PHYSICAL REVIEW B **78**, 085428 (2008)

Positronium cooling into nanopores and nanochannels by phonon scattering

S. Mariazzi, A. Salemi, and R. S. Brusa
Dipartimento di Fisica, Università di Trento and INFN, Gruppo collegato di Trento, Via Sommarive 14, I-38050 Povo, Trento, Italy

(Received 16 April 2008; revised manuscript received 17 June 2008; published 22 August 2008)

We studied the acoustic phonon scattering of a positronium (Ps) atom emitted into and then confined in closed nanopores and open nanochannels of an insulating material at low temperature. Closed nanopores were approximated by a cubic box, while nanochannels by a channel with square geometry. As a case study, calculations were carried out for nanopores and nanochannels in a silica matrix. First-order calculations allowed us to set a lower limit to the size of the pores and of the channels in order to achieve complete Ps thermalization. The Ps energy loss and the cooling time obtained from the Ps-phonon scattering model were compared to those obtained from the classical model considering Ps scattering with surface atoms with an effective mass.

DOI: 10.1103/PhysRevB.78.085428 PACS number(s): 36.10.Dr, 78.70.Bj, 72.10.Di

I. INTRODUCTION

Positronium (Ps) is the quasistable bound hydrogen-like atom formed by an electron and a positron.[1] Ps is of interest both in fundamental and applied physics.

Ps exists in two different spin states: the singlet state, parapositronium (*p*-Ps), with total spin 0 and formation probability ¼ and the triplet state, orthopositronium (*o*-Ps), with total spin 1 and formation probability ¾. In vacuum *p*-Ps has a mean lifetime of 125 ps and decays into two gamma rays, while *o*-Ps has a mean lifetime of 142 ns and decays into three gamma rays.

Ps can be formed injecting a positron in a solid.[2] In metals and semiconductors the formation of Ps in the bulk of the material is prevented by the high electron density. In these solids Ps formation is only a surface process: a thermalized positron diffusing back to the surface can capture an electron and be adiabatically emitted as Ps. This process is allowed if the Ps formation energy $\varepsilon_{\mathrm{Ps}}=\phi_+ + \phi_- - 6.8\ \mathrm{eV}\leq 0$, where ϕ_+, ϕ_- are the positron and electron work functions, respectively, and 6.8 eV is the Ps binding energy in vacuum.[3] If $\varepsilon_{\mathrm{Ps}}\leq 0$, adiabatic emission occurs at any temperature of the sample. Conversely, if $\varepsilon_{\mathrm{Ps}}>0$, Ps is formed only in a small quantity by epithermal positrons. Another possible route is a thermal-activated emission in which positrons trapped at the surface can be detrapped as Ps.[4,5]

At the surface of insulators Ps formation is usually hindered for thermalized positrons due to the high electron ionization energy. However a small fraction of Ps has been observed by epithermal positrons[6] and thermal activation.[7] Differently from metals and semiconductors, Ps can be formed in the bulk of insulators. The fraction of Ps reaching the surface by diffusion is emitted into the vacuum provided that the Ps work function $\phi_{\mathrm{Ps}}=\phi_+ + \phi_- + E_B - 6.8\ \mathrm{eV}\leq 0$, where E_B is the Ps binding energy in the material.[8]

In porous molecular materials, with pore sizes in the 2–100 nm range, Ps can be emitted into the pores and trapped until its annihilation if the relation $\phi_{\mathrm{Ps}}\leq 0$ is fulfilled. The Ps kinetic energy after emission into the pores or into the vacuum is a few electronvolts. The lifetime of *o*-Ps trapped into pores is reduced by pick-off annihilation (i.e., positron annihilation into two gamma rays with an electron of the walls of the pores).

Ps spectroscopy is becoming an import tool for characterizing dimension, distribution, and shape of pores in insulator materials[9] through the study of the lifetime and the three gamma annihilation of *o*-Ps. Besides, fundamental studies on *o*-Ps have been recently performed by promoting the formation of *o*-Ps at high density in porous materials using burst of many positrons.[10] Spin exchange between *o*-Ps atoms[11] and formation of Ps_2 (Ref. 12) have been evidenced. Bose condensation of *o*-Ps (Refs. 13 and 14) is going to be pursued confining *o*-Ps in a nanometric cavity at temperatures below 30 K. Moreover *o*-Ps can be used for antihydrogen ($\overline{\mathrm{H}}$) formation through the reaction $o-\mathrm{Ps}^{*}+\bar{p}\rightarrow\overline{\mathrm{H}}^{*}+e$, where $\bar{p}$ is an antiproton, e an electron, and $o-\mathrm{Ps}^{*}$ is an *o*-Ps excited in a Rydberg state.[15] It has been proposed to realize this reaction starting from a cold *o*-Ps beam in vacuum obtained by injecting burst of positrons in porous materials with ordered or disordered connected porosities toward the surface.[16] The *o*-Ps converter target should be held at around 100 mK. This idea is based on experimental evidence showing that *o*-Ps, emitted into pores with some electronvolt energy, is cooled by collision with the walls of the pores.[17] In the presence of interconnected porosities toward the surface, *o*-Ps may escape into the vacuum through the porosities. A fraction of *o*-Ps can emerge from the end of connected porosities with a nearly thermal energy after losing its kinetic energy by collisions with the surface of the pore.

