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2002 J. Phys.: Condens. Matter 14 13857

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Positron annihilation studies in pyrophyllite

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Received 12 July 2002, in final form 1 November 2002

Published 6 December 2002

Online at stacks.iop.org/JPhysCM/14/13857

Abstract

Results of positron annihilation studies in thermally treated natural pyrophyllite (PP) are presented. In this material we have found the positron lifetime component to range between 0.5 and 1 ns. This can be associated with voids whose evolution follows the dehydroxylation process induced by thermal treatment. The annealing of the PP at 1100 °C caused the transition of the voids to micro-pores whose estimated radius was 0.23 ± 0.01 nm where the positronium state was present. This was confirmed using the magnetic quenching phenomenon. The values of the positron lifetime found and the measured Doppler broadening of the annihilation line indicated unexpected behaviour of positrons in this mineral.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Pyrophyllite (PP) is a hydroxyaluminosilicate with the formula $\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4$, figure 1. This mineral has good technological properties under thermal treatment, e.g., low thermal conductivity and coefficient of expansion, hot load deformation, reheat stability, corrosion resistance and low heating shrinkage. Therefore it is used as a ceramic raw material in refractory compositions such as insulating firebrick or foundry specialities and also in various whiteware bodies. Several authors have studied the thermal process in PP using various methods such as thermo-gravimetry (TG), differential thermo-gravimetry (DTG), differential thermal analysis (DTA), nuclear magnetic resonance and x-ray diffraction analysis [1–4]. In the literature there have been reported positron lifetime measurements carried out on PP treated under different conditions [5]. PP exhibits a layered structure; sheets of linked tetrahedra have the composition Si_4O_{10} . Al^{3+} ions are located in (di)octahedral sites formed from inward pointing apical oxygens between two sheets. TG analysis of the PP indicates a gradual weight loss in the temperature range from 500 up to 1050 °C due to dehydroxylation of structural water. The principal endothermic broad peak centred at 700 °C has been detected by several authors. During the dehydroxylation process the PP phase retains a well organized structure up to 1150 °C. Above 1200 °C gradual crystallization of mullite occurs at the expense of

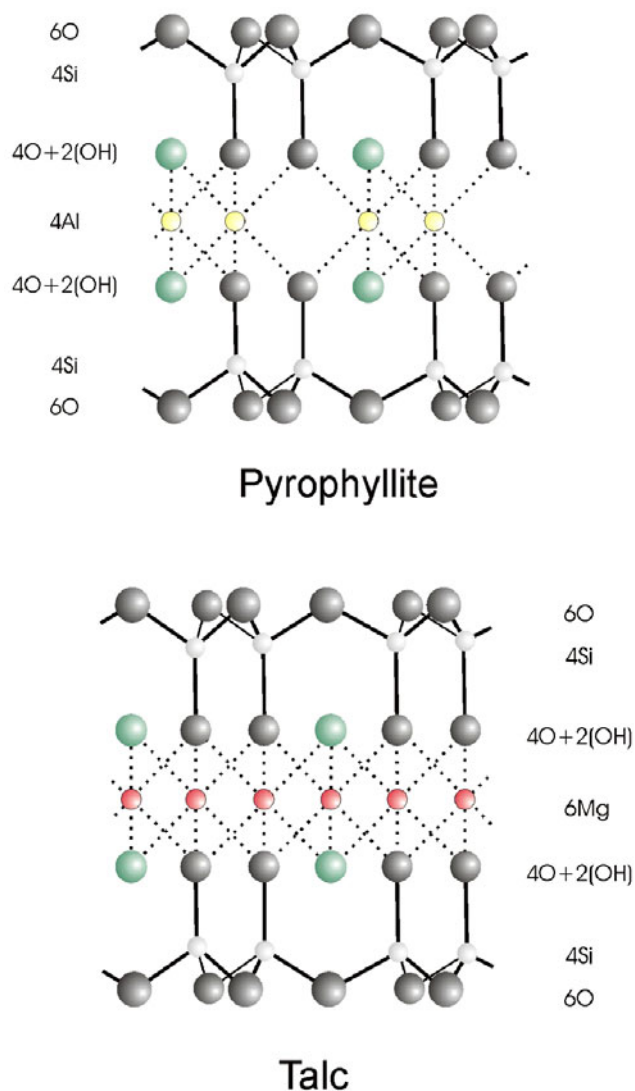


Figure 1. The structure of PP and talc.

