

## Positronium hydride in hydrogen-laden thermochemically reduced MgO single crystals

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Thermochemical reduction of hydrogen-laden MgO single crystals at  $T \sim 2400$  K results in a large concentration of both hydride ( $\text{H}^-$ ) ions and anion vacancies ( $> 10^{24} \text{ m}^{-3}$ ). Positron-lifetime experiments of these crystals provide evidence for bound positronium hydride states also referred to as  $[e^+ - \text{H}^-]$  or PsH states. The presence of the anion vacancies was found to inhibit the formation of these states. After thermally annealing out these vacancies, such that  $\text{H}^-$  concentration remains intact, two long-lived components appear in the lifetime spectrum. Furthermore, these two components correlate with the presence of the  $\text{H}^-$  ions. These results suggest the existence of bound  $[e^+ - \text{H}^-]$  states when positrons are trapped by the  $\text{H}^-$  ions, and the subsequent formation of positronium (Ps) states by the dissociation of the  $[e^+ - \text{H}^-]$  states. From the values of the intermediate lifetime component, a value of  $(570 \pm 50)$  ps is obtained for the lifetime of the PsH state located in an anion vacancy in MgO. The longest lifetime component  $\sim (1-3)$  ns is attributed to pick-off annihilation of ortho-Ps states.

### I. INTRODUCTION

One of the first models to explain the positron annihilation spectra in ionic solids was the formation of positron-anion bound states  $[e^+ - X^-]$ , where  $X^-$  refers to a halogen ion.<sup>1-3</sup> According to Ferrel's calculations,<sup>4</sup> the formation of the positronium (Ps) states was considered highly unlikely. Earlier, the long-lived component observed in the positron-lifetime spectra in alkali halides and metallic hydrides was not considered to be associated with Ps states. Efforts were then focused on the investigation of the stability of bound  $[e^+ - X^-]$  states and calculations of the corresponding annihilation rates were made.<sup>1,2,5-16</sup> The results of these calculations for bound states, such as  $[e^+ - \text{F}^-]$ ,  $[e^+ - \text{Cl}^-]$ , or  $[e^+ - \text{H}^-]$  did not agree with the experimental results.<sup>17,18</sup> In these early studies, positron trapping by lattice defects was not considered.

Later experiments verified the existence of Ps states in the alkali halides.<sup>19,20</sup> These results are satisfactorily explained if we subscribe to the formation of stable Ps states and the free positron annihilation with the external electrons of the lattice anions. More recently, evidence for positron trapping at lattice defects has been found in alkali halides. These results have led to the partial abandonment of the  $[e^+ - X^-]$  bound-state model. However, a mechanism involving a complex bound state [ion or atom- $e^+$ ] is commonly used to explain the experimental results in liquid solutions.

In the metal hydrides, a positron bound to a hydride ion,  $[e^+ - \text{H}^-]$ , also referred to as positronium hydride (PsH), has been invoked to explain the experimental results.<sup>1,3,5,18</sup> Calculations indicate that the formation of free PsH is possible<sup>1,5,8</sup> and its annihilation rate in the

ground state is between  $1.98 \times 10^9 \text{ s}^{-1}$  and  $2.46 \times 10^9 \text{ s}^{-1}$ .<sup>6,7,9-11,14-16</sup> Again, experimental and theoretical results do not agree. So far no clear experimental evidence for the existence of PsH has been reported, except for a positron annihilation study in the intercalation compound  $\text{C}_8\text{KH}_{3/2}$  in which the annihilation rate of PsH was not measured.<sup>21</sup>

The existence of PsH is important for the understanding of the physics and chemistry of the positronium. Experiments in liquids or gases are not appropriate because of the difficulties in producing  $\text{H}^-$  ions. In certain ionic crystals, the  $\text{H}^-$  ions exist as an extrinsic defect that can be controlled.<sup>22-24</sup> Therefore the  $\text{H}^-$  ion as an impurity has the important advantage over metal hydrides in that its effect on the positron annihilation spectra can be easily monitored by comparison with crystals free of  $\text{H}^-$  ions.

