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Spin depolarization of muonium in mesoporous silica

Abstract

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Spin Depolarization of Muonium in Mesoporous Silica

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Abstract. We report muon spin rotation/relaxation measurements of muonium in mesoporous silica (SBA-15) with a high specific surface area of 600 m²/g. Up to 70 percent of the incoming muons form muonium and escape efficiently into the open pores at all temperatures between 3 and 300K. We present evidence that the interaction with the silica surfaces involves both spin exchange and a transition to a diamagnetic state, possibly due to dangling bonds on the surface. At very low temperatures, below 20K, the interaction between muonium and the silica surfaces is suppressed due to a He film coating the surfaces. These results indicate that it should be possible to use muonium to probe the surfaces of uncapped nanoparticles supported in silica.

1. Introduction

Finite size can have a profound effect on the properties of a material. On general grounds one expects that any surface will have different structural, electronic and magnetic properties compared to the bulk as a result of the broken translational symmetry and in some special cases topology of the electronic structure (e.g. topological insulators). One important experimental consideration, in order to study the intrinsic finite size effects, is to isolate nanoparticles from each other. One possibility is to disperse the nanoparticles on the surface of a highly porous inert medium such as silica. Materials like silica are well known for their performance as high surface area supports for catalysts, such as Au nanoparticles, which can be decorated uniformly inside the porous silica [1]. This approach has the advantage that it can easily be extended to study uncapped nanoparticles of other materials. Although the muon is primarily known as a bulk probe of matter the high specific surface area of nanoparticles means that the muon can in special circumstances be used to probe surfaces. However it is important to first understand



the behavior of μ^+ and muonium in pure silica, before studies of embedded nanoparticles can begin.

In this paper we report measurements of the transverse and longitudinal spin relaxation rate of muonium in mesoporous silica (SBA-15). We find that a large fraction of up to 70% of the muons form muonium and reach the open pore region [2, 3, 4, 5, 6, 7, 8]. This is comparable with previous experiments on Mu in SiO_2 both in bulk [3] and thin films [8]. Surprisingly this holds true even at low temperatures, indicating that the process for muonium to reach the pores is epithermal. We also observe slow depolarization of muonium attributed to muonium scattering off the silica surfaces. There is evidence that the collisions involve both spin exchange and a transition to a diamagnetic state. We propose the active sites are dangling bonds on the surface (e.g. Si-O-) which have an unpaired spin but can also bind the muonium in a diamagnetic hydroxyl-like group Si-O-Mu. Finally at the lowest temperatures we observe that the interaction of muonium with the silica surfaces is suppressed in a He atmosphere due to coating of the surfaces with He. These results indicate that it may be possible to use muonium as a probe of the surfaces of nanoparticles supported in silica.

2. Experimental

The mesoporous silica (SBA-15) was chosen for this experiment because of its relatively stable channel structure compared to other mesoporous silicas. The sample was made at the University of British Columbia using a hydro-thermal method developed by Somorjai *et al* [9]. More details are given in a separate publication presented at this meeting (see J. Xiao *et al*). The end product is a white fluffy powder. The specific surface area measured with the Brunauer-Emmett-Teller (BET) method is $600 \text{ m}^2/\text{g}$ and the average pore diameter is about $\approx 10\text{nm}$. Non-magnetic Al sample cells with a Ag backing plate were loaded with the powder and sealed with a Kapton window using a gold O-ring. The cell was heated and pumped for 24 hours to remove moisture and oxygen. The pumping outlet tube was then crimped to close the cell, which was subsequently stored in an evacuated desiccator until the experiment. At the beginning of the experiment the cell was then loaded into a He horizontal gas flow cryostat mounted on the SFUMU spectrometer on the M15 beamline at TRIUMF.

