Chapter 10

MUON SPIN ROTATION MEASUREMENTS ON ZINC OXIDE

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Abstract: The theoretical suggestion that hydrogen might form shallow donor states in zinc oxide – and hence account for the n-type conductivity normally found in undoped samples – has been confirmed by experimental studies using muonium, a light pseudo-isotope of hydrogen. Characteristic frequencies in muon spin rotation experiments yield a hyperfine constant that is ~10^4 times smaller than that of vacuum-state muonium, indicating an extended orbital and a shallow centre. Temperature-dependence studies yield an ionization energy of about 30 meV. Band-offset diagrams and measurements on other semiconductors suggest that hydrogen forms shallow donor centres when the electron affinity of the host material is more than about 4 eV; otherwise the hydrogen level lies deep in the energy gap.

Key words: Hydrogen, muons, muonium, shallow donors

1. INTRODUCTION

The simulation of hydrogen by muons has proved to be extremely valuable in the identification of potential sites for hydrogen in semiconductors and insulators. Although the muon has a mass one-ninth that of the proton, its interaction with the host lattice, both electronically and chemically, is virtually identical to that of a proton. During its 2.2 microsecond lifetime (experiments are frequently undertaken over a timescale of up to ten lifetimes), the muon can diffuse, interact with, and adopt positions in the lattice that protons themselves would occupy. If the temperature is sufficiently low, muons can capture electrons to form muonium atoms. The reduced mass of muonium is within 0.5% of that of

hydrogen and so its Bohr radius and ionization energy are essentially the same as those of hydrogen.

Experiments using muons are generally easier and more direct than experiments\textsuperscript{1} using hydrogen itself. One reason for this is the high sensitivity of the technique, by which one can essentially ‘see’ individual muons. Another and more fundamental aspect is that hydrogen frequently forms ‘a negative-$U$ system’, making the neutral state inaccessible under thermal equilibrium conditions. Such conditions do not apply in the muon experiments, permitting observation of both the ionized (charged) and unionized (neutral) states.

The theoretical prediction\textsuperscript{2} that hydrogen forms a shallow donor state in ZnO has been confirmed by muon implantation studies\textsuperscript{3,4}. Below 40 K a distinctive beating of the muon precession signal provides the required signature. Fourier transformation reveals a central line at the muon Larmor frequency accompanied by two symmetrically disposed satellites, the separation of which yields a hyperfine constant about 10,000 times smaller than that for vacuum-state muonium. Confirmation that this signal represents the extended orbital of a shallow centre has been obtained by studies as a function of temperature, which reveal the disappearance of the satellites with an ionization energy of approximately 30 meV. More recent measurements\textsuperscript{5} in longitudinal magnetic fields provide further evidence for these findings.

2. EXPERIMENTAL DETAILS AND RESULTS

The experiments were undertaken at the ISIS pulsed muon facility at the Rutherford Appleton Laboratory situated near Oxford in England. Positive muons of energy 4 MeV and 100% spin polarized are brought to rest within a few tenths of a millimetre in powder or single-crystal samples mounted within a cryostat.

The technique of muon spin rotation involves applying a magnetic field perpendicular to the direction of the incoming beam of muons (transverse to their spin) and monitoring the resulting precession signal via the emission of positrons that are emitted preferentially in the direction of the muon spin at the moment of its radioactive decay. For the bare muons this is simply the Larmor frequency but for muonium several frequencies are observed. In the case of a small hyperfine constant, one can easily reach the so-called Paschen-Back regime in moderate fields and then a triplet of lines is seen in a Fourier transform of the raw data.