In hydrogen doped MgO single crystals the presence of  $\text{H}^-$  ions can be monitored by their infrared absorption bands near  $1000 \text{ cm}^{-1}$ .<sup>24,25</sup> Contrary to the situation in alkali halides and alkali hydrides, no evidence for Ps formation has been found in the bulk of both doped and undoped MgO single crystals.<sup>26-28</sup> In addition, positron age-momentum correlation measurements and lifetime spectra can be satisfactorily explained by using a simple model of two states corresponding to the annihilation of free positrons and positrons trapped at defects.<sup>26,28,29</sup> Thus, MgO single crystals in which a high concentration of  $\text{H}^-$  ions have been produced constitute an excellent candidate for studying the formation of positronium hydride.

In this study we produced evidence that in thermochemically reduced hydrogen-laden MgO, thermalized positrons can interact with  $\text{H}^-$  ions annihilating via either bound  $[e^+ - \text{H}^-]$  states or Ps states formed by dissoci-



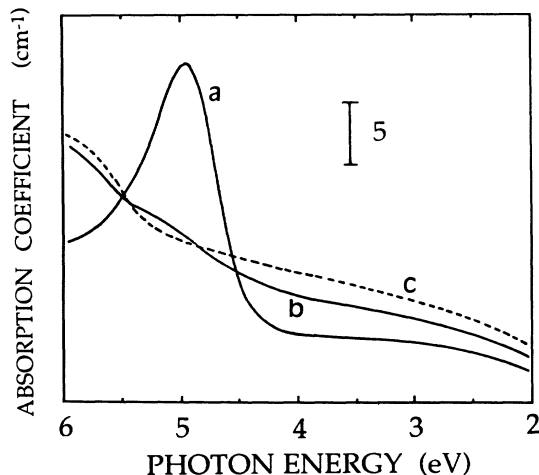


FIG. 1. Visible and uv absorption spectra for pair I after (a) TCR at 2400 K, (b) reducing treatment at 1530 K for 100 min, and (c) oxidizing treatment at 1825 K for 80 min.

closely spaced bands indicates that there exist more than one species of hydride ion perturbed by different impurities or defects. Measurements were made in two pairs of thermochemically reduced samples, hereafter named pair I and pair II. Each member of a pair had the same concentrations of anion vacancies and  $H^-$  ions. The initial concentration ratio of anion vacancies to  $H^-$  ions,  $[F, F^+]/[H^-]$ , was of the order of 0.07 and 0.01 for pair I and pair II, respectively. Figures 1 and 2 show the optical absorption spectra for a sample from pair I.

The most desirable feature of these crystals is that the

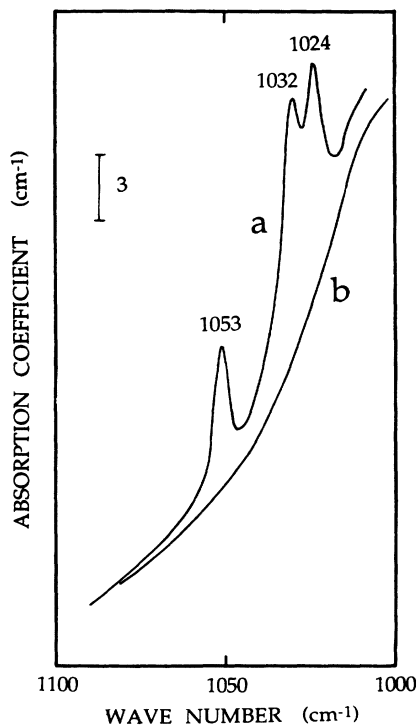


FIG. 2. IR absorption spectra for pair I after (a) TCR at 2400 K, (b) oxidizing treatment at 1825 K for 80 min.

ratio  $[F, F^+]/[H^-]$  can be diminished to any level by annealing the samples at high temperatures. The  $H^-$  ions are thermally much more stable than anion vacancies, so that anion vacancies can be completely annealed out without affecting the  $H^-$  concentration.<sup>25</sup> Table I provides the anion vacancies and  $H^-$  concentrations after different thermal treatments. Figures 1 and 2 illustrate the optical spectra after different anneals.