All measurements were taken in a spin rotated mode in which the initial muon spin polarization was oriented close to the vertical direction (\hat{x}) and perpendicular to the beam direction (\hat{z}). Two types of measurements were made as a function of temperature (1) $1/T_2$ spin depolarization rate of the muonium precession in small transverse field (TF) of 7G applied along \hat{z} and (2) $1/T_1$ spin relaxation of the muonium in longitudinal field of 28G applied along \hat{x} . Typical asymmetry plots of raw data are shown in Figs. 1 and 3 respectively. Additional TF measurements were also made for detector calibration purposes. After measurements were taken on the closed cell it was removed from the cryostat and the outlet tube was cut to open the cell to the outside. Precautions were taken to minimize any exposure to moisture in the air. The open sample cell was reinserted into the cryostat and the sample space was flushed with warm He gas and pumped down to ≈ 0.015 mbar to remove any residual oxygen that may have leaked into the cell after it was crimped. A significant decrease in the muonium $1/T_2$ was observed at room temperature as may be seen by comparing Figs. 1a and 1b. This is strong indication that the closed cell had a small partial pressure of O_2 . We estimate that 1.5 mbar of O_2 [3] at 300K would be sufficient to cause the additional $1/T_2$ relaxation in Fig. 1a compared to 1b. A second set of measurements of $1/T_1$ and $1/T_2$ were made on the open/pumped cell for comparison. In this case the powder was in direct contact with He gas of the flow cryostat, except at 300K where the sample space was evacuated. The He pressure is very low near room temperature but increases gradually at lower temperatures and reaches a few hundred mbar at 3K.

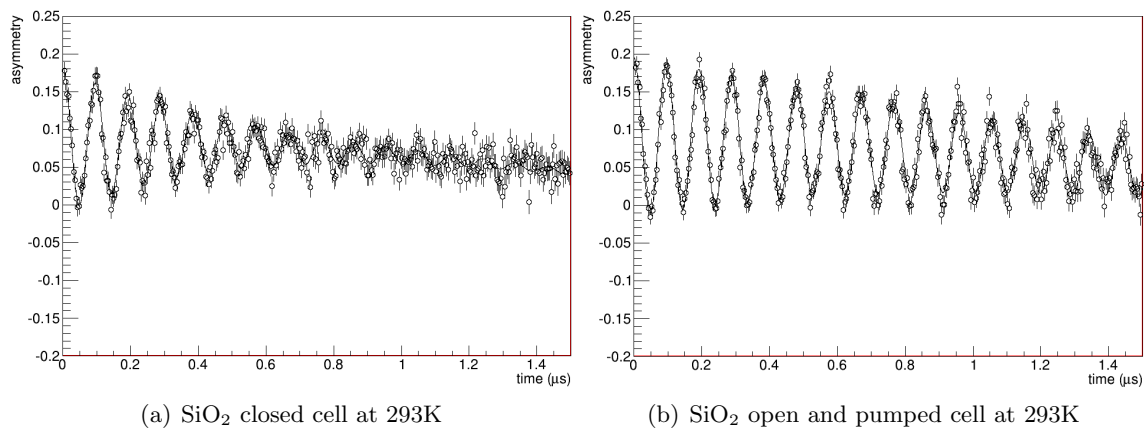


Figure 1. (a) Muonium precession signal in a weak transverse field of 7G at room temperature in porous silica (SBA-15) in a closed cell (b) same conditions as (a) except the cell has been evacuated. Note the decrease in relaxation rate which is attributed to residual amounts of O₂ trapped in the closed cell.

3. Results and Discussion

3.1. $1/T_2$ Spin Depolarization of Muonium

Figure 1 shows the TF muonium signal in SBA-15 silica at room temperature both in a closed cell (a) and an open cell environment (b). Note the $1/T_2$ relaxation rate in the closed cell is much larger than in the open cell. From this we conclude there was a small partial pressure of O₂ in the closed cell which causes spin exchange with muonium. This also demonstrates that the muonium reaches the open pores since that is the only place the oxygen gas can be. It would be interesting to compare our results with the rates measured by Himmer et al. for molecular O₂ in the gas phase [10]. This will require further measurements with a controlled amount of O₂ admitted into the cell. This will be subject of future studies in a controlled environment. The temperature dependence of $1/T_2$ in both the open and closed cells is shown in Fig. 2 (a). Note the difference between the open and closed cells is largest at room temperature where the oxygen in the closed cell is all in the gas phase. As the temperature is reduced the difference becomes smaller, indicating the effect of the oxygen is less pronounced, so that at 50K there is almost no difference. This is evidence that oxygen on the surface of the silica is much less effective in causing spin exchange. It is likely that the oxygen adsorbed on the surface dimerizes and is not paramagnetic. The two curves separate again below 20K. In particular there is a sudden drop in $1/T_2$ seen in the open cell not seen in the closed cell. We attribute this to the He atmosphere in the open cell since one expects He to form a film on the silica surfaces which shields muonium from the depolarizing collisions with the silica. A similar effect was observed in fine oxide powders [2]. In some silica powders the Mu formation probability decreases when a film of He or other gas is coating the surface [7]. However, no such decrease was observed in SBA-15 at least for He.

