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# Positron bound states on hydride ions in thermochemically reduced MgO single crystals

M. A. Monge, R. Pareja, and R. González
*Departamento de Física, Universidad Carlos III de Madrid, C/Butarque 15, 28911 Leganés, Spain*

Y. Chen
*U.S. Department of Energy, ER 131, Division of Materials Sciences, Office of Basic Energy Sciences, Washington, D.C. 20874-1290*

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Positron-lifetime and Doppler-broadening techniques were used to unambiguously identify positronium hydrides in thermochemically reduced MgO crystals at low temperatures. Positrons trapped at $H^-$ ions, forming PsH, yield a lifetime of $(640\pm 40)$ ps, independent of temperature. Complementary evidence for this identification was provided by Doppler-broadening experiments, in which positrons were trapped at $H^{2-}$ sites at low temperatures. The $H^{2-}$ ions were formed via $H^- + e^- \rightarrow H^{2-}$ by the capturing of an electron released from $Fe^+$ impurity under blue-light stimulation. [S0163-1829(96)00438-9]

## I. INTRODUCTION

The positronium atom (Ps) is a particle consisting of a positron bound to an electron, both revolving about their center of mass. This atom was predicted and experimentally discovered many years ago.[1,2] The possibility of forming molecules in which Ps is a constituent has been of considerable interest both theoretically and experimentally. The positronium hydride (PsH), also known as the bound state $[e^+ - H^-]$, is such a molecule; it is a hydrogen molecule with one of its two protons replaced by a positron. Its existence was first postulated by Ore[3] and recent calculations predict a PsH lifetime of ~ 410 ps in vacuum.[4] This molecule is important in the understanding of the physics and chemistry of the positronium. For example, the annihilation characteristics of the positronium may provide information on different processes occurring in the center of the galaxy − in particular, those annihilation processses responsible for the narrow annihilation line detected from the direction of the galactic center.[5,6] The detection of PsH and knowledge of its annihilation characteristics in condensed matter are fundamental for numerous applications of positron annihilation spectroscopy (PAS) to materials science.[7]

The formation of PsH has been reported in MgO crystals,[8] and in collisions with $CH_4$ molecules.[9] In this paper we demonstrate from positron lifetime experiments at low temperatures that PsH molecules are formed in MgO single crystals containing $H^-$ ions, which are protons each with two electrons substituting for indigenous $O^{2-}$ ions. Even though the $H^-$ ion is negatively charged, substituting for an $O^{2-}$ ion renders the site positively charged relative to the lattice and can therefore trap an electron to form a metastable $H^{2-}$ ion. A temperature-dependent positron-trapping coefficient has been obtained. In addition, by Doppler-broadening experiments we produced evidence that thermalized positrons can be trapped by substitutional $H^{2-}$ ions, induced in the crystals by blue light at low temperatures.

## II. EXPERIMENTAL PROCEDURE

The MgO crystals used in this investigation were grown by the arc fusion method[10,11] at the Oak Ridge National Laboratory using high purity grade MgO powder from the Kanto Chemical Company, Tokyo (Japan). Large concentrations of hydrogen were obtained by presoaking the MgO powder in $H_2O$. In the proccess of thermochemical reduction (TCR) the crystals were heated at high temperature (~2400 K) and under high pressure Mg vapor (~7 atm) in a tantalum bomb, followed by rapid cooling.[12,13]

To monitor the concentration of oxygen vacancies and $H^-$ ions, optical absorption measurements in the UV-VIS-IR were made with a Perkin-Elmer Lambda 9 and a Perkin-Elmer 2000 FT-IR spectrophotometers.

Two types of positron techniques were employed: lifetime and Doppler broadening. In both cases a $^{22}Na$ positron source was sandwiched between a pair of samples. Lifetime experiments were performed between 100 and 300 K inside a liquid-$N_2$ flow cryostat. A spectrometer with a resolution (FWHM) of 235 ps was used. The lifetime spectra were analyzed by means of the POSITRONFIT program. Doppler-broadening experiments were performed over a range 10 – 300 K in an optical He-closed cycle cryostat. The annihilation radiation was recorded with an intrinsic Ge detector with a resolution of 1.62 keV at the 1.33 MeV line of $^{60}Co$. Measurements were made with samples either in the dark, or under blue-light irradiation on both external surfaces by two 400 W Xe lamps colinearly arranged. An interferometric filter with a band width of 2.5 nm, in conjunction with a lens system, was used to concentrate the beams onto the samples. The irradiance on the sample was estimated to be $\cong 170$ $mW/cm^2$. The axis of the Ge detector was perpendicular to the light beams. A series of spectra with $2.5\times 10^6$ counts under the annihilation peak were alternatively collected in the dark and under blue light at different temperatures. The Doppler broadening of the annihilation peak was characterized by the line shape parameter $S$. It describes the fraction of annihilation events in the energy window of $(511.0\pm 0.8)$ keV.

