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## POSITRONS AND POSITRONIUM IN GRAINY AND POROUS SOLIDS

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Systematic investigations have been performed using positron annihilation techniques on micrograins of crystalline powders (e.g., MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>) and on various zeolites (e.g., silicalite 1, Na-X, Na-Y, ZSM-5, mordenite) aiming at a better understanding of the formation and decay of the long-lived *ortho*-positronium states. The techniques were lifetime spectroscopy, Doppler-effect measurements and the recording of the full energy distribution of the annihilation radiation. The influences of heat treatment, sample evacuation and presence of gases were investigated. Lifetimes over 130 ns and *o*-Ps fractions of about 30% were found. A strong correlation of positron annihilation technique data with a water content of the samples was evidenced. Possible pictures of the formation and decay of *ortho*-positronium in porous media are discussed.

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### 1. Introduction

Due to their comparative simplicity and cheapness, positron annihilation techniques (PAT) are popular tools for non-destructive investigation of solids. However, the interpretation of PAT data may pose difficulties in complex and/or inhomogeneous systems, like fine grained microcrystalline materials, where positronium (Ps) formation may take place to a considerable extent, resulting in the appearance of a large variety of annihilation channels. The very long lifetimes observed, up to about 100–130 ns, indicate that *ortho*-positronium (*o*-Ps) suffers only very weak interactions. Such lifetime values draw attention to the importance of recording the 3 $\gamma$ -emission events by which *o*-Ps decays in vacuum.

Applications of Ps as a probe in solid state and surface research have been initiated soon after the long-living triplet positronium (*o*-Ps) was discovered in microcrystalline powders [1]. The Ps states are sensitive to the presence of additives (e.g., surface-bound ions, gases), which can reduce both the *o*-Ps lifetime and intensity, and lead to the appearance of shorter-lived states annihilating mostly through  $2\gamma$ -annihilation. In this context, zeolites, which are of high technological importance, appeared as suitable materials for thorough studies [2–4]. Correlations between PAT parameters and, e.g., cage sizes, the presence of metal ions, the water content, etc., have been sought [5–10], but data in PAT literature exhibit a rather big scatter. Possible reasons to this could arise from incomplete optimisation for recording the  $3\gamma$ -annihilation events [11, 12] and differences in sample synthesis and treatments.

Our goal was therefore to investigate the conditions that lead to high Ps yields and the interactions that modify the *o*-Ps lifetime and intensity in microcrystalline solids (e.g., MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>) and in zeolites. The high specific surface of the microcrystalline powders relates to the outer surface of the grains, whereas for zeolites it is provided almost completely by the internal surface of channels and voids in the lattice framework. Common features and differences in the annihilation characteristics of the two classes of samples were also looked for. To gain information, the zeolites were studied both in vacuum and in gas atmosphere. The effect of water removal has also been examined.

## 2. Experimental

In addition to conventional measurements of positron lifetime spectroscopy (LT) and Doppler broadening (DB) of the annihilation line, the full energy distribution (FED) of the annihilation radiation was also recorded with the aim of establishing characteristic parameters for the quantification of the  $3\gamma$ -decay. Comparing LT with DB and FED results may help in determining the true intensities of the long-living *o*-Ps components, whose determination is systematically affected by the energy (and solid angle) dependent efficiency of recording  $2\gamma$ - and  $3\gamma$ -events. The LT measurements were carried out both in Budapest and in Strasbourg, employing high quality spectrometers set for high efficiency recording of  $3\gamma$ -events (250 and 350 ps FWHM, respectively). LT spectra with integral counts of  $5 \times 10^6$ – $4 \times 10^7$  were recorded with a time span of  $\approx 1$ – $1.5 \mu\text{s}$ .

The FED spectra were recorded with a Microfast 16k PC analyser in the 40–1350 keV range by using a Canberra HPGe detector (25% efficiency and 1.1 keV resolution at 0.5 MeV). The 1.28 MeV photopeak was used to monitor the count of positrons.

Microcrystalline MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> (with a grain size of 15–50 nm) and well-characterised zeolites (silicalite-1, X-, Y-type, etc.) were selected. Silicalite-1 (MFI structure, pure silicium dioxide with 96 SiO<sub>2</sub> per unit cell) contains free spaces in the form of straight and zigzag channels (an average diameter of 0.55 nm). Zeolites may contain a substantial amount of water (up to 25–30%) when kept in air. Water removal was studied in the Y-zeolites and mordenite while silicalite-1



was used for the study of gas capillary condensation. The Y-zeolite samples were prepared from “Grace” Na-Y (with a grain size of 1–5  $\mu\text{m}$ ).

