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Positron annihilation in insulating materials

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Abstract

We describe positron results from a wide range of insulating materials. We have completed positron experiments on a range of zeolite- γ samples, KDP crystals, alkali halides and laser damaged SiO_2 . Present theoretical understanding of positron behavior in insulators is incomplete and our combined theoretical and experimental approach is aimed at developing a predictive understanding of positrons and positronium annihilation characteristics in insulators. Results from alkali halides and alkaline-earth halides show that positrons annihilate with only the halide ions, with no apparent contribution from the alkali or alkaline-earth cations. This contradicts the results of our existing theory for metals, which predicts roughly equal annihilation contributions from cation and anion. We also present result obtained using Munich positron microprobe on laser damaged SiO_2 samples.

The behavior of positrons in metals is now well understood, and calculations based on first-principles approaches provide reliable estimates for positron observables for a wide variety of bulk metals and defects in metals (Jensen, 1989; Sterne and Kaiser, 1991; Puska, 1991; Puska and Nieminen, 1994; Sterne et al, 1999, Tang et al, 2002). The situation for insulators is markedly different. Many insulators show multiple lifetime components. In metals, this would indicate the presence of defects, but in insulators, multiple lifetimes can also arise in defect-free materials due to positronium formation (Dupasquier, 1983). The variety of possible positron states in insulators greatly complicates the interpretation of experimental data, especially since the theory that works so well for metals cannot be used reliably to provide the reference lifetimes associated with the defect-free state in insulators.

The observables associated with positronium are used routinely to measure open volumes in insulators, such as free volumes in low- k dielectric materials, polymers, zeolites etc. (Jean, 2002, Jean et. al., 2002). The interpretation of these data is based on a simple and effective empirical model that provides a calibration between the open-volume size and the long-lived ortho-positronium (o-Ps) lifetime (Brandt et al., 1960; Tao, 1972; Eldrup et al., 1981). In this model, the lifetime of o-Ps is shortened from its vacuum value of 142 ns by pickoff with electrons from the material surrounding the open-volume region. The open-volume region is generally represented as a sphere, and it is assumed that positronium can be treated as a single quantum mechanical particle within this sphere. The annihilation rate is then determined by the positronium density within a layer of fixed thickness around the outside of the sphere. This simple theory is widely used, and a number of extensions have been developed to treat cavities of different shapes (Jasinska et al., 1997, 1999; Gidley et al., 1999; Goworek, 2001), and larger sizes for which a zero-temperature ground-state solution does not give an adequate description (Gidley et al., 1999 ; Ito et al., 1999). Nevertheless, it is difficult in general to extend this simple model to address issues such as asymmetric pore shapes and changes in pore surface chemistry.

At Lawrence Livermore National Laboratory we are combining experimental and theoretical methods aimed at developing a predictive understanding of positrons and positronium behavior in insulators. The ultimate goal of this project is to develop tools for describing the quantum-mechanical behavior of positrons in insulators. As part of this project, we have completed positron measurements on a wide range of insulating materials, including alkali halides, zeolites, KDP crystals, and oxides to provide well-validated experimental data for comparison with theory. Below we summarize results from these experiments.

First we show recent results on a laser-damaged glass sample obtained with Munich positron microprobe (David et al 2001). A better understanding of the nature of the damage caused in glass under laser irradiation will aid in mitigating and developing better matched systems for final optics components for high power laser systems, such as the National Ignition Facility being built at Lawrence Livermore National Laboratory. Fig.1 shows the average positron lifetime results from a $700 \mu\text{m} \times 1400 \mu\text{m}$ area around a laser-damage site. The data is collected with a $50 \mu\text{m}$ positron beam spot. Average positron lifetime decreased around the damage site. There is significant contrast in the positron image and at present a full theoretical understanding of these variations is lacking. This demonstrates the sensitivity of positrons to defects associated with laser damage, and highlights the need for further theoretical development to enable the identification of the specific defects produced by laser damage. A similar reduction in other positron observables, such as the annihilation fraction with low momentum electrons (S-parameter) has been reported previously on SiO_2 samples subjected to ion implantation (Fujinami and Chilton, 1993).

