfa Aesar; the μSR measurements were made chiefly at the ISIS Muon Facility (UK), with some additional measurements (SnO_2, Nb_2O_5) at the Swiss Muon Source (PSI, Zurich).

We find candidate deep-donor states of muonium in Ag_2O and HgO, using a powerful variant of the μSR technique known as level-crossing resonance. Figure 1 shows two such resonances for muonium in Ag_2O. Their positions determine unpaired electron spin density both on the interstitial muon and the nearby Ag nuclei, mapping out the local electronic structure. The hyperfine parameters, like those for HgO [6], are characteristic not of a shallow or effective-mass donor but of a deeper, compact centre. In Ag_2O, this dissociates around 180K with an ionization energy defining a donor depth of between 130 and 300 meV.

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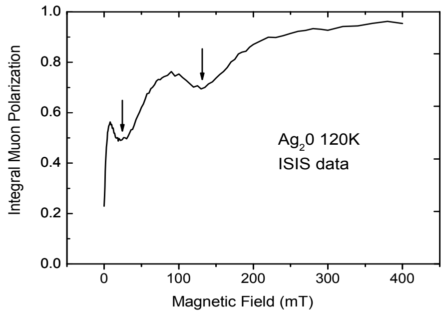

FIGURE 1. Level crossing resonances (resonant loss of polarization), characterizing hyperfine parameters for muonium in Ag_2O at 120K. This signature of the neutral deep donor is lost above about 180K.

In HfO_2, ZrO_2 and Bi_2O_3, the dominant muonium centre (from cryogenic temperatures up to room temperature and above) is the interstitial trapped atom, as it is in MgO and SiO_2. It seems likely that this corresponds to the neutral state of deep hydrogen acceptor centers. Figure 2 shows how this paramagnetic signal is lost at high temperatures – above 700K in HfO_2. It is tempting to assign this to a 0/- transition via hole ionization, with an acceptor binding energy of 0.4eV, but it could instead be an artefact of the onset of ionic conduction, or of muonium diffusion and trapping, in this material. Similar data for ZrO_2 shows the atomic muonium signal diminishing above 350K with an activation energy of 0.25eV.

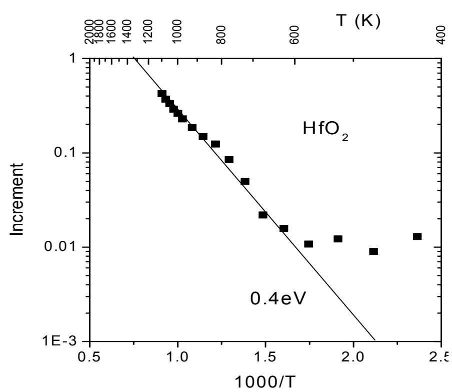

FIGURE 2. Arrhenius plot for the disappearance of atomic muonium in HfO_2, monitored from the growth of the ionic or diamagnetic μSR signal.

Pursuing the search for shallow donors, we were unable to detect a paramagnetic muonium fraction, either deep or shallow, in PbO, Nb_2O_5, Ta_2O_5, Sb_2O_5, PbO_2 or SnO_2, between room temperature and 4K. Beyond the original observation in ZnO, we so far find clear evidence for new shallow-donor states only in WO_3. Appropriate hyperfine satellites are seen in CdO, as they are in ZnO, but they disappear only above 100K with the somewhat high activation energy of 94±18meV. A possible complex with the abundant O vacancies needs to be considered. In WO_3, the hyperfine satellites are unresolved, being collapsed to a broader spectral feature by short spin-state lifetimes. Figure 3 shows that this feature has appropriate ionization characteristics, with a donor depth averaged from several data sets of 28±25meV**.** Similar spectral features are found at low temperature (discernible below about 50K) in TiO_2, ZrO_2 and HfO_2 but they are less pronounced In the case of ZrO_2 and HfO_2, the shallow-donor muonium, if confirmed, must therefore coexist with the deeper trapped-atom states. This raises the tantalizing possibility, compatible with recent theoretical treatments [7], that these candidate high-κ materials may not be immune to hydrogen-induced conductivity.

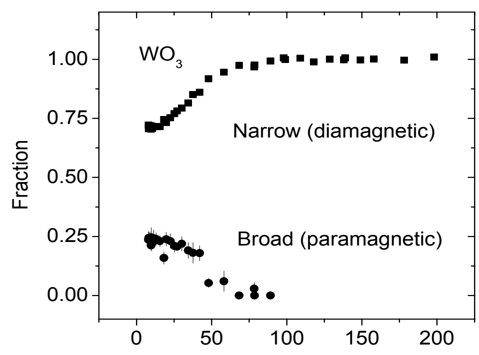

FIGURE 3. Dissociation or ionization of the putative shallow-donor muonium state in WO_3, showing growth of the ionic (upper) at the expense of the neutral (lower) fraction, seen as distinct components in the μSR spectrum.

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