All samples were pressed into pellets. The microcrystallites were heated to and kept at 450 K under constant evacuation for 24 h, then pressed (0.3 GPa) into 1–1.5 mm thick disks of 8–13 mm diameter. The zeolite powders were pressed into pellets before heating. A sandwich arrangement of the samples was used with a  $^{22}\text{Na}$  positron source of about 20 MBq activity within two thin Ni foils, giving a single-component source correction of several percent. For the silicalite-1, this assembly was kept at 353 K for 24 h under constant evacuation in a 6–10  $\text{cm}^3$  glass vial, then sealed in vacuum or after filling with spectroscopically pure  $\text{N}_2$  (*ca.* 0.085 MPa at 294 K). The water removal was studied by LT, DB, and FED measurements, employing a continuously evacuated sample-holder cryostat.

LT data for the gas-filled samples were recorded between 90 K and 400 K in a cryostat-oven with ample time allowed at each temperature to reach thermal equilibrium. The reproducibility of the LT results was checked by recording spectra again after several months.

The lifetimes and relative intensities were fitted by using a MINUIT package based program tailored specially for evaluating lifetime components ranging over three orders of magnitude.

For the evaluation of DB and FED data, parameters that denote the  $2\gamma$ - or  $3\gamma$ -annihilation events have to be defined. The  $S$  and  $W$  parameters, which describe the 511 keV annihilation peak (AP) separately or combined [13] are commonly used to characterise the  $2\gamma$ -annihilation, whereas the  $L/R$  values (left/right plateau regions of AP) may be used for typifying the  $3\gamma$ -emission in the FED data [14]. The fraction  $f_{3\gamma}$  of long-lived  $o$ -Ps, decaying by  $3\gamma$ -emission, can be estimated and scaled by combining LT and FED data [14]. It has to be underlined that the overall difference in the recording efficiency for  $2\gamma$ - and  $3\gamma$ -annihilation events, respectively, may result in an incorrect evaluation of the relative intensities. However, the circumventing of this obstacle poses some difficulties which require more precise considerations of the changes encountered.

### 3. Results and discussions

The lifetime measurements have revealed the presence of long lifetime components of 50–80 ns for the  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and MgO samples. It was found that the setting of the energy window on the stop detector line strongly influences the effective relative intensity of these components, denoting the presence of  $3\gamma$ -annihilation. It may be noted that these components exhibit about a half of the vacuum lifetime (142 ns), showing so only about one half of the “birth intensity” of the vacuum-like  $o$ -Ps component. Most usually, the origin of such components is ascribed to  $o$ -Ps atoms formed at the surface of the grains and undergoing interactions upon collisions with surface impurities and radicals. Consequently, their intensity and lifetime should depend both on the grain size and on the size of the average intergrain free space. Effectively, it appears that the smaller the grain size, the higher the relative surface and the higher the intensity of the long-lived component, whereas

its actual lifetime depends on the inertness of the surface and on the quality of the vacuum.

The first measurements on zeolites performed in our laboratories did not give such long-lived components, and lifetimes of 10–20 ns only were recorded. It is only after prolonged heating in vacuum, in some cases up to 620 K, that significantly longer lifetimes could be observed. With such treatments thus, lifetimes as long as 90–130 ns were found in all samples, in contrast to earlier literature data, reporting only 20–40 ns components for ZSM5, X-, Y-zeolites, and mordenites.

Evaluation of the LT spectra was carried out on the basis of four independent lifetime components, yielding in most cases satisfactory fits. The various components may be categorized as follows:  $\tau_1$  with 0.2–0.5 ns combining the *p*-Ps and  $e^+$  annihilations,  $\tau_2$  with 1–4 ns for *o*-Ps probably trapped in small voids of the lattice,  $\tau_3$  with 10–90 ns for *o*-Ps decaying in internal channels of the zeolites and  $\tau_4$  with 100–135 ns for *o*-Ps *a priori* decaying outside of the crystallites, in the intergrain space. Some typical data are shown in the Table.

TABLE

Positron lifetime parameters for some zeolite samples at 294 K in vacuum and in N<sub>2</sub> gas (lifetimes  $\tau_i$  are given in ns, intensities  $I_i$  in %, relative errors are about 2%).