Several experiments carried out on different porous materials have shown that at room temperature, the *o*-Ps kinetic energy can be reduced close to the thermal energy within its lifetime of 142 ns.[17–20] Nevertheless, few measurements[21–26] and theoretical studies[27] exist concerning the lifetime and annihilation of *o*-Ps at low temperature of the sample.

Since the lifetime and pick-off rate of *o*-Ps are affected by the occupation of energy levels,[27] the study of *o*-Ps energy loss process is important both for the morphological study of the pores and the production of cooled *o*-Ps in the vacuum or inside a buried cavity.

At room temperature the energy loss of Ps confined into pores is usually simulated using a model originally developed for the classical interaction between Ps and gas molecules.[28] In the extended model for Ps interaction with a surface, the guess parameter is constituted by the effective mass of the atoms on the pore walls.[19] However, Saito and Hyodo[29] doubted the capability of the classical model to describe the cooling of Ps atoms at low temperature.

Dull *et al.*[27] have extended the Tao-Eldrup model[30–32] to a rectangular pore [rectangular Tao-Eldrup (RTE) model] to obtain the lifetime of *o*-Ps as a function of the sample temperature and of the pore dimensions. However this model seems to fail in describing lifetime measurements at low temperature.[21,26] One limit of the RTE model is considering the *o*-Ps as immediately thermalized after its emission into the pore. Conversely *o*-Ps spends time to cool down from its initial energy of few electronvolt.

In this paper we analyze the cooling of Ps by creation and destruction of phonons at the surface of nanopores and nanochannels in samples held at low temperature. First we consider the general case of a Ps atom confined in a pore schematized by a rectangular box. Then the specific cases of a cubic box with different sizes and a channel with square geometry will be examined. Finally, the energy loss and cooling time will be studied in a one-dimensional potential well.

We present results for nanostructures in SiO_2. This material is interesting for the study of confined Ps (Refs. 12 and 13) or production of Ps beams[16] because of its high Ps yield.[6,33] However the results can be easily extended to different materials.

II. Ps-PHONON INTERACTION

The Ps atom is considered to be confined in a rectangular box with infinite potential barriers and the Ps wave function is assumed to overlap with phonons in a region R from the wall of the potential well. In our model we consider a sample temperature below which the interactions with optical phonons can be neglected and the acoustical branch of the dispersion relation can be assumed to be linear. Since Ps is a neutral particle, interactions with the polar-optical modes are expected to be weaker than other phonon interactions.[34–37] In the case of silica the optical deformation potential contribution to Ps scattering was found to be absent for temperatures below 701 K.[36,37] These studies have also shown that in the case of MgF_2 the contribution of nonpolar optical scattering becomes important only above 200 K.

Based on the above considerations, the Ps-phonons interaction in the near-wall surface region is treated only in terms of acoustic deformation potential[34,35,37,38]

$$W = E_d \sum_q \left[\sqrt{\frac{\hbar}{2NM\omega_q}} iq(a_q e^{i\vec{q}\cdot\vec{r}} - a_q^+ e^{-i\vec{q}\cdot\vec{r}}) \right],$$

where N is the number of atoms in the sample, M their effective mass, $\vec{q}$ and ω_q the phonon momentum and angular frequency, respectively. a_q and a_q^+ are the destruction and creation operators, respectively. The Ps position is given by the vector $\vec{r}$. The interaction term E_d depends on the material. In the case of SiO_2, it has been estimated to be around 3.6 eV[37] by measuring the *p*-Ps momentum in bulk materials as a function of the temperature.

Ps can lose or increase its energy by creating or destroying phonons. The Ps transition probability P_{kk^I} from momentum magnitude k to k^I is calculated as a function of the Ps momentum by using the first-order perturbation theory:

$$P_{kk^I} = \left| -\frac{i}{\hbar} \int_0^t \sum_q \langle k^I | E_d \frac{1}{\sqrt{N}} \left[\sqrt{\frac{\hbar}{2M\omega_q}} iq(a_q e^{i\vec{q}\cdot\vec{r}} - a_q^+ e^{-i\vec{q}\cdot\vec{r}}) \right] | k \rangle e^{[i(E_{(o\mathrm{Ps})\mathrm{final}} - E_{(o\mathrm{Ps})\mathrm{initial}} + \Sigma_q \hbar\omega_q (n_q^I - n_q))t]/\hbar} dt \right|^2. \quad (1)$$

At low temperatures (below about 30 K) the dispersion relation indicates that the angular frequency is $\omega_q = v_s q$, where v_s, the sound speed in SiO_2, is around 4900 m/s.[39] $|k\rangle = |\mathrm{Ps}(\vec{r})_k\rangle \Pi_q |n_q\rangle$ and $|k^I\rangle = |\mathrm{Ps}(\vec{r})_{k^I}\rangle \Pi_q |n_q^I\rangle$ are the wave functions of the total system before and after Ps scattering, respectively. $|n_q\rangle$ is the wave function of n_q phonons with momentum magnitude q, and $\hbar$ is Planck's constant. The wave function of a Ps atom with momentum k, $|\mathrm{Ps}(\vec{r})_k\rangle$, is assumed to be the one of a particle in an infinite rectangular well of side lengths a, b, and c, i.e.,

$$|\mathrm{Ps}(\vec{r})_k\rangle = \sqrt{\frac{2}{a}} \sqrt{\frac{2}{b}} \sqrt{\frac{2}{c}} \sin(k_x x) \sin(k_y y) \sin(k_z z).$$

