Positron and positronium studies of silica aerogel

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Abstract. Variable-energy positron annihilation spectroscopy (VEPAS) has been used to probe the structure of gold nanoparticles suspended in a silica aerogel matrix by measuring the annihilation parameters $S$ and $W$ and the ortho-positronium (o-Ps) fraction parameter $F$, as a function of incident positron energy. Correction methods have been developed to improve the sensitivity of $F$ by removing background contributions to the number of recorded o-Ps annihilation events. Charging effects have also been observed and investigated.

1. Introduction
Aqueous colloids (suspensions) of gold nanoparticles in water have attracted attention because of applications in photonics technologies such as ultrafast switching, surface-enhanced Raman scattering, and plasmonic sensing [1]. Silica aerogel is a highly porous form of silica glass made of a rigid, open network of tiny intersecting silica strands about 5 nm thick. The average size of the pores between the strands is 40 nm, and over 90% of the total volume is air. The refractive index of aerogel is $\sim 1.05$ and the optical loss due to Rayleigh scattering can be as low as 0.1 dB/cm at a wavelength of 900 nm [2].

Gold nanoparticle-implanted aerogels can be incorporated into waveguides using techniques developed by Bath’s Centre for Photonics and Photonics Materials (CPPM) [3,4]; the resulting devices are stable with time, as the nanoparticles are ‘locked in’ by the silica network.

Past positron studies such as those by Hyodo and colleagues have looked at silica aerogel surface and bulk positronium (Ps) interactions using positron age–momentum correlation [5] as well as angular correlation of annihilation radiation, positron lifetime and Doppler broadening [6]. Other studies have used silica aerogel as a Ps formation medium [7]. Initially, the study described here was aimed at using VEPAS to investigate the gold nanoparticles within the aerogel medium, but it was found that the positron response was dominated by the structure of the aerogel itself.

2. Experimental details
2.1. Aerogel formation
In previous reports, doped aerogels have suffered from nanoparticle aggregation or other limitations. The CPPM group made sol using aqueous gold colloid, resulting in a purple-looking wet gel and aerogel, Fig. 1 (middle). Using TEM it was confirmed that the purple colour is correlated with nanoparticle aggregation due to the presence of methanol. A two-step procedure was developed to stop this in wet gels of the same composition. Using the modified wet gel process prevents aggregation while retaining control over gel time, allowing nanoparticles of diameter $\sim 40$ nm to be embedded at various concentrations in aerogel, Fig. 1 (sample (3), bottom) and Fig. 2. The samples used during this experiment were those shown in Fig. 1, with $\sim 30\%$ gold in (2) and (3). The samples were all initially cleaved in half down their lengths to reveal as clean a surface as possible for the measurements.
2.2. Slow positron beam
All the measurements described herein were performed on the magnetic-transport positron beam at the University of Bath [8]. The energy spectra of annihilation gamma photons from the sample were recorded by a Ge detector, yielding the Doppler-broadened linewidth parameters $S$ and $W$ [9] and the parameter $P:V$ – the ratio of spectrum counts in the 511keV annihilation photopeak to those in the valley region between ~ 400-500 keV - for each incident positron energy $E$ from 0.5 – 30 keV (corresponding to mean depths of 0.13 – 92 µm). Beam energy and position, together with all aspects of data collection, are computer-controlled.

3. Data analysis

3.1. Normalisation method for $S$ and $W$
Doppler broadening parameters can be affected by drifts in the Ge detector resolution and electronic instabilities. The resultant changes in both the $S$ and $W$ parameters can be larger than the real changes within and between data sets, rendering comparisons meaningless. In order to minimize the effect of such drifts the sample is positioned on the holder above a reference sample – here the aerogel sample without nanoparticles - in the vertical plane with a ~3 mm gap between. The two orthogonal trim coils, normally used to position the beam at different energies, then deflect the ~8 mm diameter 30 keV beam by ~11 mm from the base of the sample of interest to the top of the reference sample, and spectra are collected (and $S$ and $W$ evaluated) alternately for the two bulk samples. The average ratio between the parameters at 30 keV is then used to evaluate normalised $S$ and $W$ relative to the reference sample. Figs. 3 and 4 show the difference between the results before and after this procedure.