### B. Positron annihilation measurements

The positron annihilation results for pair I after successive thermal treatments are also summarized in Table I. Initially, this pair showed a two-component spectrum as has also been observed for undoped and doped MgO single crystals, as well as for MgO crystals containing a high concentration of  $F$  and  $F^+$  centers.<sup>34</sup> Heating for 10 min at 1400 K in a reducing atmosphere induced a dramatic change in the positron annihilation spectrum. The new spectrum exhibited three components. Successive reducing treatments produced a monotonic increase of the parameter  $\tau^*$ , defined as

$$\tau^* = \sum_{i=1}^3 I_i \tau_i, \quad (1)$$

where  $\tau_i$  and  $I_i$  are the lifetime and the intensity associated with the corresponding spectral component, respectively. This increase in  $\tau^*$  was mainly due to the increase of the lifetime of the long-lived component. The annihilation parameters  $I_2$ ,  $I_3$ , and  $\tau_3$  showed a tendency to increase as the concentration of anion vacancies decreased during the annealing. After the anneals the  $H^-$  ion concentration remained constant and no significant changes occurred in the  $\tau_1$  values. After the first oxidizing treatment at 1775 K the  $H^-$  concentration was below the level of detection. A noticeable change in the spectrum was induced: The  $\tau_1$  and  $\tau_3$  values increased and the  $I_3$  intensity decreased. After oxidation at 1825 K pair I exhibited an almost two-component spectrum. The value of  $I_3$  was very low and  $\tau_2$  was close to the value obtained initially for the as-TCR samples. It should also be noted that both the ratio  $I_3/I_2$  and  $\tau_2$  remain practically constant for all three-component spectra, except for the spectrum obtained after the 1825 K oxidation (see Table I). The lifetime spectra of pair I are shown in Fig. 3 for the samples after (a) TCR, (b) reducing treatment at 1530 K, and (c) oxidizing treatment at 1825 K.

The behavior observed in the annihilation parameters of pair II was similar to that observed for pair I. There were some differences in the  $\tau_1$  and  $\tau_3$  values and in the spectral intensities. However, the  $\tau_2$  value and the  $I_3/I_2$  ratio also remained constant, except after the last two oxidizing treatments (1550 and 1825 K). The average values for  $\tau_2$  and the  $I_3/I_2$  ratio obtained for both pairs of samples were  $(430 \pm 30)$  ps and  $0.25 \pm 0.03$ , respectively. The differences in  $\tau_1, \tau_3$ , and the spectral intensities between the two pairs are attributed to the initial difference in the  $H^-$  and anion vacancy concentrations.

Three observations are emphasized in the present results: (1) The lifetime spectra of TCR MgO crystals were

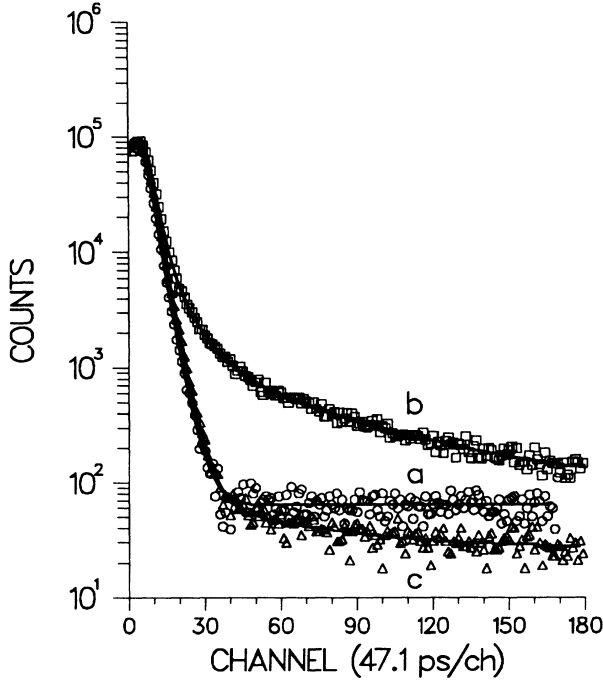


FIG. 3. Positron lifetime spectra for pair I after (a) thermochemical reduction at 2400 K, (b) reducing treatment at 1530 K for 100 min, and (c) oxidizing treatment at 1825 K. The time scale is 47.1 ps per channel.