## III. RESULTS AND DISCUSSION

During TCR, the main defects formed are $H^-$ ions and oxygen vacancies.[12,13] The latter can exist in two charge

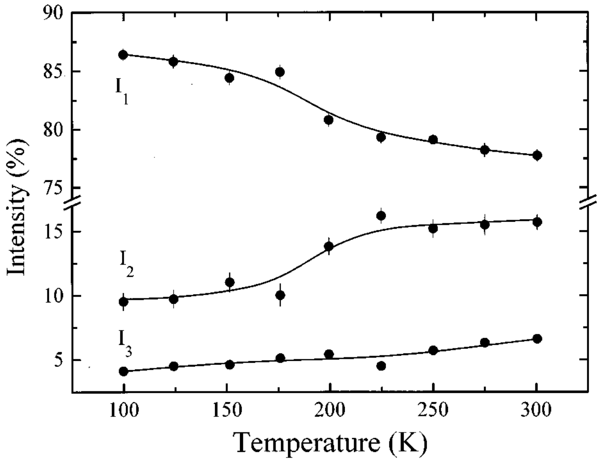

FIG. 1. Intensities of the positron lifetime spectrum against temperature for MgO crystals with an $H^-$ concentration of $1\times10^{18}$ $cm^{-3}$ and no F centers.

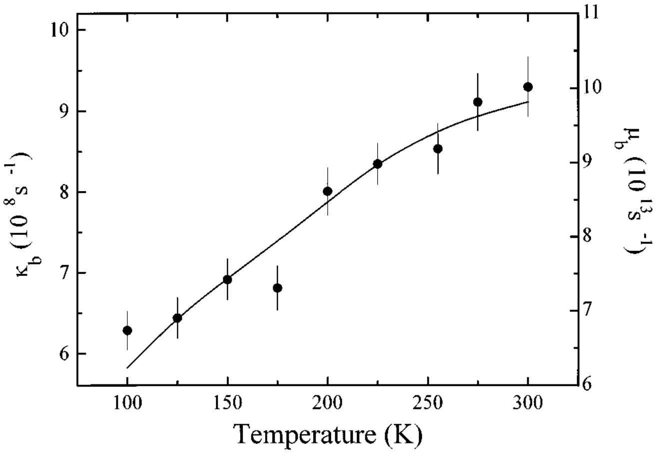

FIG. 2. Temperature dependence of the positron trapping rate ($\kappa_b$) and of the trapping coefficient ($\mu_b$) for $H^-$ ions.

states, with one or two electrons ($F^+$ and F centers, respectively), with the F centers as the dominant species. The optical absorption bands of both centers are broad and can be identified by peaks coinciding at the same wavelength (250 nm).[14] The $H^-$ ions are identified by local vibrational modes at 1053, 1032, and 1024 $cm^{-1}$.[12,13] From the corresponding optical absorption bands, the concentrations of the anion vacancies (F plus $F^+$ centers) and $H^-$ centers were estimated to be $\sim5\times10^{18}$ $cm^{-3}$ and $1\times10^{18}$ $cm^{-3}$, respectively. The $H^-$ ions are thermally much more stable than the oxygen vacancies.[13] In a reducing atmosphere, they are stable even at 1900 K, whereas anion vacancies anneal at $T = 1350$ K. Since F centers were shown here to compete with hydride ions for positrons, it was possible to take advantage of the stability of the hydride ions and either partially or completely anneal out the anion vacancies at 1470 K.

Thermochemical reduction also results in valence change of impurities such as iron, from $Fe^{3+}$ to $Fe^+$. Exciting the crystal with blue light (400–430) nm releases electrons via $Fe^+ \rightarrow Fe^{2+} + e^-$. (The absorption at these wavelengths is sufficiently small that this process can be considered to be uniform throughout the crystal.) The electron is then trapped at an $H^-$ site, forming a metastable $H^{2-}$ ion.[15–17] At room temperature the paramagnetic $H^{2-}$ ion will release an electron, reverting back to an $H^-$ ion; at sufficiently low temperatures, $<$ 150 K, it is thermally stable.[17] In the present study we chose to work at low temperatures precisely to maximize the concentration of $H^{2-}$ ions.