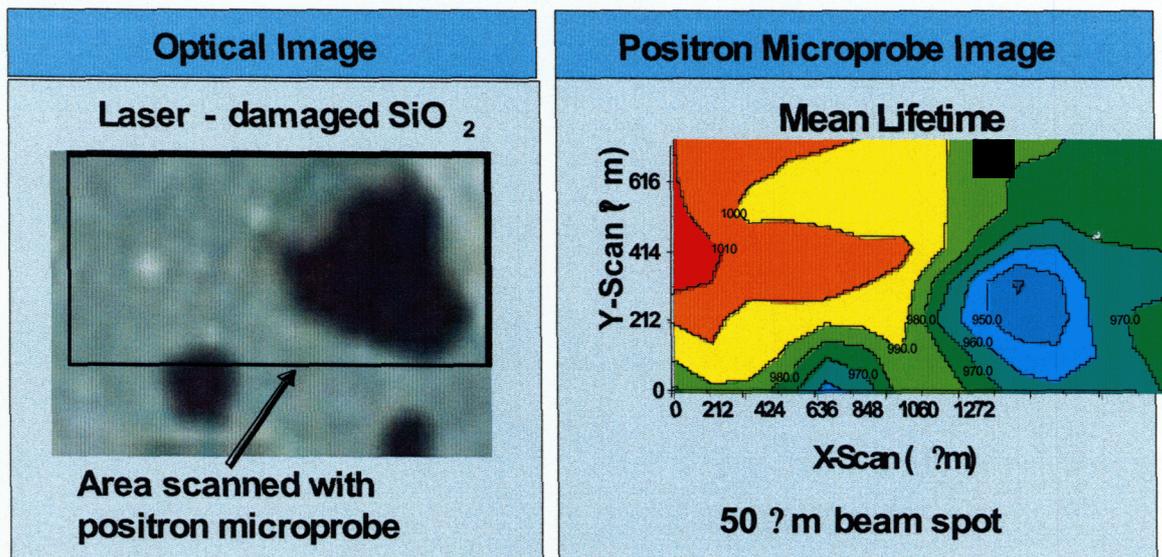


Fig. 1. Positron lifetime image of laser-damaged glass obtained using Munich pulsed positron microprobe. For comparison an optical image of the scanned region is also shown. The different contour regions correspond to different average lifetime values.

Potassium dihydrogen phosphate, KH_2PO_4 (KDP) crystals have attracted wide interest due to their optical properties and crystals of sizes up to 90 cm have been grown as

system components for the National Ignition Facility. It is also known for its ferroelectric transition at 122K. At room temperature, it has a tetragonal structure and is paraelectric and changes to orthorhombic structure with a ferroelectric phase at 122 K. A detailed understanding of the atomic process associated with this transition is still under debate (Zhang et al, 2001). We studied a large KDP crystal (5 cm × 5 cm × 0.8 cm) using electron momentum measurement. Previous studies using angular correlation measurements showed small variations around 122K (Saito and Hyodo 2001). However, our measurements showed no such variation around the transition point. Instead, as shown below, we observed large variations depending on the location of the sampled region across the sample, suggesting presence of defects that are influencing positron observables at low temperatures. Further investigations are necessary to understand the nature of these defects.

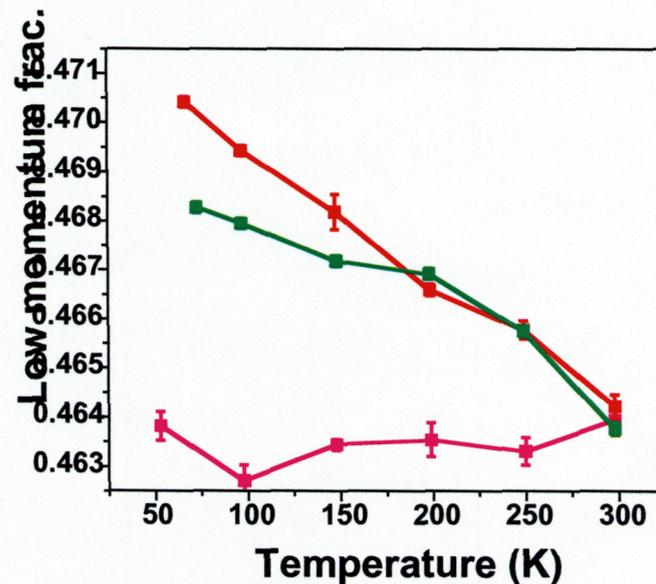


Fig. 2. Figure shows annihilation fraction with low momentum ($<0.38 \text{ a.u.}</math>) electrons from a KDP crystal as a function of temperature. Three sets of data correspond to three different locations across the sample that are 4mm apart from each other. The diameter of the positron beam spot was about 3 mm. Positrons emitted from a ^{22}Na source are guided to the sample with a 1 kG magnetic field. Therefore, these data points have only small contributions from the surface region of the sample.$