two component. The value of the second lifetime component was close to that attributed to annihilation at vacancy defects when the ratio  $[F, F^+]/[H^-]$  is about 0.07.<sup>34</sup> (2) The positron-lifetime spectrum becomes three component, two of them being long lived, when the ratio  $[F, F^+]/[H^-]$  decreased to a value  $\sim 0.03$  after reducing treatments. (3) The  $\tau_2$  values and  $I_3/I_2$  ratios remained constant when the samples contained a significant concentration of  $H^-$  centers.

#### IV. POSITRON DECAY IN MgO CONTAINING $H^-$ IONS

The aforementioned results show unambiguously that the appearance of the long-lived components of  $\sim 430$  ps and 1–3 ns is related with the presence of  $H^-$  ions and the absence of anion vacancies in the samples. In previous experiments it was found that undoped MgO crystals having a high concentration of anion vacancies ( $\sim 10^{24} \text{ m}^{-3}$ ), but no  $H^-$  ions, exhibited a two-component spectrum; the second component of about 200 ps was attributed to positrons trapped at  $F$  centers.<sup>34</sup> Our results indicate that these long-lived components are induced by  $H^-$  ions and that  $F$ -type centers inhibit their appearance. Because the  $(430 \pm 30)$  ps value found for  $\tau_2$  is consistent with the calculated values for free PsH,<sup>6,7,9–11,14–16</sup> it is reasonable to associate this component with positron annihilation in the ground state of the bound  $[e^+H^-]$  system. In Sec. V we will use this  $\tau_2$  value to calculate the lifetime of the PsH state in anion vacancies in MgO. The existence of PsH states in MgO appears to be energetical-

ly possible since the electrostatic energy of a substitutional  $H^-$  ion in the MgO lattice must be smaller than the electrostatic energy per ion in MgO [9.36 eV (Ref. 35)]. Even this value is not high enough to compensate for the PsH ground-state energy,  $-21.47$  eV.<sup>16</sup> In a first approximation the effect of the lattice ions on the PsH energy would be to increase this energy by the electrostatic term.<sup>4</sup> Thus the effect of the surrounding ions would be to raise the PsH to an excited state with a certain probability of being dissociated into PsH and H. Moreover in MgO the nearest-neighbor ions to an anion vacancy move outwards, due to electrostatic repulsion, the radial displacements being around 7–10% of the lattice parameter,  $a_0 = 4.21 \text{ \AA}$ .<sup>36</sup> According to recent calculations,<sup>16</sup> the size of the PsH is estimated to be 3.86  $\text{\AA}$ , a value compatible with the anion vacancy size. The long-lived component  $\tau_3$ , 1–3 ns, cannot be attributed to positron annihilation in the excited  $[e^+H^-]$  states since the  $\tau_3$  value was not constant but seemed to increase when the  $H^-$  concentration was lowered during the first two oxidizing treatments (1550 and 1825 K). Moreover, a faint long-lived component of about 1–2 ns still remained after the component associated with the  $[e^+H^-]$  ground state disappeared. The fact that the  $\tau_3$  values are characteristic of pick-off annihilation of ortho-Ps states and that they increased with decreasing  $H^-$  concentration suggests that this long-lived component could actually be due to pick-off annihilation of ortho-Ps states, which might be prevented by the presence of  $H^-$  ions.