The corresponding permitted energy levels are given by

$$E = \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m} = \frac{\hbar^2 k^2}{2m},$$

where m is the mass of Ps. The transition probability, obtained by solving Eq. (1), is

$$P_{kk^1} = \frac{\pi^2 tR}{Mv_s} \frac{2m}{\hbar^2} \left| \frac{E_d}{abc} \frac{1}{\sqrt{N}} \right|^2 [Q_+ + Q_-]. \quad (2)$$

Q_+ and Q_- are associated with the creation and destruction of a phonon and are given by

$$Q_\pm = \sum_j q_j \delta\left(k^{I2} - k^2 \pm \frac{2mv_s}{\hbar} q_j \right) (n_{q_j} + \xi) \quad (3)$$

with ξ equal to 1 and 0, respectively. The q_j terms are expressed by

$$q_1=\sqrt{(k_x^I-k_x)^2+(k_y^I-k_y)^2+(k_z^I-k_z)^2},$$

$$q_2=\sqrt{(k_x^I-k_x)^2+(k_y^I+k_y)^2+(k_z^I-k_z)^2},$$

$$q_3=\sqrt{(k_x^I+k_x)^2+(k_y^I-k_y)^2+(k_z^I-k_z)^2},$$

$$q_4=\sqrt{(k_x^I+k_x)^2+(k_y^I+k_y)^2+(k_z^I-k_z)^2},$$

$$q_5=\sqrt{(k_x^I+k_x)^2+(k_y^I+k_y)^2+(k_z^I+k_z)^2},$$

$$q_6=\sqrt{(k_x^I-k_x)^2+(k_y^I-k_y)^2+(k_z^I+k_z)^2},$$

$$q_7=\sqrt{(k_x^I-k_x)^2+(k_y^I+k_y)^2+(k_z^I+k_z)^2},$$

$$q_8=\sqrt{(k_x^I+k_x)^2+(k_y^I-k_y)^2+(k_z^I+k_z)^2}.$$

Dirac's deltas in Eq. (3) do not belong to quadratic deltas with simple analytical solutions.[40] However, geometrically, it is possible to observe that the deltas impose the following relationship between the momentum of Ps before and after the interaction:

$$\vec{k}^I=\vec{k}-\left(\pm\frac{2mv_s}{\hbar}+2|k|\cos\alpha\right)\hat{\gamma}, \tag{4}$$

where α is the angle between $\vec{k}-\vec{k}^I$ and $\vec{k}$, $\hat{\gamma}$ is the unit vector of $\vec{k}-\vec{k}^I$, the momentum of the phonon involved in the process. This relation imposes that the momentum magnitude of Ps after the interaction is in the range

$$|k|-\frac{2mv_s}{\hbar}\le|k^I|\le|k|$$

and

$$|k|\le|k^I|\le|k|+\frac{2mv_s}{\hbar}$$

for phonon creation and destruction, respectively. Thus, the maximum variation admitted for the momentum magnitude of Ps is

$$||k|-|k^I||_{\mathrm{MAX}}=\frac{2v_sm}{\hbar}\approx 1.7^{*}10^{8}\ \mathrm{m}^{-1}. \tag{5}$$

Equation (5) points out that no transition occurs at the first order if the distance between two close Ps momentum levels in the box is higher than this value. In the following we discuss the possibility of thermalization by interactions at the first order for closed pores and open porosities. Closed and open pores were modeled by a cubic box and a square channel, respectively.

A. Cubic box

The distance between two generic momentum levels of a Ps atom trapped in an infinite potential well with dimensions $a=b=c$ is in magnitude

$$\begin{aligned}||k|-|k^I||&=\frac{\pi}{a}\Big|\sqrt{n_x^2+n_y^2+n_z^2}\\&\quad-\sqrt{(n_x+\alpha)^2+(n_y+\beta)^2+(n_z+\gamma)^2}\Big|\\&=\frac{\pi}{a}\Big|\sqrt{n^2}\\&\quad-\sqrt{n^2+\alpha^2+\beta^2+\gamma^2+2\alpha n_x+2\beta n_y+2\gamma n_z}\Big|,\end{aligned} \tag{6}$$

where n_x, n_y, and n_z are the principal quantum numbers and α, β, and λ their variations. Since $\alpha^2+\beta^2+\gamma^2+2\alpha n_x+2\beta n_y+2\gamma n_z$ is an integer, the distance between close momentum levels is

$$||k|-|k^I||=\left|\frac{\pi}{a}[\sqrt{n^2}-\sqrt{n^2\pm 1}]\right|. \tag{7}$$

It is worth noticing that Eq. (7) underestimates the momentum distance because given the principal quantum numbers n_x, n_y, and n_z, it is possible to have no values of α, β, and γ, which returns

$$\alpha^2+\beta^2+\gamma^2+2\alpha n_x+2\beta n_y+2\gamma n_z=\pm 1. \tag{8}$$

The condition for the permitted transitions between close levels is obtained by combining Eq. (7) and Eq. (5):

$$\frac{2v_sm}{\hbar}\ge\left|\frac{\pi}{a}[\sqrt{n^2}-\sqrt{n^2\pm 1}]\right|. \tag{9}$$

The lower accessible n_m value for Ps is given by the minimum n value, which satisfies both Eq. (9) and the condition $n=\sqrt{n_x^2+n_y^2+n_z^2}$ with n_x, n_y, and n_z integers ≥ 1.