### A. Positronium hydride formation

Severe thermochemical reduction of hydrogen-doped MgO crystals provides all the necessary ingredients to observe the PsH, even though optimization of parameters and elimination of undesirable defects are necessary.

After TCR, the MgO samples showed a two-component lifetime spectrum with a second component lifetime of 225 ps which is attributed to trapped positrons at F centers. In spite of the high F center concentration, no positron trapping saturation was observed. When most of the F centers were annealed out, the lifetime spectrum was observed to be three-component. The second component is due to annihilation of bound positron states at $H^-$ ions, i.e., bound $[e^+ - H^-]$ states, and the third component with lifetime values of 1.4–1.9 ns has been attributed to pickoff annihilation of ortho-Ps states created by dissociation of $[e^+ - H^-]$ states.[8] The lifetime values of these three components do not exhibit a significant temperature dependence but their spectral intensities do. Figure 1 depicts the spectral intensities versus temperature after the F centers were completely annealed out. The increase of $I_2$ and $I_3$ indicates both an increase of the bound $[e^+ - H^-]$ states and their dissociation into Ps and H. Using a more elaborate positron decay model than that proposed in Ref. 8, the positron trapping rate $\kappa_b$ for $H^-$ ions and the lifetime of the PsH state $\tau_{PsH}$ was obtained.[18]

The positron trapping coefficient $\mu_b$ is related to the positron trapping rate $\kappa_b$ by $\kappa_b = \mu_b C_{H^-}$, where the measured $H^-$ ion concentration $C_{H^-}$ in the samples is $9.3\times10^{-6}$ $atom^{-1}$. Figure 2 shows the $\kappa_b$ and $\mu_b$ values against temperature. These values increase with temperature, as predicted for a positively charged vacancy in wide-gap crystals.[19] Calculations in semiconductors indicate that a positively charged vacancy can hold bound positron states even though its positron trapping coefficient is very low.[19,20] Thus, in MgO crystals positrons can be trapped at $H^-$ ions after more effective positron traps such as F centers have been removed. Experiments in a pair of samples where the concentration of F centers was varied as the samples were annealed at increasing temperatures, yield a lifetime for the PsH state of $(640\pm40)$ ps, independent of temperature. This value agrees with that previously obtained from room-temperature experiments.[8]

Doppler broadening of the 511 keV annihilation photopeak provides information on the momentum distribution of the annihilating electrons. A low $S$ implies a low probability that positrons annihilate with low momentum electrons. Also, $S$ depends on the positron trapping coefficient $\mu_b$. The temperature dependence of S measured in the dark for samples with different F center concentrations is shown in Fig. 3. For comparison, $S$ for a sample with only F centers (without $H^-$ ions) is shown. In all cases, $S$ increased with temperature. These results indicate a strong temperature effect on the positron trapping coefficient for $H^-$ ions.

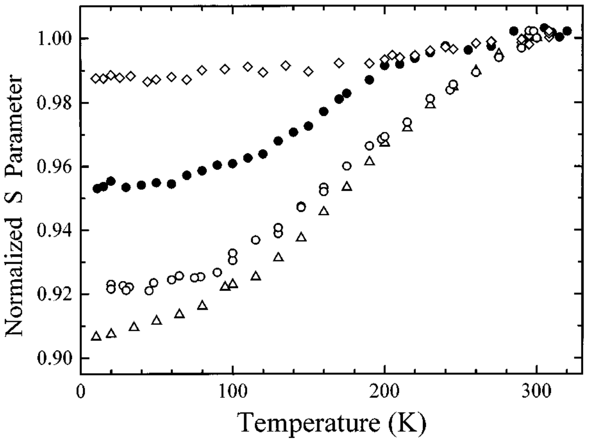

FIG. 3. Temperature dependence of the $S$ parameter, normalized to the room-temperature value, for MgO crystals with $[F]\sim 5\times 10^{18}$ cm$^{-3}$(◇); $[F]=5\times 10^{17}$ cm$^{-3}$ and $[H^{-}]=1\times 10^{18}$ cm$^{-3}$(●); $[F]=1\times 10^{17}$ cm$^{-3}$ and $[H^{-}]=1\times 10^{18}$ cm$^{-3}$(○); and $[H^{-}]=1\times 10^{18}$ cm$^{-3}$(△).