Given that (1) thermalized positrons move as Bloch positrons and can be trapped by lattice defects in MgO and (2) Ps states are not formed in MgO free of  $H^-$  ions,<sup>26,28,29</sup> we propose the following model: In the absence of other possible positron traps, free positrons can be trapped by  $H^-$  ions resulting in bound  $[e^+H^-]$  states. Accordingly, positrons can be annihilated in (1) free states, (2) bound  $[e^+H^-]$  states, and (3) Ps states that can be created by the dissociation of the  $[e^+H^-]$  states into H and free Ps. These last  $[e^+H^-]$  states can be in excited levels. If we accept that the ortho-Ps  $\leftrightarrow$  para-Ps conversion is negligible, as is currently assumed for solids, the positron kinetic decay would be given by the following equations:

$$\begin{aligned} \frac{dn_f}{dt} &= -(\lambda_f + \kappa_b)n_f, \\ \frac{dn_b}{dt} &= \kappa_b n_f - (4\Gamma_{Ps} + \lambda_{PsH})n_b, \\ \frac{dn_{3S_1}}{dt} &= 3\Gamma_{Ps}n_b - \lambda_{3S_1}n_{3S_1}, \\ \frac{dn_{1S_0}}{dt} &= \Gamma_{Ps}n_b - \lambda_{1S_0}n_{1S_0}, \end{aligned} \quad (2)$$

with the boundary conditions  $n_f(0) = 1$  and  $n_b(0) = n_{3S_1}(0) = n_{1S_0}(0) = 0$ . Here  $n_f$ ,  $n_b$ ,  $n_{3S_1}$ , and  $n_{1S_0}$  are the fraction of free positrons, bound  $[e^+H^-]$  states, ortho-Ps and para-Ps, respectively;  $\lambda_f$ ,  $\lambda_{PsH}$ ,  $\lambda_{3S_1}$ , and  $\lambda_{1S_0}$  their

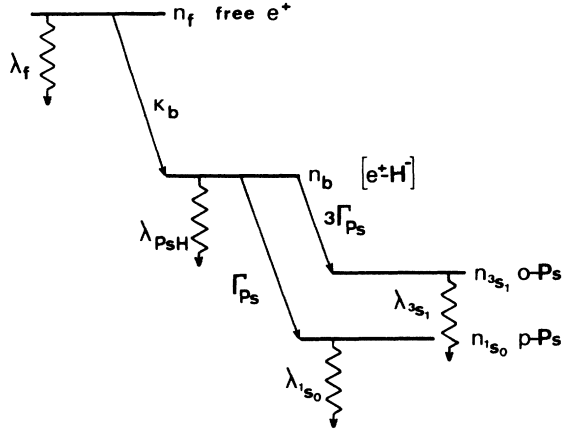


FIG. 4. Positron decay scheme in MgO containing  $H^-$  ions.

corresponding annihilation rates;  $\kappa_b$  the transition rate into bound  $[e^+H^-]$  states; and  $4\Gamma_{Ps}$  the dissociation rate of the  $[e^+H^-]$  states into H and Ps. The transition rate  $\kappa_b$  will obviously be proportional to the  $H^-$  ion concentration  $c_b$ , i.e.,  $\kappa_b = \mu_b c_b$ , where  $\mu_b$  is the specific positron trapping rate per unit of  $H^-$  ion concentration. For this model the positron decay scheme is shown in Fig. 4.

Solving the Eqs. (2), the fraction of positrons in the samples at time  $t$ ,

$$N(t) = n_f(t) + n_b(t) + n_{3s_1}(t) + n_{1s_0}(t)$$

is obtained (see Appendix)

$$N(t) = \sum_{i=0}^3 I_i \exp(-\lambda_i t). \quad (3)$$

## V. DISCUSSION

Although the proposed model yields a four-component lifetime spectrum, the experimental spectra can reliably be decomposed into only three exponential terms. The reason is that the values of  $\lambda_0$  (expected to be  $\sim 8.0 \times 10^9 \text{ s}^{-1}$ ) and  $\lambda_1$  are very close, and therefore their corresponding exponential terms cannot be resolved in the analysis. On the other hand, it is expected that  $\lambda_{PsH}$  and  $\lambda_{3s_1}$  are smaller than  $\lambda_1$  and very different from one another. So, while the exponential terms related to  $\lambda_2$  and  $\lambda_3$  can be resolved by the computing analysis, those related to  $\lambda_0$  and  $\lambda_1$  cannot. Thus, experimentally the fraction of positrons in the samples  $N(t)$  would be given by

$$N(t) = I_1 \exp(-\lambda_1 t) + I_2 \exp(-\lambda_2 t) + I_3 \exp(-\lambda_3 t), \quad (4)$$