Found n_m, the minimum kinetic energy

$$E=\frac{\hbar^2\pi^2}{2m}\left(\frac{n_m}{a}\right)^2$$

and the minimum temperature

$$T=\frac{2}{3k_B}E=\frac{\hbar^2\pi^2}{3k_Bm}\left(\frac{n_m}{a}\right)^2,$$

attained by a Ps atom in the cubic box can be estimated. k_B is Boltzmann's constant.

The minimum temperature that a Ps atom can reach in a cubic box is shown in Fig. 1 as a function of the pore size a, while the temperature corresponding to the ground state is indicated as a dashed line. Figure 1 points out that in cubic pores with size smaller than six nanometers, a Ps atom cannot reach the ground state by scattering with one phonon, thus remaining in an excited state until its annihilation. For instance, in a cubic pore with size $a=5$ nm, the lower accessible level for Ps is reached with $n_m=\sqrt{6}$, corresponding to a Ps temperature of 345 K. This happens even for very low temperatures of the host material. Conversely, in larger pores, Ps can reach the ground state and its temperature is set by the ground energy. For instance, pore sizes >20 nm are required in order to cool *o*-Ps below 10 K. It is important to outline that for cube sizes smaller than 6 nm, the ground state can still be reached but only through two-phonon

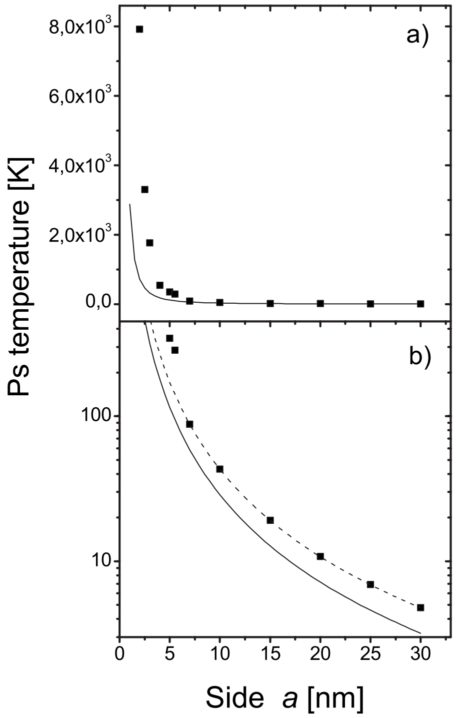

FIG. 1. (a) Minimum temperature permitted for a Ps atom confined in a cubic well (squares) and in a square channel (solid line) as a function of side a of the cube and of the channel base, if phonon-Ps interaction at the first order are considered. (b) Detail of the low-temperature region. The dashed line represents the temperature of a Ps atom in the ground state of a cubic well. Calculations are carried out for nanostructures in a SiO_2 matrix.

acoustic scattering, which is a second-order process.

Model simulations can give insights not only in setting pore dimensions for achieving *o*-Ps cooling, but also in correlating *o*-Ps lifetime with the pore dimensions. The formation and annihilation of Ps at low temperatures as a function of the pore dimensions was investigated only in two experimental works. Fisher *et al.* (Ref. 21) measured the three gamma annihilation of *o*-Ps in mesoporous-based silica films with different pore sizes for sample temperature in the 50–400 K range. Experimental data were compared to the RTE model (Ref. 27) and agreement was observed between 400 and 200 K. Below 200 K, deviations from the RTE model were present, which depended on the pore size. For pore diameters smaller than about two nanometers the pick-off rate was higher than predictions. On the contrary, for pore diameters around 3 nm, the pick-off rate was lower than the value predicted by the RTE model.

Thraenert *et al.* (Ref. 26) measured the *o*-Ps lifetime for temperatures in the 50–500 K range in porous silica glasses and they also compared the data to the RTE model. The agreement between the experimental data and the model was good at 300 K, while a disagreement was observed for lower temperatures. Thraenert *et al.* observed, with respect to model predictions, a reduced pick-off annihilation rate in samples with pores of diameters around 2.5–4 nm and a higher pick-off annihilation rate in samples with larger pores (5 and 27 nm in diameter).

As shown in the RTE model[27] the pick-off annihilation rate of *o*-Ps is directly correlated with the overlap between the *o*-Ps wave functions of the occupied energy levels and the surface region of the pore. The pick-off annihilation rate results larger in the excited states than in the ground state. In the RTE model the *o*-Ps is assumed to immediately reach the thermal equilibrium when injected into a pore, and to sample all states with probability governed by Boltzmann's equation.

A possible discussion about the trend of the observed experimental deviations from the RTE model at low temperatures could be done starting from the two following points:

(a) For pore dimensions smaller than few nanometers single-phonon scattering does not allow to reach the ground state, so two-phonon scattering process has to be invoked. This could reduce the probability of Ps-phonon energy exchange, lengthening the permanence of Ps in excited states.

(b) The time required by Ps to reach the minimum energy level increases with pore size due to both the increase in the time to cross the well (i.e., the Ps frequency of collision with the pore walls decreases) and the decrease in the rate of energy loss (see third paragraph).