3.2. $1/T_1$ Spin Relaxation of Muonium

Typical asymmetry plots showing the $1/T_1$ spin relaxation rate of muonium in a longitudinal field of 28 G are shown in Fig 3. Note there is much faster relaxation near room temperature in the closed cell. This is consistent with spin exchange from O₂ in the closed cell. However there is still observable $1/T_1$ spin relaxation in the open cell where all the oxygen has been removed. This is attributed to spin exchange with unpaired electronic spins on the silica surface, most likely Si-O- dangling bonds.

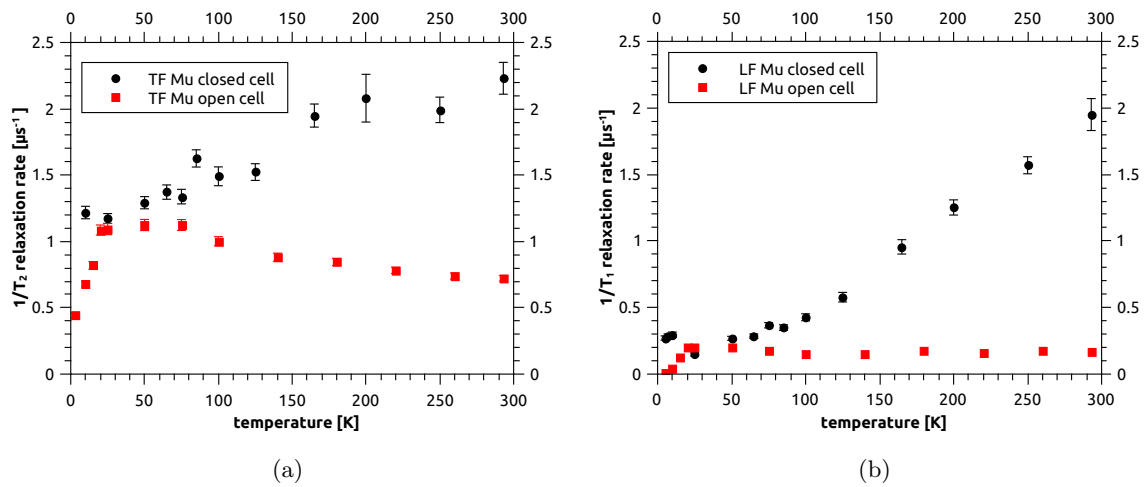


Figure 2. (a) $1/T_2$ spin relaxation rate of Mu in a small transverse field of 7G versus temperature. Black points are for the closed cell and red points are the open cell. (b) $1/T_1$ spin relaxation rate of Mu in a longitudinal field of 28G versus temperature. Note both $1/T_1$ and $1/T_2$ decrease sharply below 20K in the open cell due to the coating of the surfaces with a thin film of He.

