Initial Study of Positively Charged Muonium Motion in ZnO, CdO, TiO$_2$, and SnO$_2$

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Abstract

Transparent conducting oxide materials ZnO, CdO, TiO$_2$ and SnO$_2$ are being studied to determine the motional characteristics of diamagnetic muonium. These materials are being studied with an eye for future applications in solar cells, LEDs, and other transparent electrode applications. Theoretical studies show that H$^+$ is the only stable form of hydrogen seen in these materials; therefore we expect to only observe a Mu$^+$ state except at the very lowest temperatures. Zero field muon spin depolarization measurements have been performed to determine Mu$^+$ motional characteristics in these samples; with the aim of addressing a controversy regarding the diffusion barrier for hydrogen in ZnO. The results of initial data fits are discussed and interpreted in light of the data on H diffusion. We observe ionization of shallow donor Mu states at low temperatures, confirming earlier observations that are consistent with hydrogen as an n-type dopant in these compounds.

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1. Introduction

Transparent conducting oxides (TCO) are commonly used as electrodes/transparent windows in semiconductor based optical devices, such as LED’s and solar cells. The efficiency of these devices is partially dependent on the ability to emit or absorb light through the TCO electrode. The degradation of the TCO electrode over time plays a part in the lifetime of the device. The diffusion of hydrogen, in both
the TCO and semiconductor layers, may therefore play an important role in the degradation of the electrode transparency. By understanding the mechanics of hydrogen diffusion, it will be possible to create longer lasting and more efficient electrodes and devices.

MuSR (Muon Spin Research) uses positive muons as a substitute for protons to create short lived hydrogen analogs. The short lifetime of the muon (2.2 $\mu$s) allows for detection of the properties of isolated muonium ($\text{Mu: } \mu^+ e^-$) defects in materials. The properties of Mu defects can be translated to H defects in the same material. $\text{Mu}^0$ shallow donors have been seen in ZnO [1,2] and other oxide materials [3,4] at low temperatures. Theoretical modeling has shown that hydrogen is only stable in the positive charge state, $\text{H}^+$ [5]. Excess electrons in the conduction band from the ionized H dopes the material n-type. Therefore, $\text{Mu}^+$ will be the only charge state of interest regarding the motional characteristics. Zero magnetic field (ZF) depolarization measurements are needed to study the $\text{Mu}^+$ diffusion. This MuSR technique creates a sample area in which there is a net zero magnetic field and monitors $\text{Mu}^+$ spin depolarization due to fluctuating local magnetic fields and/or motion of $\text{Mu}^+$ in the material. In the samples of interest here, the local magnetic fields are created by nuclear moments in the host atoms and the percentage of atoms with nuclear moments is low for these compounds. Oxygen has no stable isotope with a non-zero nuclear moment. The depolarization rate of these materials is slow due to the low percentages of nuclear magnetic moments, 4% Zn, 25% Cd, 13% Ti, and 17% Sn, making for a difficult experimental challenge.

2. Experimental results

2.1. ZnO

Zero field muon spin depolarization measurements were taken for ZnO from 20 K to 400 K at ISIS, UK and from 300 K to 660 K at TRIUMF in Vancouver, Canada. The data below room temperature has been preliminarily fit with a dynamic Kubo-Toyabe function [6], a static Kubo-Toyabe function [6], and a function roughly constant with temperature. The dynamic Kubo-Toyabe function provides the hop rate of the $\text{Mu}^+$ center as a function of temperature. This is shown in figure 1a. The rise in hop rates at 100 K is assigned to thermally activated tunneling among equivalent oxygen anti-bonding sites, based on theoretical models [7,8]. The decrease in hop rates near 225 K indicates a transition into a second site. This second site is assigned to a bond center site parallel to the c-axis, which is the lowest energy site based on theory [7]. Since the bond center site is the lowest energy site, it should also be occupied at the lower temperatures. The width parameter ($\Delta$) of the dynamic signal we used in the current analysis is therefore a weighted average of the width parameters associated with the two different $\text{Mu}^+$ sites. Based on the theoretical results, we have tentatively assigned the second low-temperature state to the three equivalent oxygen anti-bonding sites oriented at 71 degrees to the c-axis, the so-called AB$_1$ sites. The activation energy for the low temperature motion from a fit to the hop rate plot is 56.5 (7.4) meV with a very low prefactor. Given our site assignments and these motion parameters, this can be taken to be thermally activated tunneling among the three AB$_1$ sites around a single oxygen atom. The barrier energy for a transition out of this locally tunneling state into the room temperature bond center site obtained from the data in figure 1a is 441 (16) meV. If we assume that only the low energy BC$_\parallel$ site is occupied from 320 to 360 K, we get a static width parameter $\Delta_{BC} \sim 17$ kHz. It has been difficult to separate the signals in the data from TRIUMF due to a high background signal. The present results suggest the onset of $\text{Mu}^+$ diffusion near 400 K. However, the simple analysis used thus far suggests that the $\text{Mu}^+$ centers may go through multiple trap and release cycles at elevated temperatures. Data at higher temperatures, and with a lower background, are needed in order to extract the $\text{Mu}^+$ global diffusion barrier energy and to further investigate the trap and release dynamics associated with the trap limited diffusion regime.
Fig. 1: (a) Hop rate of Mu\(^+\) in ZF as a function of temperature in ZnO. The solid line is the calculated fit. (b) CdO ZF signal amplitudes as a function of temperature. The open circles are the total amplitude, the diamonds are a diamagnetic state, the squares are the shallow donor signal, and the filled circles are a third signal, as yet unidentified.