Sample	$\tau_2$	$\tau_3$	$\tau_4$	$I_2$	$I_3$	$I_4$
Na-Y	2.2	15.2	110	23.2	11.4	21.2
mordenite	0.7	2.7	105	40.0	13.2	9.5
silicalite-1	2.28	22.3	133.2	24.4	2.6	28.7
silicalite-1 + (N <sub>2</sub> )	4.23	20.5	113.7	10.7	10.3	19.0

Due to the high time/channel setting used, which is absolutely necessary to span over at least 1  $\mu$ s range for the inclusion of the long-lived components, the absolute values of the shortest lifetimes, especially  $\tau_1$ , are less reliable than the longer ones and will not be discussed here further. Note that due to the difference in the detecting efficiencies for the 2 $\gamma$ - and 3 $\gamma$ -events, the intensities  $I_4$  and  $I_3$  are sensitive to changes in the counting geometry.

To evaluate the long lifetimes, the trapping of *o*-Ps in a potential well is usually assumed [5, 6, 15, 16]. The confined *o*-Ps wave function is supposed to penetrate into the walls of the trap, and, depending on the overlap, a shorter lifetime than in vacuum is expected. Thus, for literature data quoting lifetimes of about 10–30 ns, the above model gives sizes of the localization sites that are very close to what is expected on crystallographic grounds. However, there is no such agreement when dealing with lifetimes about and over 100 ns. Applying this model (on the basis of data in the Table) for localised *o*-Ps in order to calculate  $\tau_3$  and  $\tau_4$ , it turns out that taking the channel and channel crossing sizes, e.g., for silicalite-1, lifetimes well below the actually measured values are calculated. This result most probably underlines insufficiencies of the model with respect to the proper description of the expansion of the Ps wave function outside the trap

towards the lattice bulk. Turning to the shorter lifetime values, on the basis of this confinement model, for example, the actual value of  $\tau_2$  in silicalite-1 would correspond to a void of about 0.31 nm radius. As, however, there seems to be no crystallographic free space of that size in the lattice, the related component may thus possibly originate from *o*-Ps annihilating in defected sites, which are not evidenced and expected by other methods. Note that as concerns the quantitative estimation of such long lifetimes, the simplest versions of the confined *o*-Ps-model do not represent a proper approach.

The strong influence of an intense vacuum heat treatment of the samples obviously indicates that the absorbed water (or gas) has a strong effect on the formation and/or survival of *o*-Ps in zeolites. Various samples have been investigated in this respect, the LT spectra have been recorded at various stages of the heating procedure and the *o*-Ps proportions have been determined via *in situ* FED measurements during the heating-cooling cycles (Fig. 1). Different samples behave surprisingly differently: a substantial increase in the intensity of the long-lived components has been found just as well as a decrease or practically no change in other cases. Thermogravimetric measurements were also carried out, and a correlation between the water loss and the *o*-Ps fraction [17] is indicated. However, as these measurements were performed in dry nitrogen, it is only the trends but not the absolute values which might be transposed to the case of heat treatment in vacuum. Water removal was also investigated by *in situ*  $^{57}\text{Fe}$  Mössbauer effect

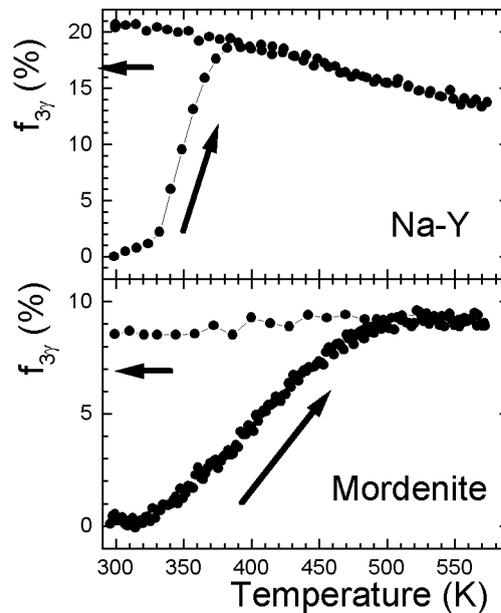


Fig. 1. The effect of water removal by vacuum heating of mordenite and Na-Y-zeolites. Increase in the  $f_{3\gamma}$  ratio indicates not only the high *o*-Ps formation but also an increasing “survival chance”.

(ME) measurements in MFI zeolites [18, 19] and it was concluded that the positron methods are sensitive to changes of the adsorbed water in the range of 280–330 K, whereas in ME only the removal of crystalline water is seen, above 450 K.