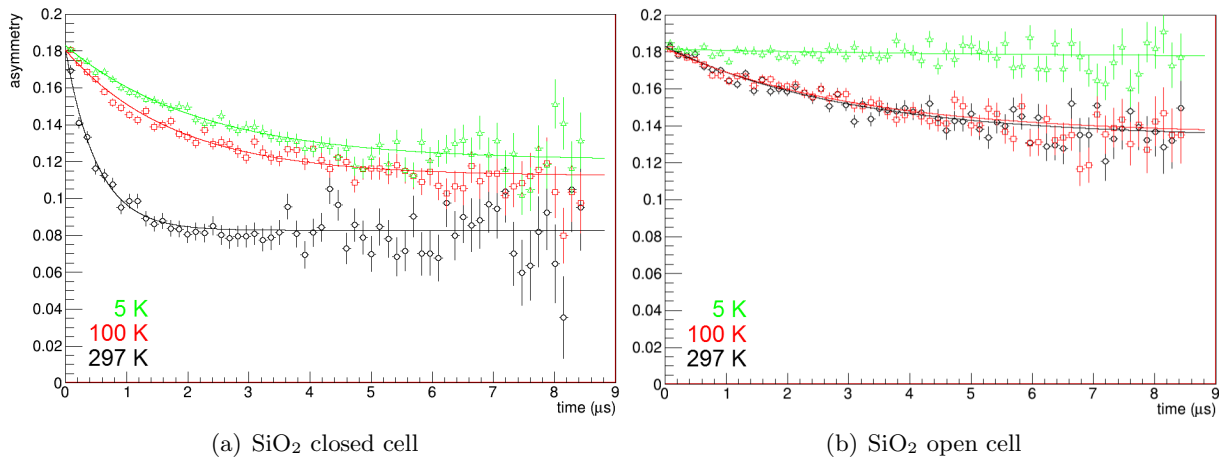


Figure 3. LF spectra in a field of 28G at various temperatures for both samples

The data fit well to a two component transition model over the whole temperature range in which there is a relaxing term and non relaxing term. As mentioned above the relaxation is due to spin exchange from oxygen and unpaired spins on the silica surface, whereas the non relaxing component is due to a transition to a diamagnetic muon state. A simple transition model yields the following form:

$$P_z(t) = A_{\mu^+} + A_{Mu} \cdot \left\{ \frac{\nu}{\lambda + \nu} + \left(1 - \frac{\nu}{\lambda + \nu} \right) \exp(-(\lambda + \nu) \cdot t) \right\}, \quad (1)$$

where $\lambda = 1/T_1$ is the relaxation rate from spin exchange and ν is the reaction rate describing the transformation from Mu to μ^+ . A_{Mu} describes the muons that form Mu when implanted into the sample. A_{μ^+} , the fraction of the muons that stay diamagnetic, was held constant in the fit based on TF results. From the fitted values at 7G TF (Fig. 1) we obtain an average relative

Mu fraction $F_{Mu} = 2A_{Mu}/(2A_{Mu} + A_{\mu+})$ of $0.67 \pm 0.02\%$ for the closed cell and $0.69 \pm 0.02\%$ for the open cell. The fitted value for the reaction rate ranges between 0.1 and $0.3 \mu s^{-1}$ and varies weakly with temperature. The fitted values for $1/T_1$ are shown in Fig. 2. Note at 293K $1/T_1$ is much larger in the closed cell (with oxygen) than in the open cell (without oxygen). This is consistent with a large spin exchange rate from O_2 in the pores at room temperature in the closed cell. Also the difference between the open and closed cell diminishes with decreasing temperature as in the case of $1/T_2$. This is confirmation that the spin exchange rate for oxygen on the silica surface is much less than in the gas phase. Finally we note there is a dramatic drop in $1/T_1$ in the open cell below 20K which is not seen in the closed cell. This also confirms our interpretation that a He film shields the muonium from spin depolarizing interactions with the silica surface.

4. Summary and Conclusions

We have measured the spin depolarization of muonium in mesoporous silica (SBA-15) with a high specific surface area in the presence of oxygen and helium. A large fraction of the incoming muons form muonium and escape efficiently into the open pores at all temperatures down to 3K. We have identified two distinct processes for the way muonium interacts with the silica surface. The muonium may spin exchange with unpaired spins on the surface but there is also evidence for a transition to a diamagnetic state. The active sites are most likely dangling bonds which have an unpaired electronic spin but may also bind the muonium in a diamagnetic state. At very low temperatures, below 20K, the interaction between muonium and the silica surfaces can be suppressed in a He atmosphere due to the formation of a thin He film. These results suggest it may be possible to land polarized muons efficiently to the surface of nanoparticles supported in silica.

Acknowledgments

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