the dehydroxylate phase [6]. At 1300 °C the cristobalite phase starts to appear followed by crystallization at 1325 °C. The structural reorganization induces exothermic DTA peaks at 1215 and 1325 °C.

The aim of this paper is to add to the thermal investigations of the PP positron annihilation methods. A positron implanted into the material inspects mainly the interstitial positions in the crystalline structure and is able to detect changes in the electronic structure, creation of defects, free volumes or small pores. The last are important for ceramic materials because the positron annihilation technique is able to detect even closed and very small pores whose radius ranges from 0.2 up to 15 nm. In our studies we performed measurements of positron lifetime and Doppler broadening of the annihilation line. These are the commonly used experimental positron annihilation techniques.

2. Sample preparation and experimental technique

We have performed our investigations using samples of 2 cm × 1 cm and 2 mm thick cut from the commercially available natural PP called Lava produced by Myrland Lava Company, Inc. According to the producer, this material, after heat treatment at 1100 °C for 45 min in air, is converted into a very hard material and changes colour from grey to pink; this was detected in our studies as well. All measurements of the positron characteristics were performed at room temperature after the heat treatment of the samples. After isochronal annealing during 45 min in air, the samples were left to cool down to room temperature inside the furnace. We used the isotope ^{22}Na with an activity 20 μCi closed in an envelope made from thin kapton foil 7 μm thick as a positron source. The source was sandwiched by the two PP samples. The positron lifetime (PL) spectra were measured using a conventional *fast-fast* coincidence lifetime spectrometer with BaF_2 scintillators with a time resolution (FWHM) of 240 ps for the ^{22}Na energy window. Data were analysed using the LT version 2.5 computer program [7]. In the analysis of the PL spectra, the background and the correction for the source were taken into account. From our previous experience on well annealed metallic samples we have assumed for each spectrum one lifetime component for the source equal to 342 ps with the intensity 16%. The Doppler broadening of the annihilation line spectra was measured using a high purity Ge detector with the energy resolution of 1.20 keV interpolated at 511 keV. From the spectra we extracted the so-called *S*-parameter, which is the most commonly used parameter in positron annihilation studies. This quantity is sensitive to the presence of low momentum electrons, which are mainly located in vacancies or their clusters. This parameter is defined as the ratio of the area under the fixed central part to the total area under the whole annihilation line.

In our studies we have used also the coincidence Doppler broadening of the annihilation line spectrometer which allows us to observe positron annihilation with tightly bound high momentum electrons. The Doppler coincidence spectrometer consisted of one high purity Ge detector, with an energy resolution 1.4 at 511 keV, and one NaI scintillator detector. The detection of two annihilation quanta allowed us to achieve the pick to background parameter close to 4400:1. The spectra were corrected by the background subtraction using the procedure described in [8].

3. Results and discussion

3.1. Positron lifetime measurements

Two lifetime components were detected in the lifetime spectrum for the raw Lava PP material at room temperature. The first lifetime component, $\tau_1 = 286 \pm 2$ ps with intensity $I_1 = 88 \pm 1\%$, could be associated with the annihilation of free positrons in the bulk material. The origin of the second lifetime component, $\tau_2 = 522 \pm 7$ ps and of lower intensity I_2 , is vague. This value suggests that a positron could be localized and then annihilated in a very large void, whose radius is close to 0.5 nm if the analogy with metals is taken into account. Nevertheless, in a large void a bound state between the positron and an electron can also be created. In this state, called positronium (Ps), the positron can annihilate in the *pick-off* process after time longer than 1 ns. It is not excluded that the origin of the second component could be attributed to delocalized Ps, as it is in $\alpha\text{-SiO}_2$. We will prove below that it is attributed to the presence of voids.