The increase in the pick-off observed in pores with very large dimensions[26] or dimensions smaller than few nanometers[21] could be correlated with a possible long permanence of Ps in excited states. The permanence in excited states could be due to the two reasons (a) and (b). The effect of point (b) vanishes going to small pore dimensions, while the confining effect of point (a) starts to have a role only in pores with dimensions below few nanometers.

According to the above picture, the pick-off rate is expected to reach a minimum in an intermediate pore dimension region. This would be compatible with the data reported in Ref. 21 and 26. Our model seems to suggest the existence of a minimum pick-off annihilation rate at very low temperature in cubic pores with size around 6 nm, corresponding to a Ps mean free path $l=(2/3)a$ of 4 nm.[27]

The above discussion is valid assuming that other phenomena do not change the pick-off rate, specifically: (i) changes in the chemistry of the pores walls,[41,42] (ii) preferential trapping of Ps in pores of different dimensions,[21] (iii) different Ps formation probability and Ps diffusion at different temperatures, and (iv) production of paramagnetic centers at low temperature.[23,24]

The modification of the total or partial decoration of the pore walls with the temperature is expected to change the pick-off rate. Points (ii) and (iii) could hinder the correlation between changes in annihilation properties and pore size. The last point must be taken into account in presence of high irradiation of the sample, for example using bunch of many positrons. Paramagnetic centers can have different formation and relaxation probability with temperature, leaving memory effects on the sample.

B. Square channels

If the side of the infinite potential well along the z axis tends to infinite we obtain a channel with a quadratic base of side $a=b$ in the $x-y$ plane. This infinite well simulates a regular open channel with the z axis perpendicular to the sample surface. A Ps atom emitted into the channel can escape into the vacuum after losing part of its energy by collisions with the channel walls. In this case the magnitudes of k_x and k_y momenta are quantizated, but the k_z value tends to be a continuous. In a channel Ps can attain its minimum energy level without any limitations because the distance between the two momentum levels of Eq. (6) has no lower limit, i.e.,

$$||\vec{k}| - |\vec{k^I}|| \leq \frac{2mv_s}{\hbar}.$$

In fact the left term of Eq. (8) can attain any value since in this case the γ term is a real number. This is illustrated in Fig. 2, where it is shown that a Ps with a generic momentum k can jump to a lower momentum level until it reaches the lowest one.

In the infinite well the minimum momentum has magnitude $k=\sqrt{2}\pi/a$ in the $x-y$ plane, corresponding to a minimum energy of $E=(\hbar^2\pi^2)/(ma^2)$. In Fig. 1 the minimum temperature $T=(2E)/(3k_B)$ that a Ps atom can reach in a square channel is reported as a function of the channel side a. The minimum temperature is always lower than that in a cubic box with the same dimension a. As a comparison, Ps cooling below 10 K can occur only in a square channel if a is around 17 nm. It is worth to notice that if Ps is injected at a sufficient channel depth and reach the minimum momentum in the $x-y$ plane, its direction of emission depends only on the k_z component. The emission angle with respect to the z axis increases together with the energy loss until the limit set by $k_z=0$ is reached. This means that for obtaining Ps cooled at 10 K, with small emission angle with respect to the z axis, channels with side $a>17$ nm would be necessary. This behavior could be experimentally checked and it could also give information on different conditioning of the surfaces of the channels.

III. Ps ENERGY LOSS IN ONE-DIMENSIONAL WELL

In order to obtain an evaluation of the time required by Ps to cool down, Eq. (1) can be analytically solved in the case of a one-dimensional infinite potential well. It reads

$$P_{kk^1} = \sum_q \frac{2tR\pi^2 q}{Mv_s} \left| \frac{E_d}{a} \frac{1}{\sqrt{N}} \right|^2 [(n_q+1)\delta(E_{(o\mathrm{Ps})\mathrm{final}} - E_{(o\mathrm{Ps})\mathrm{initial}} + \hbar\omega_q) + (n_q)\delta(E_{(o\mathrm{Ps})\mathrm{final}} - E_{(o\mathrm{Ps})\mathrm{initial}} - \hbar\omega_q)]$$
$$\times[\delta(k^I - k + q) + \delta(k^I - k - q) + \delta(k^I + k + q) + \delta(k^I + k - q)]. \qquad (10)$$

The average energy variation can be calculated in the hypothesis that a Ps atom absorbing or creating a phonon has always an available energy level for the transition in the potential well. This hypothesis is satisfied if the distance between close energy levels is comparable to or smaller than the permitted momentum variation $|\vec{k^I}|-|\vec{k}|=\pm 2mv_s/\hbar$, as predicted by Eq. (4) in the one-dimensional case. In terms of well size this means dimensions larger or equal to 25 nm.

The transition probability from states with momentum k to states with momentum k^I can be obtained by transforming the summation in Eq. (10) into an integral on all possible

$$q{:}P_{kk^I} = \sum_q \to \frac{L}{2\pi}\int_0^\infty dq,$$

where $L/(2\pi)$ is the normalizing term and L is the length of the linear lattice.