where the first term describes, approximately, the sum of the first two terms of the predicted spectrum. Now, it would be reasonable to assume that

$$I_1 = I_0 + I_1,$$

and

$$\lambda_I = \frac{\lambda_0 I_0 + \lambda_1 I_1}{I_0 + I_1}.$$

Taking into account the statistical ratio between para-Ps and ortho-Ps and assuming that all ortho-Ps annihilate by a pick-off process, the relationship  $I_3 = 3I_0$  would be expected for the intensities associated with para-Ps and ortho-Ps. The experimental values for pair I indicate that the values for  $I_0$  should range from 1 to 2.2 %, which means that the difference between  $\tau_I = \lambda_I^{-1}$  and  $\tau_1 = \lambda_1^{-1}$  is smaller than 2 or 3 ps, even in the most unfavorable situations. These deviations are within the experimental error of  $\tau_1$ . Consequently, it is reasonable to assume that  $\lambda_1 = \lambda_I$ .

From Eqs. (A12) and (A13)  $\Gamma_{Ps}$  is obtained as a function of the experimental parameters and the  $\lambda_0$  value

$$\Gamma_{Ps} = \frac{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)}{3 \left[ (\lambda_1 - \lambda_2) \frac{I_2}{I_3} + (\lambda_1 - \lambda_3) \right] - \frac{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)}{\lambda_0 - \lambda_2}}. \quad (6)$$

A good approximation for  $\lambda_0$  is the theoretical value of the self-annihilation rate of the para-Ps state in vacuum,<sup>37</sup> i.e.,  $\lambda_0 = 8.0 \times 10^9 \text{ s}^{-1}$ . Taking into account that  $\lambda_1 = \lambda_I$ ,  $\Gamma_{Ps}$  can be determined from the experimental results using Eq. (6). Equation (A7) now gives the annihilation rate of the PsH states,  $\lambda_{PsH}$ . The values found for  $\Gamma_{Ps}$  and  $\lambda_{PsH}$  are given in Table I and are reasonably constant considering the experimental errors. Their mean values are  $(1.59 \pm 0.17) \times 10^8 \text{ s}^{-1}$  and  $(1.75 \pm 0.14) \times 10^9 \text{ s}$ , respectively. The lifetime of the PsH state,  $\tau_{PsH} = \lambda_{PsH}^{-1}$ , would be  $(570 \pm 50)$  ps. This value is between  $\sim 70$  and  $\sim 160$  ps, longer than the values calculated for the lifetime of the ground state of free PsH.<sup>6,7,9-11,14-16</sup>

In light of our results and of the proposed model, it seems realistic to regard the value of  $(570 \pm 50)$  ps as a reasonable approximation to the lifetime of the PsH in MgO. It should be noted that the discrepancy between our experimental  $\tau_{PsH}$  value in MgO and the calculated  $\tau_{PsH}$  values for the PsH ground state in vacuum could be explained on the assumption that indigenous ions may noticeably perturb the PsH lifetime and induce its dissociation into H and Ps. Calculations have shown that the PsH annihilation rate is quite sensitive to its electron-electron correlation and binding energy.<sup>14,16</sup> The PsH annihilation rate in an anion vacancy in MgO can be modified by the lattice ions in two ways: (a) reducing the PsH binding energy and (b) perturbing the correlation term. As mentioned in Sec. IV, PsH in the MgO lattice could be created in an excited state due to the electrostatic energy associated with the substitutional  $H^-$  ions. The PsH binding energy against dissociation into Ps and H would decrease, thus increasing the probability that this dissociation may be observed because of the long lifetime of the PsH. Also, as the PsH is located at an anion vacancy, the electron-electron correlation term would be

deeply perturbed by the neighbor  $\text{Mg}^{++}$  ions; it is clear that the overlapping between the electron wave functions and the positron wave function would be reduced because of the  $\text{Mg}^{++}$  ion screening.