After annealing of the PP the value of the second lifetime component changes in a wide range for a temperature above 400 °C as shown in figure 2. At this temperature the value of τ_2 increases up to 1040 ± 22 ps. The next annealing, at 900 °C causes a decrease of this value

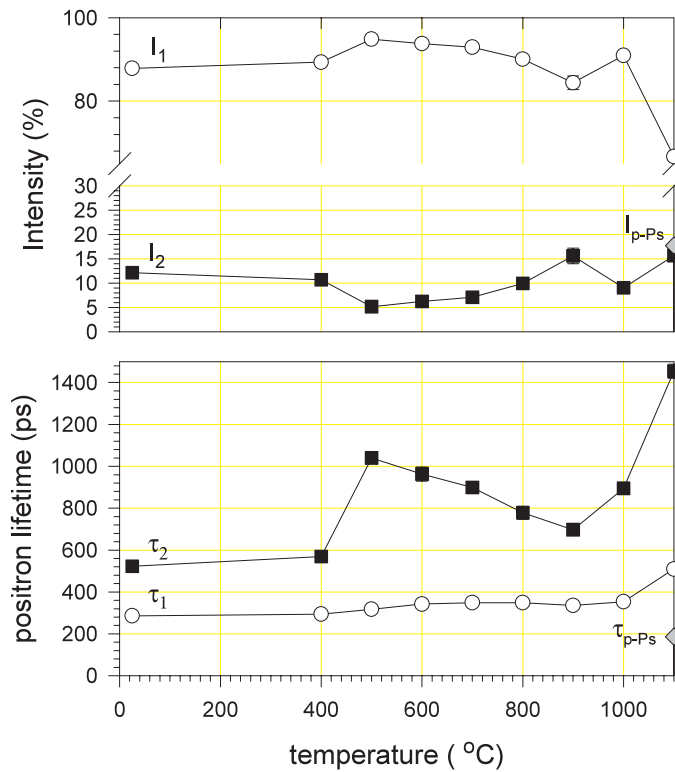


Figure 2. Positron lifetime components and their intensities as a function of temperature in the isochronal annealing.

to 697 ± 27 ps. It is worth noticing that such values of the positron lifetime are rather rarely detected in condensed matter. For example Uedono *et al* [9] detected positron lifetime close to 630 ps in voids in diamond. If we take into account the fact that within this temperature range the dehydroxylation process takes place we could argue that the second lifetime component is associated with this process and the presence of the OH^- group in the crystalline lattice of the PP. The loss of the structural water induces the change in the structure of the void where the positron is localized. Within this temperature range the first lifetime component slightly increases up to 335 ± 4 ps.

At temperatures above 900°C the second lifetime component rapidly increases. But after thermal treatment at 1100°C we detect in the positron lifetime spectrum three lifetime components. (This is the maximum temperature suggested by the producer, and also the authors of the paper [3].) The first one was 186 ± 18 ps, the second one 509 ± 10 ps and the last one 1454 ± 34 ps. This unambiguously suggests that the void is converted to a pore where the Ps is created and/or localized. Now the first lifetime component can be associated with the self-annihilation of the singlet state of the *para*-Ps (*p*-Ps) and the last value with the annihilation of the *ortho*-Ps (*o*-Ps) in the *pick-off* process. If we consider the well known model proposed by Tao, which is commonly used in polymer physics, we can use the following equation [10]:

$$\tau \text{ (ns)} = \frac{1}{2} \left[1 - \frac{R}{R + 0.1656 \text{ (nm)}} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + 0.1656 \text{ (nm)}}\right) \right]^{-1}, \quad (1)$$