The average energy variation at a fixed momentum is given by

$$\langle \Delta E(k) \rangle = \frac{a}{\pi}\int \Delta E P(\Delta E) d\Delta E = \frac{a}{\pi}\int \frac{\hbar^2}{2m}(k^2 - k^{I^2})P_{kk^I}dk^I, \qquad (11)$$

which when solved gives

$$\langle \Delta E(k) \rangle = \left| \frac{E_d}{a}\frac{1}{\sqrt{N}} \right|^2 \frac{aL}{2\pi^2}\frac{8mtR\pi^2}{M\hbar}\left[\left(2k + \frac{2v_s m}{\hbar}\right) e^{-\frac{\hbar v_s\left(2k+\frac{2mv_s}{\hbar}\right)}{K_B T}} - \left(2k - \frac{2v_s m}{\hbar}\right) e^{-\frac{\hbar v_s\left(2k-\frac{2mv_s}{\hbar}\right)}{K_B T}} - \left(2k - \frac{2v_s m}{\hbar}\right)\right]. \qquad (12)$$

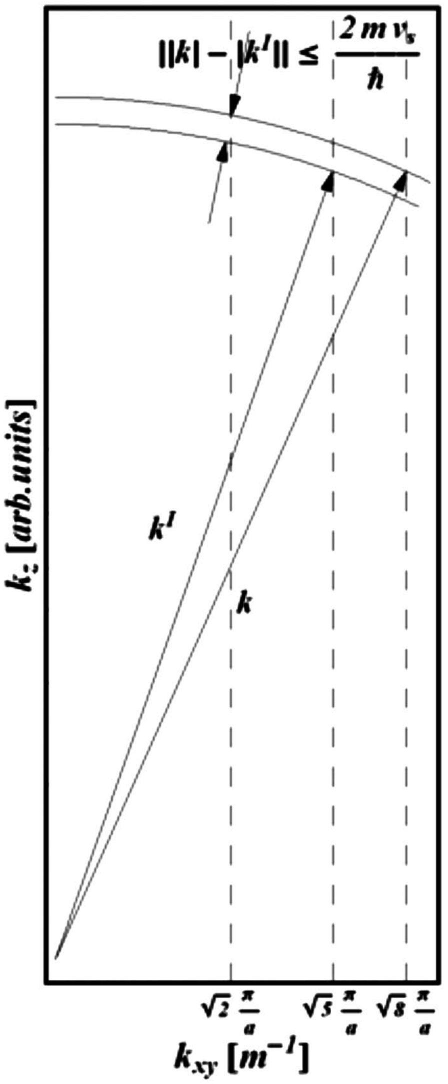

FIG. 2. Ps momentum levels in a channel with infinite length along z axis and quadratic base of side $a=b$ in the $x-y$ plane. The points on the dashed vertical lines represent allowed Ps momentum levels. $k_{xy}=\sqrt{k_x^2+k_y^2}$ is the magnitude of the Ps momentum in the $x-y$ plane. A Ps atom, with generic momentum magnitude k, can always lose momentum according to the condition $||\vec{k}|-|\vec{k}^I|| \leq 2mv_s/\hbar$, thus reaching the allowed minimum momentum $\sqrt{2}\pi/a$.

In Eq. (12), t represents the time spent by Ps in the interaction region R. This time can be approximated by

$$t = \frac{R}{v} \approx 2\frac{Rm}{\hbar k},$$

where v is the velocity of Ps. The energy of Ps as a function of time can be obtained by solving[28]

$$\frac{dE}{dt} = \left\langle \frac{\Delta E(k)}{\tau} \right\rangle$$

and assuming the time to cross the well equal to be $\tau = a/v \approx 2am/\hbar k$. The time spent by Ps to reach its final minimum energy increases at increasing pore size a.

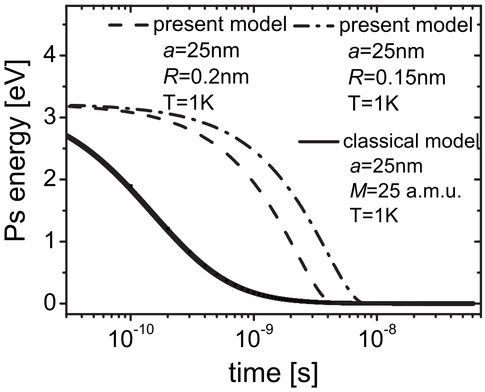

FIG. 3. Ps energy vs time in an infinite one-dimensional potential well with size $a=25$ nm in a matrix of SiO_2 at the temperature of 1 K. Dash-dotted and dashed curves correspond to present model calculations with interaction region $R=0.15$ nm and $R=0.20$ nm, respectively. The solid curve is calculated by the classical model of Ref. 19 assuming an effective mass $M=25$ a.m.u.

In Fig. 3 we report the Ps energy E as a function of time in the case of an infinite potential well with dimension $a=25$ nm in a SiO_2 matrix at the temperature of 1 K.

The R parameter is assumed to be in the range 0.15–0.2 nm, according to the estimation of the overlap between the o-Ps wave function and the surface region of the pore carried out with the Tao-Eldrup (TE) (Refs. 30–32) and RTE (Ref. 27) models. At time zero, i.e., when Ps is emitted into the pore, the energy of Ps is assumed to be $|\phi_{Ps}|=3.27$ eV.[43]

Ps loses its momentum in about 8 ns and 5 ns for R equal to 0.15 nm and 0.2 nm, respectively. For comparison, the momentum loss curve calculated with the classical model,[19,28] assuming $M=25$ a.m.u. according to Ref. 19, is shown in Fig. 3. In the case of second-order processes, involving two-phonon scattering, the thermalization time is expected to be further reduced. The momentum decreases more quickly below few nanoseconds in the classic picture, but complete thermalization is achieved in a longer time than in the Ps-phonon interaction model.