An apparent discrepancy between the experimental results and the proposed model, however minor, seems to arise from the observation that a long-lived component of  $\sim 1\text{--}2$  ns, with a very weak intensity of  $\sim 0.4\text{--}0.6\%$ , still remained in the spectrum after the lifetime component attributed to PsH states has completely disappeared following the last thermal treatment. The origin of this faint long-lived component could be due to pick-off annihilation of Ps states created by a process such as  $e^+ + \text{H} \rightarrow \text{H}^+ + \text{Ps}$  or another type of reaction involving molecular hydrogen that is still present in MgO crystals after high-temperature treatments.

The intensities  $I_3$  and  $I_2$  are related, respectively, to the number of  $e^+e^-$  pairs annihilated in ortho-Ps states and in bound  $[e^+ \text{--} \text{H}^-]$  states. The ratio  $I_3/I_2$  is thus a measure, although somewhat indirect, of the dissociation probability of an  $[e^+ \text{--} \text{H}^-]$  state into Ps and H; this probability should be a constant. Actually,  $I_3/I_2$  is related to the ratio of the  $e^+e^-$  pairs annihilated in ortho-Ps states to the  $e^+e^-$  pairs annihilated in  $[e^+ \text{--} \text{H}^-]$  states. This fraction, according to the proposed model, is given by the ratio  $3\Gamma_{\text{Ps}}/\lambda_{\text{PsH}}$ . The experimental results yield an  $I_3/I_2$  value that is essentially constant for both pairs of samples, i.e.,  $0.25 \pm 0.03$ , and a value of  $0.27 \pm 0.05$  is obtained for the ratio  $3\Gamma_{\text{Ps}}/\lambda_{\text{PsH}}$ . Although this result is quite satisfactory, it must be emphasized that the ratio  $I_3/I_2$  is not exactly the fraction of  $e^+e^-$  pairs annihilated in an ortho-Ps state per  $e^+e^-$  pair annihilated in a PsH state, as is easily seen when  $I_3/I_2$  is obtained from Eqs. (A12) and (A13). The spectra of pair II generally exhibited a long-lived component that was significantly longer and an intensity that was higher than those observed for pair I, although the resulting ratios for  $I_3/I_2$ , and the values of  $\tau_2$  and  $\tau_1$  were essentially the same as those of pair I. We attribute both discrepancies to the higher hydrogen content in samples of pair I, not only in the  $\text{H}^-$  configuration but also in the total  $\text{H}_2$  content, as attested by the cloudiness of the samples. The presence of very small bubbles of  $\sim 20$  Å in diameter, might increase the  $\tau_3$  values if this hydrogen is involved in the pick-off annihilation of the ortho-Ps or in the formation of the Ps states. Larger cavities containing hydrogen have already been observed in MgO crystals.<sup>31</sup>

## VI. CONCLUSIONS

Thermochemically reduced MgO crystals contain  $\text{H}^-$  ions and anion vacancies. A requirement for significant positron trapping by  $\text{H}^-$  ions is that the anion vacancy concentration be at least 2 orders of magnitude smaller

than the concentration of  $\text{H}^-$  ions in the samples. This observation indicates that anion vacancies are very effective positron traps as indeed they are for protons, which was how  $\text{H}^-$  ions were formed in the first place.

Experimental results for positron annihilation in MgO containing  $\text{H}^-$  ions are consistent with a positron decay model that suggests the formation of bound  $[e^+ \text{--} \text{H}^-]$  states by positron trapping by  $\text{H}^-$  ions and Ps states due to dissociation of a fraction of these  $[e^+ \text{--} \text{H}^-]$  states. Two long-lived components of  $\sim 430$  ps and  $1\text{--}3$  ns were observed. The former component is associated with positron annihilation in PsH states, and the latter with pick-off annihilation of ortho-Ps states. From the value of the 430 ps component, a value of  $(570 \pm 50)$  ps is obtained for the lifetime of the PsH state in anion vacancies in MgO. Assuming the standard two state trapping model<sup>38</sup> for positrons in samples having a high concentration of  $F$  centers, the specific trapping rate per unit of anion vacancy concentration has been determined to be about  $9 \times 10^{14} \text{ s}^{-1}$ . Indeed,  $\text{H}^-$  ions seem to be less effective as positron traps since their specific trapping rate, evaluated from the  $\kappa_b$  values, is

$$(1.16 \pm 0.15) \times 10^{14} \text{ s}^{-1},$$

i.e., about 1 order of magnitude smaller.