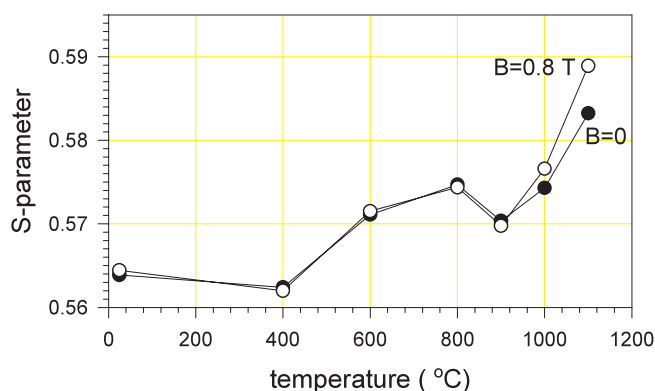


Figure 3. S -parameter versus annealing temperature. The open circles were obtained when an external magnetic induction of 0.8 T was applied.

which links the pore radius R and the lifetime component τ associated with the o -Ps annihilation in the *pick-off* process. From that we can extract the radius of the pore: $R = 0.23 \pm 0.01$ nm. The increase of the second lifetime component up to 509 ps suggests that after annealing at 1100 °C the density of electrons in the interstitial positions in the crystalline structure decreases; this induces the increase of the free positron lifetime.

3.2. Doppler broadening measurements

The explanation presented above may be confirmed by measurements of the S -parameter as a function of annealing temperature. Figure 3 depicts this dependence. The S -parameter rises for temperatures above 400 °C, then slightly decreases, and above 1000 °C rapidly increases again. Such a behaviour points to the presence of open volume defects like voids in the structure, whose size is changing as well. This behaviour is correlated with the increase of the value τ_2 , indicating that the radius of the voids increases in comparison to the raw material. The rapid increase of the S -parameter above 1000 °C is correlated with the appearance of Ps in the structure (the self-annihilation of p -Ps contributes mainly to the high value of the S -parameter in this case).

In order to confirm additionally the presence of Ps and to prove the void origin of the second lifetime component in the structure of the PP we performed measurements of the DB of the annihilation line in an external magnetic field produced by permanent magnets ($\text{BaF}_{12}\text{O}_{19}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$). It is known that in external magnetic field the phenomenon of magnetic quenching of o -Ps takes place, due to the Zeemann mixing of the p -Ps state and the $m = 0$ substate of o -Ps. The magnetic field induces more events of self-annihilation of the resultant pseudo p -Ps and causes an increase in the S -parameter. This effect is well described in the literature and it is a convenient tool for detection of the Ps in the system. The magnetic field does not affect the annihilation of free positrons or those trapped in voids. As presented in figure 3, for temperatures above 1000 °C a magnetic field of 0.8 T induced an increase in the S -parameter. This proves the presence of pores because only here can the Ps be created and annihilated. It is worth noticing that from the PL spectrum it was difficult to find Ps in the samples annealed at 1000 °C, but from the measurement of the S -parameters in the magnetic field we were able to detect that pores started to be created at this temperature. Below 1000 °C no effect of the magnetic field on the S -parameter was observed. This indicates that positrons are annihilated in voids and no Ps was created, probably because the size of the void is too small to create such a state.

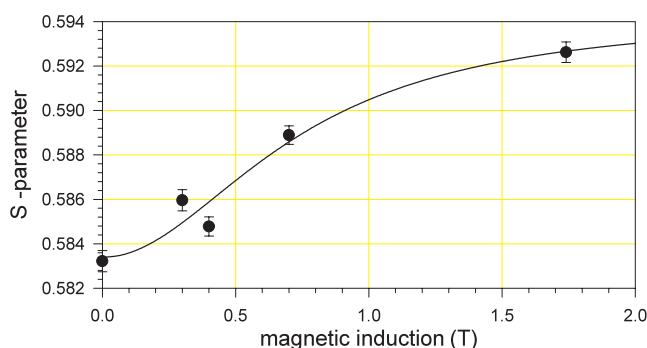


Figure 4. The dependence of the S -parameter on magnetic field for the PP samples annealed at 1100°C. The solid curve presents the best fit to equation (2).

It is known from quantum mechanics that this is not possible if the void radius is lower than 0.18 nm [12]. This experiment excludes also the existence of delocalized Ps at temperatures below 1000°C because magnetic quenching phenomena are also present for this state.