2.2. CdO

Zero field muon spin depolarization measurements have been taken for CdO from 2 K to 320 K. Three signals were seen over this temperature range. The preliminary fits included three static Kubo-Toyabe functions. The amplitudes of these signals are seen in figure 1b. The signals have not been assigned to specific sites yet. The highest amplitude signal (diamonds) is assigned to Mu\(^+\) centers. The second signal (squares) has been assigned to a Mu\(^0\) shallow donor signal and should be fit as a rapidly damped oscillation. The reduction in amplitude of this second signal at 100 K is associated with the ionization of the shallow neutral center. The ionization energy is found to be \(\sim 100\) meV. The width parameters are related to the second moment of the local magnetic field. The width parameter for the third signal (\(\Delta \sim 0.25\) MHz) is large enough to suggest that this is either a second shallow Mu\(^0\) or a Mu\(^+\) state at an impurity with a nuclear moment. However, it is unlikely that this is a shallow donor since it does not ionize below room temperature. The increasing amplitude of the first and third signals, while the second signal is reduced, indicates that the Mu\(^0\) center is being converted into the states responsible for the first and third signals, which supports a Mu\(^+\) assignment for both.

2.3. TiO\(_2\)

Zero field muon spin depolarization measurements have been taken on TiO\(_2\) from 2 K to 320 K. Three signals were observed at low temperatures: the neutral shallow donor and two Mu\(^+\) diamagnetic signals. The amplitudes of these signals are seen in figure 2a. The shallow donor ionizes around 10 K, as seen by the reduction in the static signal amplitude. The second signal is fast relaxing at the lowest temperatures, and the relaxation rate increases above 40 K. This is currently assigned to a transition into the ground state of Mu\(^+\). The ground state Mu\(^+\) signal has four regions of interest regarding motional characteristics. In the first region, below 8 K, the center is stationary or tunneling locally among equivalent sites at a constant rate. The second region, between 8 K and 40 K, sees a reduction in relaxation rate indicating some form of motional narrowing. The third region, from 40 K to 120 K, is typical of a transition to a more stable (static) state, or trapping at an impurity, since the relaxation rate is increasing. The fourth region, from 120K to room temperature, shows a release from this site, indicated by a decrease in relaxation rate.
Zero field depolarization measurements were taken for SnO$_2$ from 2 K to 320 K. Preliminary fits show two signals, one a shallow donor and the second a diamagnetic Mu$^+$ center. The amplitudes of these two signals are seen in figure 2b. The shallow donor ionizes below 200 K with an ionization energy of about 103 meV. The correlation between the amplitudes of the two signals indicates that the Mu$^0$ most likely ionizes to Mu$^+$ at the same site, which has not been determined yet. Above 200 K the Mu$^+$ relaxation rate decreases, indicative of an increase in hop rate, and suggests the onset of motion.

3. Further discussion

Further analysis of the data collected is currently being done and will include the proper oscillatory signals for the Mu$^0$ shallow donor signals and dynamic functions for the motional Mu$^+$ signals. Data will be taken to higher temperatures in order to determine the onset of global motion and the diffusion barrier energies. The ZnO high temperature data will be retaken at ISIS, where there is a lower background signal. The goal will be to have a more complete analysis of the Mu$^+$ motional characteristics and the diffusion barrier energy. Data on similar oxides have indicated that the high temperature analysis will need a two process trap-and-release model with the capture and release rates determined properly in order to obtain the true barrier for Mu$^+$ diffusion.

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References