The suggested model allows us to evaluate the lifetime of the PsH in anion vacancies from positron-lifetime measurements.

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## APPENDIX

From Eqs. (2) and assuming  $n_f(0) = 1$  and

$$n_b(0) = n_{3S_1}(0) = n_{1S_0}(0) = 0,$$

the following positron fractions in each state are obtained:

$$n_f(t) = \exp(-\lambda_1 t), \quad (\text{A1})$$

$$n_b(t) = \frac{\kappa_b}{\lambda_1 - \lambda_2} [\exp(-\lambda_2 t) - \exp(-\lambda_1 t)], \quad (\text{A2})$$

$$n_{1S_0}(t) = \frac{\Gamma_{\text{Ps}} \kappa_b}{(\lambda_0 - \lambda_1)(\lambda_0 - \lambda_2)} \left[ \exp(-\lambda_0 t) + \frac{(\lambda_0 - \lambda_1)}{(\lambda_1 - \lambda_2)} \exp(-\lambda_2 t) - \frac{(\lambda_0 - \lambda_2)}{(\lambda_1 - \lambda_2)} \exp(-\lambda_1 t) \right], \quad (\text{A3})$$

$$n_{3S_1}(t) = \frac{3\Gamma_{\text{Ps}} \kappa_b}{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)} \left[ \exp(-\lambda_3 t) + \frac{(\lambda_2 - \lambda_3)}{(\lambda_1 - \lambda_2)} \exp(-\lambda_1 t) - \frac{(\lambda_1 - \lambda_3)}{(\lambda_1 - \lambda_2)} \exp(-\lambda_2 t) \right], \quad (\text{A4})$$

where

$$\lambda_0 = \lambda_{1S_0}, \quad (\text{A5})$$

$$\lambda_1 = \lambda_f + \kappa_b, \quad (\text{A6})$$

$$\lambda_2 = 4\Gamma_{Ps} + \lambda_{PsH}, \quad (\text{A7})$$

$$\lambda_3 = \lambda_{3S_1}. \quad (\text{A8})$$

The positron fraction present in the samples at time  $t$  would be

$$\begin{aligned} N(t) &= n_f(t) + n_b(t) + n_{1S_0}(t) + n_{3S_1}(t) \\ &= \sum_{i=0}^3 I_i \exp(-\lambda_i t), \end{aligned} \quad (\text{A9})$$

here

$$I_0 = \frac{\Gamma_{Ps}\kappa_b}{(\lambda_0 - \lambda_1)(\lambda_0 - \lambda_2)}, \quad (\text{A10})$$

$$I_1 = \left[ 1 - \frac{\kappa_b}{\lambda_1 - \lambda_2} \left[ 1 + \frac{\Gamma_{Ps}}{\lambda_0 - \lambda_1} - \frac{3\Gamma_{Ps}}{\lambda_1 - \lambda_3} \right] \right], \quad (\text{A11})$$

$$I_2 = \frac{\kappa_b}{\lambda_1 - \lambda_2} \left[ 1 + \frac{\Gamma_{Ps}}{\lambda_0 - \lambda_2} - \frac{3\Gamma_{Ps}}{\lambda_2 - \lambda_3} \right], \quad (\text{A12})$$

$$I_3 = \frac{3\Gamma_{Ps}\kappa_b}{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)}. \quad (\text{A13})$$

The observed rate of positron annihilation, i.e., the annihilation spectrum is given by

$$\frac{d}{dt}[1 - N(t)] = -\frac{dN(t)}{dt} = \sum_{i=0}^3 \lambda_i I_i \exp(-\lambda_i t), \quad (\text{A14})$$

The parameter  $\tau^*$  defined as

$$\tau^* = -\int_0^\infty t \frac{dN}{dt} dt \quad (\text{A15})$$

turns in

$$\tau^* = \sum_{i=0}^3 I_i \lambda_i^{-1}. \quad (\text{A16})$$

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