In figure 4 we depict the dependence of the S -parameter on magnetic induction for samples annealed at 1100°C. The increase of the S -parameter can be described if we take into account the theory of the magnetic quenching of Ps, presented e.g. in [11]. The solid curve presents the best fit to the relation

$$S(B) = S_0 + aF_{2\gamma}(B), \quad (2)$$

where a and S_0 are constants and the function $F_{2\gamma}(B)$ is the fraction of the two-gamma annihilation of the Ps, see the appendix. From the fit we are able to extract the relative contact density of Ps equal to $\kappa = 0.21 \pm 0.07$ assuming the pick-off annihilation rate from the lifetime measurement. (The contact density is defined as the ratio of the hyperfine structure splitting between o - and p -Ps in material and in vacuum, see the appendix.) For example, the contact density parameter obtained, for α -SiO₂, has a value of 0.31 ± 0.02 [11].

3.3. The kinetic process at high temperature

In order to detect how the heat treatment time affects the size of the pores we annealed two samples of Lava material at 1100°C for 10 min in air and then cooled them to room temperature and the positron annihilation characteristics were measured. The procedure has been repeated in order to reach the total annealing time equal to 50 min. In figure 5 we presents the results of the deconvolution of the PL spectra versus annealing time. We observe a slight increase of the value of the longest lifetime component from 1444 ± 40 to 1512 ± 50 ps with the time increase. This points out that the pore radius is slightly increasing from 0.23 ± 0.04 to 0.24 ± 0.06 nm. The value of the second lifetime τ_2 component remains also unchanged. Slight changes only with the increasing annealing time are observed in the measured value of the S -parameter as well, figure 6.

3.4. Results for talc

It was interesting also to measure the PL spectrum for talc. This mineral has the formula Mg₃Si₄O₁₀(OH)₂ and has a similar crystalline structure to PP but the Al³⁺ ion is replaced by the Mg²⁺ ion, figure 1. We studied two types of natural talc rock, the most common one with grey colour, and the yellow rock found in the Ural mountains in Russia. For the first rock

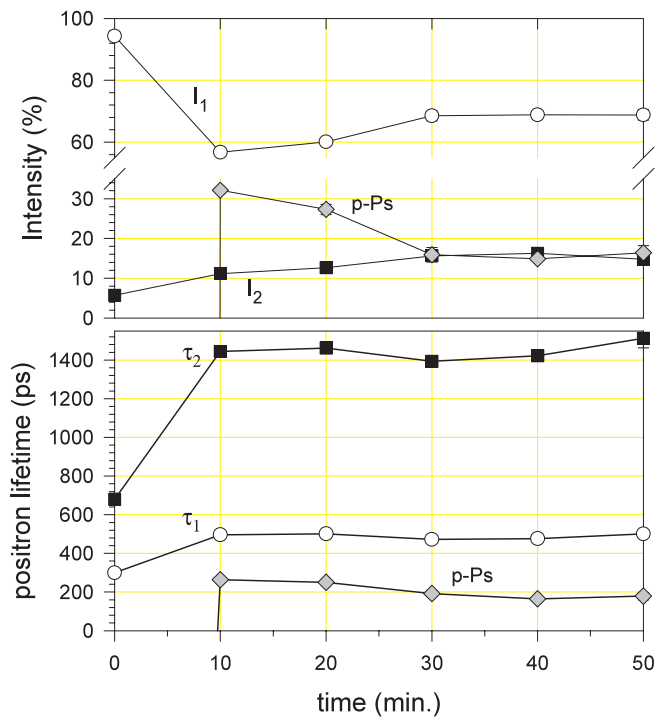


Figure 5. Positron lifetime components and their intensities as a function of the time of annealing of the PP samples at 1100 °C.