We have examined a series of alkali halide crystals using a 3 MeV positron accelerator at Lawrence Livermore National Laboratory. Positron annihilation lifetimes and electron momenta determined by the coincidence Doppler broadening technique were both determined for a set of samples known to emit positronium into vacuum. Orbital electron momentum measurements examined the chemical specificity of the positron annihilation sites in alkali halides. The quality of our samples is determined by the consistency of our measured positron lifetime values with previous results on high quality samples. The electron momentum data at high momentum values indicate the ionic species that are contributing electrons for the annihilation. Fig. 3 shows the electron momentum spectra obtained from several insulating materials with a halogen as one of the constituents. The momentum spectra

are normalized to a reference element, Ge, to highlight the contributions of high momentum orbital electrons. The top panel shows results from crystals with fluorine as a common element, while the bottom panel shows potassium compounds in which halogen is varied from fluorine to iodine. Momentum distributions from crystals containing fluorine show a broad peak centered at 1.3 atomic units, while results from crystals containing Cl, Br, and I show different behavior with less pronounced peak and centroids shifted to lower momentum values.

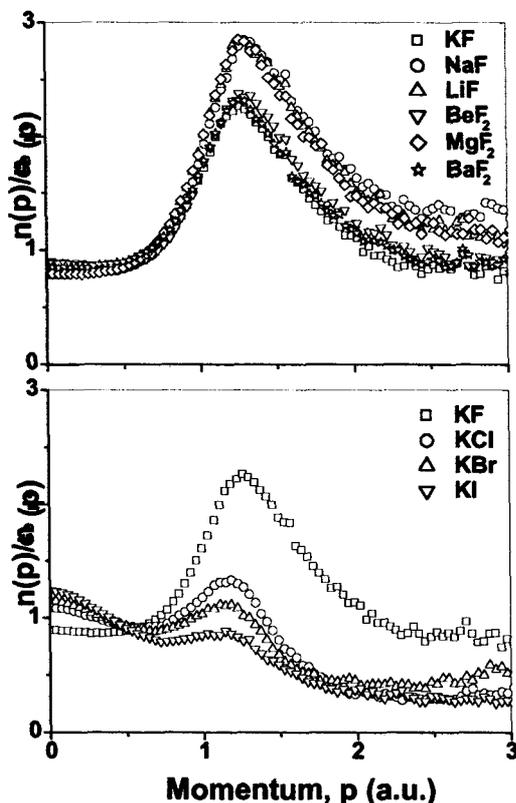


Figure 3. Electron momentum distributions for several alkali halide and alkaline earth-halide compounds plotted as a ratio to Ge. These results are consistent with positron annihilation with only the halide electrons.

Figure 4 shows the corresponding calculations for the alkali and alkaline-earth metals (top panel) and the halides (bottom panel). The close correspondence with the halide spectra in the theoretical curves confirms that the experimentally observed variations in the orbital momentum spectra are due to the halide ions. It might appear that preferential annihilation of positrons with anions is consistent with the charge distributions around the anions, since the negative ion might be expected to attract the positively-charged positron. However, our calculations using existing theoretical methods that work well for metallic systems suggest that the positron's preference for the anions is not that strong and both ionic species should make sizable contributions to the total annihilation spectrum.

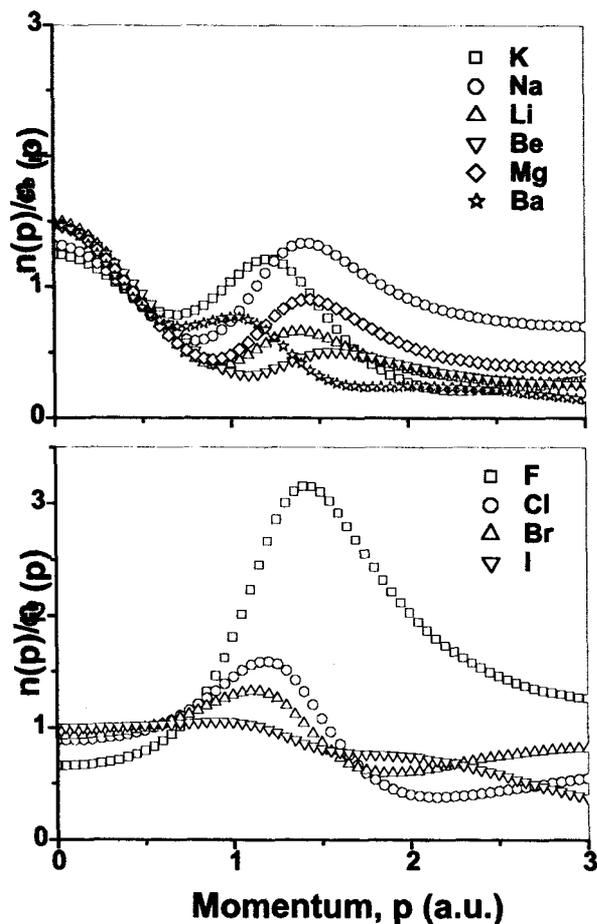


Figure 4. Calculated electron momentum distributions for the alkali and alkali-earth metals (top panel) and the halogen series normalized to Ge.