For a sample containing high F and $H^{-}$ concentrations, $S$ was unaffected by illumination with 400 or 425 nm light. This result was not surprising since the concentration of $H^{2-}$ ions[16] produced by blue irradiation was estimated to be $10^{16}$ – $10^{17}$ cm$^{-3}$. The concentration of anion vacancies was 2 orders of magnitude higher. It was previously shown that F centers are effective positron traps;[8] therefore, the fraction of positrons annihilated at $H^{2-}$ ions would be negligible.

### B. Positron trapping at $H^{2-}$ centers

Next we demonstrate the effect of blue light on $S$ via $H^{-}+e^{-}\rightarrow H^{2-}$. Since F centers compete with $H^{2-}$ ions for positron trapping, to enhance positron trapping at $H^{2-}$ sites, anion vacancies were annealed out. After heating the samples at 1470 K for 120 min in a reducing atmosphere, anion vacancies completely vanished. Under blue-light stimulation, the $H^{2-}$ concentration was estimated to be at least 1 order of magnitude lower than that of the $H^{-}$ ion.[16] However, the $H^{2-}$ ion is expected to be a more effective positron trap because of the more negative potential. The $S$ values under 400 nm light stimulation were lower than those measured in the dark at $T<100$ K. At $T>100$ K, the S values measured in the dark and those under light were indistinguishable. Figure 4 plots $(S_d-S_i)$ versus temperature, where $S_d$ refers to $S$ in the dark, and $S_i$ to $S$ under light stimulation. A Fourier analysis of the difference curve reveals predominant frequencies, indicating that $(S_d-S_i)$ is a real effect induced by the blue-light irradiation. A low $S$ value implies that positron annihilations with low momentum electrons are less probable. Consequently, the above results indicate that the annihilation with low momentum electrons are less probable when the samples are illuminated with 400 nm light. We attribute the $(S_d-S_i)$ difference to photoconversion of $H^{-}$ ions which capture electrons released from $Fe^{+}$ impurities resulting in $H^{2-}$ ions.

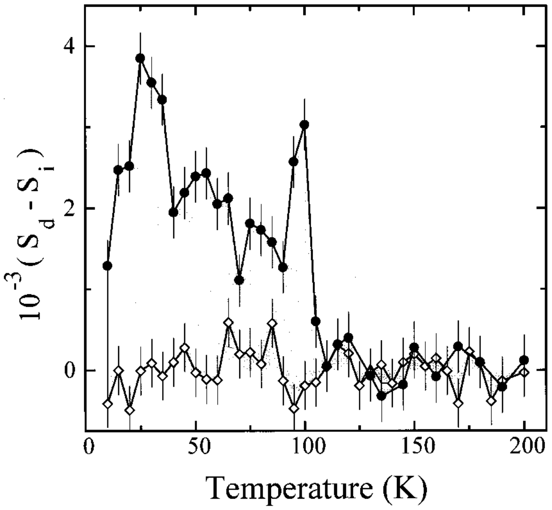

FIG. 4. Difference curve $(S_d-S_i)$ vs temperature for 400 nm light stimulation (●); points ( ◇ ) correspond to the difference between the $S$ values of two successive measurements performed in the dark. Each point represents the mean value of three measurements.

We propose that this is the only plausible interpretation. The effect is not due to temperature increase produced by the light absorption, because $(S_d-S_i)$ would be negative. Measurements were also made using unfiltered (white) light from the Xe lamp. No difference was observed between $S_d$ and $S_i$. Since low-momentum annihilations are controlled by the annihilation of para-Ps states produced by the thermally activated dissociation of PsH-like states, we attribute the observed results to a reduction in the creation of PsH-like states due to the photoconversion $H^{-}\rightarrow H^{2-}$ ions and subsequent formation of bound $[e^{+}-H^{2-}]$ states. Annihilating $e^{-}-e^{+}$ pairs at $[e^{+}-H^{2-}]$ states have lower momenta than pairs annihilating at PsH states. However, it appears that this effect is overcome by a reduction in the probability of forming para-Ps states induced by the PsH dissociation.

## IV. CONCLUSIONS

Low-temperature positron annihilation experiments demonstrate that $[e^{+}-H^{-}]$ and $[e^{+}-H^{2-}]$ states are formed in thermochemically reduced H-doped MgO crystals after anion vacancies were annealed out. The positron trapping coefficient for $H^{-}$ centers increases with temperature. The lifetime of the PsH state is (640±40) ps and is temperature independent. At temperatures below 100 K, the values of the parameter $S$ under blue-light (400 nm) stimulation were lower than those in the dark, indicating that the $[e^{+}-H^{2-}]$ state does not annihilate via dissociation into a Ps state and an $H^{-}$ ion.

## ACKNOWLEDGMENTS

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