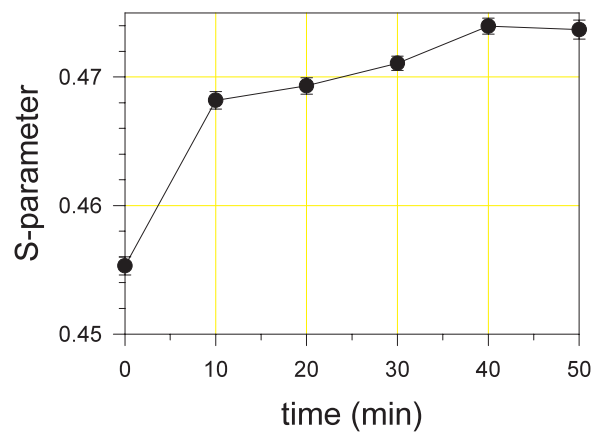


Figure 6. *S*-parameter as a function of the annealing time of the PP samples at 1100 °C.

we detected at room temperature in the PL spectrum two lifetime components, 321 ± 1 ps at $98 \pm 1\%$ and the second lifetime component 731 ± 100 ps at $2 \pm 1\%$. It was similar for the yellow rock: 332 ± 1 and 2160 ± 270 ps with the intensity $0.4 \pm 0.3\%$. The first lifetime components in both cases differ only slightly; the second ones exhibit a difference but their intensities are very small. The long lifetime component in the yellow rock points out the presence of a small amount of Ps and voids which are not present in the grey rock.

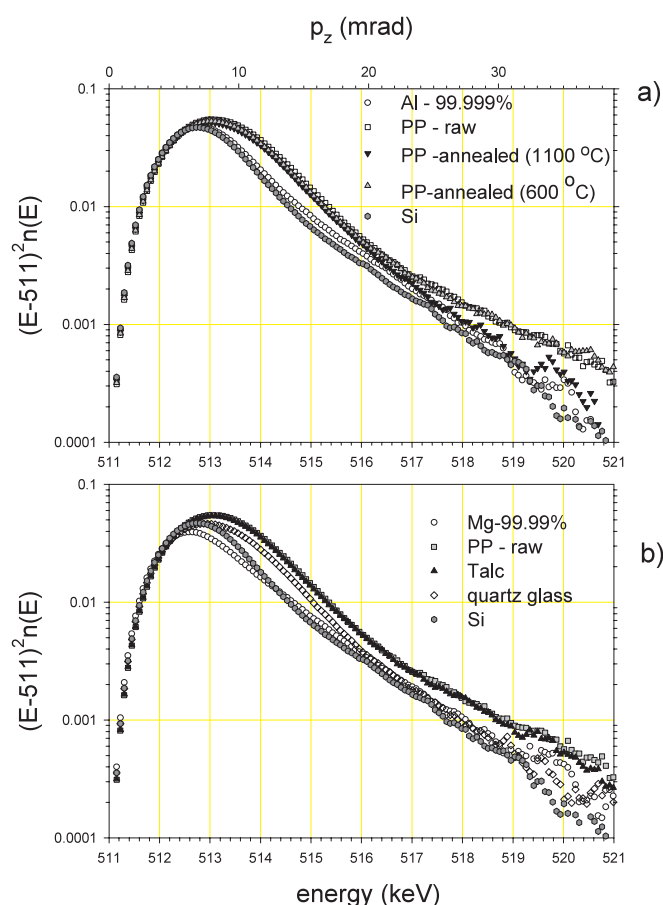


Figure 7. The DB spectra measured for raw PP, PP annealed at 600 °C and at 1100 °C (a) and talc (b). We have added also the spectra measured for Al (a), Mg (b) quartz glass and Si.

We can conclude a significant difference in the electronic structure of PP and talc, despite the similarities in their crystalline structure.

3.5. Coincidence Doppler broadening measurements

In figure 7 we depict the DB spectra measured using the coincidence spectrometer. The spectra measured for raw PP and PP annealed at 600 and 1100 °C are shown in figure 7(a), and those for talc samples in figure 7(b), respectively. The DB spectra of the measured samples are presented in comparison with the spectra of elements, Al (99.999%), Mg (99.9%) and Si (single crystal), and quartz glass. For the presentation of the experimental results we decided to put on the coordinate axis the counts per channel ($n(E)$) times the square of the momentum of the annihilation pair, which is proportional to $(E - 511)^2$, where E is the energy of annihilation quanta. The reason is to enhance the high and see more detail in the lower momentum part of the spectra.