To gain information on the  $o$ -Ps formation and decay in the highly porous zeolite structure, the influence of gas has been studied. At room temperature, there is little influence of  $N_2$  (about 1 atmosphere pressure) but upon cooling, which results in capillary condensation of the gas into the zeolite, the long-lived components of 40–130 ns disappear [20] and only lifetimes of several ns subsist. In other words, this means, that the intensity of the longest-living components diminishes whereas the short-lived components become dominant (Fig. 2). This strongly indicates that it is not the basic formation of  $o$ -Ps which is hindered but rather that the  $o$ -Ps lifetime appears to be shorter due to the new kind of interactions arising from the new surroundings brought about by the presence of the capillary condensed gas.

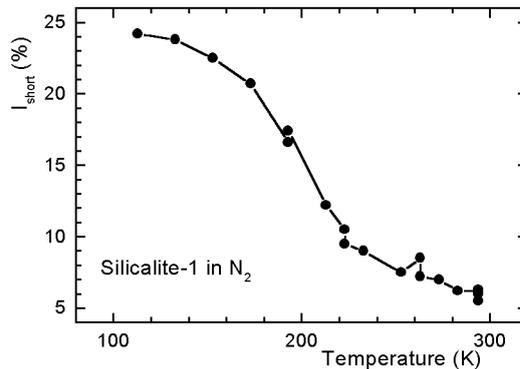


Fig. 2. The intensity of the short-living  $o$ -Ps component vs. temperature measured for a silicalite-1 sample in nitrogen (0.085 MPa at room temperature).

It is remarkable that the influence of the water uptake and that of the gas capillary condensation on the  $f_{3\gamma}$   $o$ -Ps fraction show great similarities. It is also very remarkable that in both cases the uptake of only a small fraction (about 10 percent) of the total possible capacity of either water or gas absorption of the samples results in the complete disappearance of  $f_{3\gamma}$ .

These results still do not give an unequivocal information on the origin of  $\tau_3$  and  $\tau_4$ , but it is hoped that applying various gases of different pressures and filling liquids with different molecular sizes may help to clarify these questions.

#### 4. Conclusions

Due to its ill-defined energy discrimination features and also to the influence of the difference in sensitivity for  $2\gamma$ - or  $3\gamma$ -annihilation, LT spectroscopy alone can provide misleading data as regards the relative intensity values of the very long-lived components, liable to  $3\gamma$ -decay.

A comparison of PAT results for microcrystallites and zeolites reveals that whereas in the case of “solid” grains the longest-living component must be formed at the surface and most probably decays in the intergrain space, in the “sponge-like” zeolites similar states should be formed mostly inside, along the inner surfaces of the channels, although possibly also decaying outside in the intergrain space. However, in neither case the simplest models for *o*-Ps confined in a potential well, albeit commonly applied for a large variety of matrices, can provide satisfactory quantitative estimations of the lifetimes.

A model of “trapping” and “detrapping” of *o*-Ps between channels, voids, and intergrain volumes should be worked out in details. However, the rich variety of possibilities complicates this task substantially.

A distribution of lifetime values, in contrast to the “discrete lifetime components” approach, might also be considered. It should also be investigated, with respect to the medium- and short-lived components, whether irradiation effects caused by the source during the rather long measuring times could cause slight changes just at the level of significance. Insensitivity towards irradiation appears as a prerequisite for fruitful applications in radioactive waste management.

For zeolites,  $3\gamma$ -decaying *o*-Ps seems to be a particularly sensitive probe for the study of the effect of additives and physico-chemical stimuli (localisation and chemical state of dilute additives, like heavy ions, magnetic impurities, capillary condensation, dehydration, acidity, temperature treatment, etc). However, special care has to be taken, as the sample treatment may change the PAT features of zeolites, masking the changes we aim to investigate. To establish some basic correlations more profoundly, there are also further basic processes to investigate in more details. Such are, e.g., determination of *p*-Ps and *o*-Ps contributions, that of the “thermalisation state” of Ps, corrections of PAT spectra due to the change in the occurrence of  $3\gamma$ - $2\gamma$  annihilation for various long- or shorter-lived *o*-Ps states, etc.

When changes in the intensities of the *o*-Ps states are observed, it is essential to identify transitions between the various annihilation channels. This may request specific time settings to study the very short and very long lifetimes simultaneously, and a combined application of various positron annihilation methods. This seems to be a necessary and advantageous further step in the PAT studies of meso- and nanoporous media.

A broader use of liquids and gases, together with the concomitant measurement of the gas uptake, should be fruitful. The similarities between the water loss process and gas desorption starting from capillary condensation should be investigated in details.

It would be also of interest to assess how the present results on the dominantly SiO<sub>2</sub>-based zeolites might be exploited for the SiO<sub>2</sub> insulator widely used in semiconductor technology.

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