Our experimental results indicate that the annihilation is essentially entirely associated with the anion electrons. Existing theories that include the possibility of both cation and anion annihilation do not explain these results. The experimental observation of essentially 100% overlap of the positron with the halide atoms becomes even more significant when we recall that positronium, a neutral state, dominates the positron state in these materials. For this selectivity to occur in a positronium state either the positronium system is highly polarizable, leading to self-trapping, or the positronium is trapped at a structural defect surrounded by halide atoms, e.g. an alkali vacancy.

We have completed a series of experiments on a set of Zeolite-Y samples after baking in vacuum to remove water and other gaseous contaminants. The resulting positron lifetime data show a clear separation into two distinct sample sets based on the cation form and the Si/Al ratio. We obtained lifetime components centered at 0.6-0.8 ns and 3-4.5 ns, with an additional longer lifetime component (30-45 ns) associated with positronium in the large

intergranular regions. Surprisingly, there is no lifetime component at the value expected (2 and 8 ns) for the cage structures in zeolite-Y. We suggest that the observed lifetime value of 3-4.5 ns is the average of these two cage structures. In order to test these lifetime assignments, we measured the changes in lifetimes when three molecules of different sizes (and hence different cage occupancies) are introduced into the samples. As shown in fig. 5, when the zeolite-Y is filled with CCl_4 , a molecule that can enter the larger cage structure but not the smaller one, a lifetime component consistent with positronium sampling of the smaller cage structure is observed at 1.8 ns.

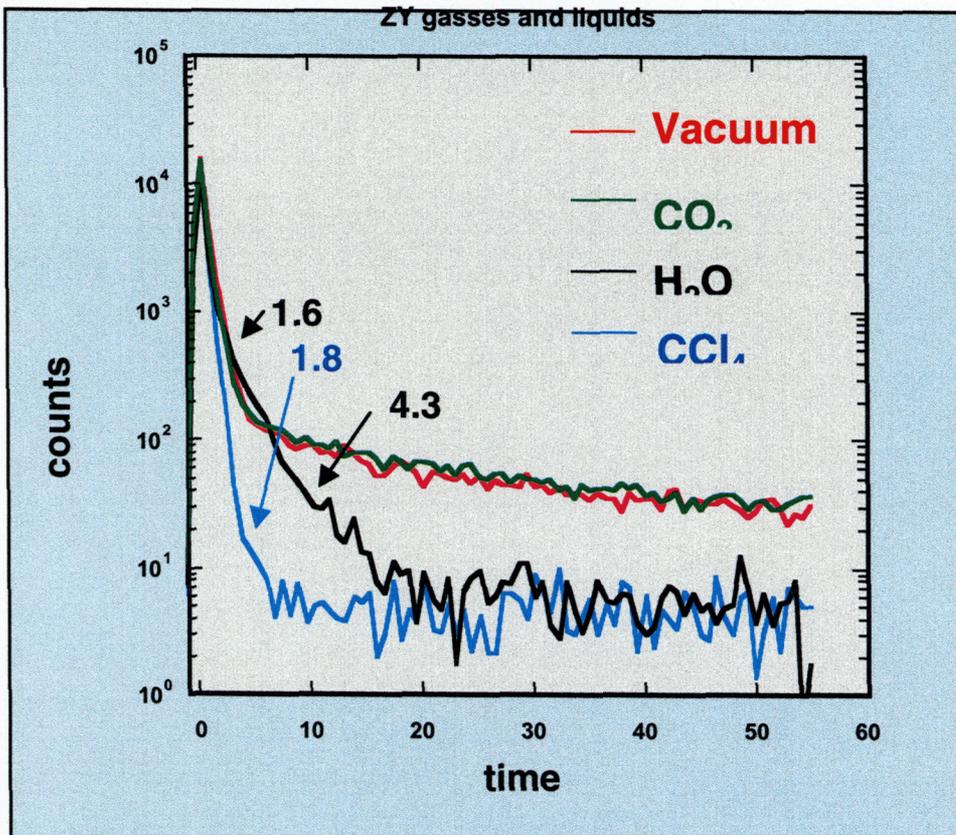


Fig. 5. Plot shows the lifetime spectrum from Zeolite-Y samples when filled with different molecules.

We provided several examples of recent experimental activities at Lawrence Livermore National Laboratory designed to shed additional light on positron and positronium behavior in insulators. Existing theoretical frameworks are unable to fully account for the observed experimental features. We are currently developing new theoretical tools to better describe these experimental findings.

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