In figure 7(a) there are clearly visible significant differences in the shape of the raw PP spectrum and the spectrum for Al and Si. The differences which occur at momentum higher than 20 mrad or gamma energy higher than 517 keV indicate that the positron wavefunction

does not overlap the core regions of Al and Si and the annihilation with electrons from this region is not visible. It is the same for the PP samples annealed at 600 °C. The slight difference between the raw PP and that annealed at 600 °C one can notice in the spectrum in the range between 10 and 20 mrad. The annealing of PP at 1100 °C causes essential changes in the spectrum at higher momentum. We can conclude that this process has induced changes in the crystalline structure that push the positron wavefunction in the direction of Al ions. That is the reason why the high momentum part of the spectrum follows the Al spectrum above gamma energy of 516 keV. Above we concluded the positrons were localized at voids; we can now add that the voids are located close to the Al ion in the crystalline structure.

It is interesting to see a similarity of the DB spectrum for the raw PP and the talc (yellow rock) except a little difference at gamma energy higher than 519 keV, figure 7(b). (We did not find significant differences between the DB spectra measured for grey and yellow rock.) In this picture we depict the DB spectrum of Mg and quartz glass. In the case of talc the positron wavefunction does not overlap the Mg core region as well. It is the same with the Si core regions. At this stage it is difficult to find the shape of the positron wavefunction. We cannot also explain the increase in the high momentum part of the DB spectrum of both minerals. Theoretical work is needed for this explanation.

4. Conclusions

In the PP samples using positron annihilation methods large voids were detected; the annealing process of the PP induces an increase in the size of the void in which positrons are trapped. Only for the samples annealed at 1100 °C is the void large enough to allow the creation of Ps. This was confirmed by the observation of magnetic quenching. The changes in the void size are correlated with the dehydroxylation process of the PP. The positron lifetime in this void ranges from 0.5 to 1 ns depending on the temperature at which the samples were annealed. We detected also an enhancement in the high momentum part of the DB spectra of the PP and talc which cannot be explained by the positron annihilation with the electrons from the core region on Al, Si and Mg. Only the annealing of PP at 1100 °C allows us to localize positrons close to the Al region.

Appendix

In the magnetic field, the Zeemann mixtures of p -Ps and the $m = 0$ substate of o -Ps contribute to the two-gamma annihilation. In the absence of the o -Ps \rightarrow p -Ps conversion reaction one can obtain the fraction of the two-gamma annihilation of the Ps as follows [11]:

$$F_{2\gamma}(B) = \frac{\lambda_p}{4(1+y^2)} \left(\frac{y^2}{\lambda_+ + \lambda_{po}} + \frac{1}{\lambda_- + \lambda_{po}} \right), \quad (\text{A.1})$$

where $\lambda_+ = (\lambda_0 + y^2\lambda_p)/(1+y^2)$, $\lambda_- = (\lambda_p + y^2\lambda_0)/(1+y^2)$, $y = x/(1 + \sqrt{1+x^2})$, $x = 4\mu B/\Delta E$ and $\Delta E = \kappa \Delta E_0$. B is the value of the magnetic field, ΔE_0 is the hyperfine structure splitting in vacuum between o -Ps and p -Ps and μ is the magnetic moment of the electron. The parameter κ is called the relative contact density of the Ps. $\lambda_0 = \kappa \lambda_0^0$ and $\lambda_p = \kappa \lambda_p^0$, where $\lambda_0^0 = 1/142$ ns and $\lambda_p^0 = 1/125$ ps are the annihilation rates of o -Ps and p -Ps in vacuum, respectively, and λ_{po} is the *pick-off* annihilation rate. In our calculations presented in figure 4 we assumed $\lambda_{po} = 1/1454$ ps.

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