![Figure 1. Aerogel samples: (1) (top) with no nanoparticles: (2) (middle) with clustered nanoparticles: (3) (bottom) with ~ 40nm diameter spherical nanoparticles.](image1)

![Figure 2. Aerogel: a rigid open network of tiny intersecting silica strands with air-filled pores between them (on average about 40 nm across). Over 90% of the total volume is air.](image2)

![Figure 3. $S$ parameters for samples (1)-(3) normalised to average bulk $S$ value for sample (1).](image3)

![Figure 4. $S$-Parameter data normalised using the alternating sample method.](image4)
3.2. Correction method for P:V ratio

The P:V ratio is particularly sensitive to the probability that ortho-positronium (o-Ps) is formed in the aerogel and survives to decay into three gamma photons. (Higher P:V means less o-Ps.) o-Ps decay photons contribute to the valley counts V.

V, however, also contains a background contribution associated with the peak P (due to incomplete charge collection in the Ge detector) as well as from other background sources. To correct for this a background spectrum (collected with the slow positron beam switched off) was measured and background counts \( V_B \) subtracted from a Si spectrum (with no Ps) to find the contribution \( V_P \) to V from incomplete charge collection as a fraction of P. Using this information, \( V_B \) and \( V_P \) were computed and subtracted from each measured V, which was then used to calculate the ‘true’ P:V ratio.

Fig. 5 shows the raw P:V ratios for the three samples. The corrected ratios in Fig. 6 show a fourfold increase in sensitivity to o-Ps annihilation between samples 1 and 2. The raw P:V for Cz Si had an average P:V = 8.4 whereas when the corrected ratio was 18.9.

4. Charging Effects

Charging effects in sample (1) were investigated by consecutively repeating one \( S(E) \) run (\( E = 0.5 \) to 30 keV) ten times (Fig. 7). Each run took 12.5 h. The lower \( S \) parameters at \( E < 1.5 \) keV are associated with epithermal positron annihilation. Over time the charging effect increased, with the formation of a saturated state in the 1.5–4.5 keV region, shown also in the \( S-W \) plot in Fig. 8. This effect causes the P:V ratio to increase (and o-Ps formation to decrease) dramatically with time in the 1.5–4.5 keV region. The subsurface field appears to be drifting positrons toward the surface at epithermal energies, with a consequently lower Ps formation probability.
5. Final Results
Whereas there is a real difference between the normalised S-Parameters for the three cleaved aerogel samples (Fig. 4), there is a much smaller difference between corrected P:V ratios the two gold samples (Fig.6), but there is a difference between the gold and plain silica aerogel sample.

To test whether the gold nanoparticles could be a catalyst for increased o-Ps formation, more samples were obtained with various gold nanoparticle concentrations between 0 and 29% (Fig. 9). The first set of results used the standard normalisation method described above. In the second set measurements were made separately at the centre of the samples with no normalisation. The third set is identical to the first except that the centres of each sample are measured rather than the ends. The fourth set comprises two repeats of the first measurement of the 14% Au sample. The fifth set is a data point from normalisation run of the original cleaved sample (3). The point at 0% Au is for sample (1).

Some of the results show agreement but others have differences far outside statistical fluctuations, suggesting that positrons and Ps are very sensitive to differences in the structure of the aerogel itself.

6. Conclusions
Doped silica aerogel was investigated initially to look at the positron response to the gold nanoparticles, the P:V ratio being the parameter of choice. Techniques were developed to improve both the sensitivity and reliability of the P:V ratio and S-Parameter. The findings suggest, however, that while P:V was sensitive to the presence of the nanoparticles, there is little or no sensitivity to aggregation. Further investigations with different concentrations of gold nanoparticles revealed that the differences and similarities we originally found appear to be dependent upon the on the face and lateral part of sample probed by the positrons. We have to conclude that the structure of the silica aerogel itself may dominate VEPAS results, and further work may lead to information on aerogel structure of importance to its novel applications in photonics and other fields.

References
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