IV. CONCLUSIONS

In the limit of the present model, choosing the appropriate parameters E_d and v_s, a minimum dimension of pores or channels to obtain the thermalization of Ps and its cooling time can be estimated in any material at low temperature. However in the case of o-Ps formation at the surface of pores and channels in metallic or semiconductor materials, there is a very high probability of annihilation with an unpaired spin of the medium (pick-off annihilation) for each o-Ps collision with the walls of the cavities. The strong competition between the two scattering routes, pick-off and phonon scattering, prevents the cooling of Ps in these materials. In the case of insulator materials, the cooling of o-Ps can be limited by the reduction of its lifetime through quenching phenomena. In addition to pick-off annihilation on the pore walls we recall the spin conversion due to induced paramagnetic centers at low temperature by positron irradiations.[23,24]

According to our model the Ps thermalization times are of the order of some nanoseconds. *p*-Ps confined in nanostructures at low temperature is not allowed to reach thermal equilibrium due to its very short lifetime, whatever the material type. *p*-Ps is expected to annihilate hot with high momentum of the positron-electron pair. The annihilation of hot *p*-Ps causes a larger Doppler shift of the photon energy influencing the shape of the 511 keV annihilation line when detected by Doppler broadening (DB) spectroscopy. Similarly its larger momentum enlarges angular correlation (ACAR) measurements. Thus, if porosities are studied at low temperature by DB or ACAR, these effects must be taken into account.

Although restricted to the Ps-phonon interaction at the first order, the present model provides channel size limits for designing targets for production of *o*-Ps beams at low temperature and points out the necessity to improve *o*-Ps lifetime calculations in the case of *o*-Ps confined into pores at low temperature. It raises the need of more experimental works in porous materials at low temperature to discriminate among the several effects that can influence the formation and annihilation probability of Ps and of second-order phonon-scattering calculations in the case of small size nanostructures.

---

[1] S. Berko and H. N. Pendleton, Annu. Rev. Nucl. Part. Sci. **30**, 543 (1980).

[2] A. P. Mills, Jr., in *Positron Solid-State Physics*, edited by W. Brandt and A. Dupasquier (North-Holland, Amsterdam, 1983), p. 432; K. G. Lynn, *ibid.*, p. 609.

[3] A. P. Mills, Jr., in *Positron Spectroscopy of Solids*, edited by A. Dupasquier and A. P. Mills, Jr. (North-Holland, Amsterdam, 1995), p. 209; T. Hyodo, *ibid.*, p. 419.

[4] K. G. Lynn and D. O. Welch, Phys. Rev. B **22**, 99 (1980).

[5] A. P. Mills, Jr., Phys. Rev. Lett. **41**, 1828 (1978).

[6] S. Van Petegem, C. Dauwe, T. Van Hoecke, J. De Baerdemaeker, and D. Segers, Phys. Rev. B **70**, 115410 (2004).

[7] P. Sferlazzo, S. Berko, and K. F. Canter, Phys. Rev. B **32**, 6067 (1985).

[8] P. J. Schultz and K. G. Lynn, Rev. Mod. Phys. **60**, 701 (1988).

[9] D. W. Gidley, K. G. Lynn, M. P. Petkov, M. H. Weber, J. N. Sun, and A. F. Yee, in *New Directions in Antimatter Chemistry and Physics*, edited by C. M. Surko and F. A. Gianturco (Kluwer, Dordrecht, 2001), p. 151.

[10] A. P. Mills, Jr., Radiat. Phys. Chem. **76**, 7 (2007).

[11] D. B. Cassidy and A. P. Mills, Jr., Phys. Rev. Lett. **100**, 013401 (2008).

[12] D. B. Cassidy and A. P. Mills, Jr., Nature (London) **449**, 195 (2007).

[13] P. M. Platzman and A. P. Mills, Jr., Phys. Rev. B **49**, 454 (1994).

[14] A. P. Mills, Jr., Nucl. Instrum. Methods Phys. Res. B **192**, 107 (2002).

[15] C. H. Storry, A. Speck, D. Le Sage, N. Guise, G. Gabrielse, D. Grzonka, W. Oelert, G. Schepers, T. Sefzick, H. Pittner, M. Herrmann, J. Walz, T. W. Hänsch, D. Comeau, and E. A. Hessels (ATRAP Collaboration), Phys. Rev. Lett. **93**, 263401 (2004).

[16] A. Kellerbauer, M. Amoretti, A. S. Belov, G. Bonomi, I. Boscolo, R. S. Brusa, M. Büchner, V. M. Byakov, L. Cabaret, C. Canali, C. Carraro, F. Castelli, S. Cialdi, M. de Combarieu, D. Comparat, G. Consolati, N. Djourelov, M. Doser, G. Drobychev, A. Dupasquier, G. Ferrari, P. Forget, L. Formaro, A. Gervasini, M. G. Giammarchi, S. N. Gninenko, G. Gribakin, S. D. Hogan, M. Jacquey, V. Lagomarsino, G. Manuzio, S. Mariazzi, V. A. Matveev, J. O. Meier, F. Merkt, P. Nedelec, M. K. Oberthaler, P. Pari, M. Prevedelli, F. Quasso, A. Rotondi, D. Sillou, S. V. Stepanov, H. H. Stroke, G. Testera, G. M. Tino, G. Trénec, A. Vairo, J. Vigué, H. Walters, U. Warring, S. Zavatarelli, D. S. Zvezhinskij, and (AEGIS Proto-Collaboration), Nucl. Instrum. Methods Phys. Res. B **266**, 351 (2008).

[17] R. S. Yu, T. Ohdaira, R. Suzuki, K. Ito, K. Hirata, K. Sato, and Y. Kobayashi, Appl. Phys. Lett. **83**, 834966 (2003).

[18] C. He, M. Muramatsu, N. Oshima, T. Ohdaira, A. Kinomura, and R. Suzuki, Phys. Lett. A **355**, 73 (2006).

[19] C. He, T. Ohdaira, N. Oshima, M. Muramatsu, A. Kinomura, R. Suzuki, T. Oka, and Y. Kobayashi, Phys. Rev. B **75**, 195404 (2007).

[20] R. S. Vallery, P. W. Zitzewitz, and D. W. Gidley, Phys. Rev. Lett. **90**, 203402 (2003).

[21] C. G. Fischer, M. H. Weber, C. L. Wang, S. P. McNeil, and K. G. Lynn, Phys. Rev. B **71**, 180102(R) (2005).

[22] S. Mariazzi, L. Toniutti, N. Patel, and R. S. Brusa, Appl. Surf. Sci. (to be published).

[23] N. Djourelov, T. Suzuki, V. Shantarovich, and K. Kondo, Radiat. Phys. Chem. **72**, 723 (2005).

[24] H. Saito, Y. Nagashima, T. Hyodo, and T. Chang, Phys. Rev. B **52**, R689 (1995).

[25] T. Goworek, B. Jasinska, J. Wawryszczuk, R. Zaleski, and T. Suzuki, Chem. Phys. **280**, 295 (2002).

[26] S. Thraenert, E. M. Hassan, D. Enke, D. Fuerst, and R. Krause-Rehberg, Phys. Status Solidi C **4**, 3819 (2007).

[27] T. L. Dull, W. E. Frieze, D. W. Gidley, J. N. Sun, and A. F. Yee, J. Phys. Chem. B **105**, 4657 (2001).

[28] Y. Nagashima, M. Kakimoto, T. Hyodo, K. Fujiwara, A. Ichimura, T. Chang, J. Deng, T. Akahane, T. Chiba, K. Suzuki, B. T. A. McKee, and A. T. Stewart, Phys. Rev. A **52**, 258 (1995).

[29] H. Saito and T. Hyodo, in *New Directions in Antimatter Chemistry and Physics*, edited by C. M. Surko and F. A. Gianturco (Kluwer, Dordrecht, 2001), p. 101.

[30] M. Eldrup, in *Positron Annihilation*, edited by P. G. Coleman, S. C. Sharma, and L. M. Diana (North-Holland, Amsterdam, 1982), p. 753.

[31] S. J. Tao, J. Chem. Phys. **56**, 5499 (1972).

[32] M. Eldrup, D. Lightbody, and J. N. Sherwood, Chem. Phys. **63**, 51 (1981).

[33] L. Liszkay, C. Corbel, P. Perez, P. Desgardin, M.-F. Barthe, T. Ohdaira, R. Suzuki, P. Crivelli, U. Gendotti, A. Rubbia, M. Etienne, and A. Walcarius, Appl. Phys. Lett. **92**, 063114 (2008).

[34] A. Dupasquier, in *Positron Solid-State Physics*, edited by W. Brandt and A. Dupasquier (North-Holland, Amsterdam, 1983), pp. 510–580.

[35] M. Tuomisaari, R. H. Howell, and T. McMullen, Phys. Rev. B **40**, 2060 (1989).

[36] I. V. Bondarev, Y. Nagai, M. Kakimoto, and T. Hyodo, Phys. Rev. B **72**, 012303 (2005).

[37] Y. Nagai, M. Kakimoto, T. Hyodo, K. Fujiwara, H. Ikari, M. Eldrup, and A. T. Stewart, Phys. Rev. B **62**, 5531 (2000).

[38] C. M. Wolfe, N. Holonyak, Jr., and G. E. Stillman, *Physical Properties of Semiconductors*, Prentice Hall Series in Solid State Physical Electronics (Prentice-Hall, Englewood Cliffs, NJ, 1989).

[39] R. Vacher and J. Pelous, Phys. Rev. B **14**, 823 (1976).

[40] L. M. Guelfand and G. E. Chilov, *Les Distributions* (Dunod, Paris, 1972), Vol. 1.

[41] M. P. Petkov, M. H. Weber, K. G. Lynn, K. P. Rodbell, and S. A. Cohen, Appl. Phys. Lett. **74**, 2146 (1999).

[42] D. W. Gidley, H. Peng, and R. S. Vallery, Annu. Rev. Mater. Res. **36**, 49 (2006).

[43] P. Sferlazzo, S. Berko, and K. F. Canter, Phys. Rev. B **35**, 5315 (1987).