

Positron Lifetimes in Metal Hydrides (*).

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Summary. — Positron-decay curves in commercially available metal hydrides have been measured, using a delayed coincidence system with 0.37 ns (FWHM) prompt time resolution. Evidence was found that the annihilation is complex, with two exponential decays of comparable intensities. In alkali-metal hydrides as in alkaline-earth hydrides, the annihilation rates I_1 and I_2 are found to increase with molecular densities. The experimental results are against the crude application of the simple decay model of the positron bound to a single H^- ion of the lattice. This model seems realistic only in the limit of very low molecular densities. Positron lifetimes in TiH_2 and ZrH_2 are found to be considerably shorter than lifetimes in divalent alkaline earth hydrides, probably owing to the presence of the highly polarizable electrons in the conduction band.

1. - Introduction.

Information about the annihilation features of slow positrons in solids is mainly given by measurements of angular correlation of photons from the two-gamma decay and by positron lifetime spectra. The first method gives the density of momenta of the annihilating particles, the second gives the lifetimes of the positron in the material and the fraction of positron annihilations which occur by various modes. In the past few years some efforts were made in the above direction, in order to get some knowledge of the electron structure of matter. The decay mechanism of the positron, in spite of the abundance of experimental data, is not yet clearly understood.

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FERREL⁽¹⁾ discussed the formation of the positronium atom in ionic crystals and concluded that this possibility is destroyed mainly by the fact that the positronium atom is confined to a space of very small dimensions with a great lowering of its internal binding energy. It was then suggested that in ionic crystals the positron interacts electrostatically with the negative ions and annihilates with the outer electron shells. This argument was supported by accurate experimental data⁽²⁾ on the angular correlation of photons from positron annihilation in two systematic series of alkali halides, all the sodium halides and all the alkali chlorides: the positive ions have very little influence on the momentum distribution in comparison with the negative ions. This conclusion was supported also by the observation that angular correlation curves for LiH and NaH are hardly distinguishable⁽³⁾. Serious difficulties arise when the experimental densities of momenta are compared with the distributions calculated from the wave-function products given by various models of electron and positron wave functions in the crystal. This is probably due to the fact that positrons annihilate chiefly with the electrons of the valence band which are more polarizable than others, and whose wave functions differ from the Hartree-Fock free-ion wave functions because of the crystal potential and the presence of the positron itself. Therefore a significant comparison with experimental data requires a detailed knowledge of the electron charge distribution in the crystal.

At the present, accurate experimental data about positron lifetimes in alkali halides are available^(4,5). For these substances the annihilation spectra are complex and show the contribution of two or more lifetime components. The interpretation of these results is not immediate but it is seen that the annihilation features show regularities within each series of alkali halides.

Owing to the main result pointed out by experiments that the annihilation process is chiefly concerned with the electronic properties of the negative ions, it is useful to get experimental data about the most simple series of ionic crystals, that is metal hydrides. Moreover the most demanding theoretical works about positron annihilation in ionic crystal are performed in LiH because of its simple electronic structure^(6,7). Finally the experimental investigation of positron lifetimes in solids is now more accurate than in the past few years because of improved experimental techniques.

(1) R. A. FERREL: *Rev. Mod. Phys.*, **28**, 308 (1956).

(2) A. T. STEWART and N. K. POPE: *Phys. Rev.*, **120**, 2033 (1960).

(3) A. T. STEWART and R. H. MARCH: *Phys. Rev.*, **122**, 75 (1961).

(4) A. BISI, A. FIORENTINI and L. ZAPPA: *Phys. Rev.*, **134**, A 328 (1964).

(5) C. BUSSOLATI, A. DUPASQUIER and L. ZAPPA: *Nuovo Cimento*, **52** B, 529 (1967).

(6) V. J. GOL'DANSKII, A. V. IVANOVNA and E. P. PROKOP'EV: *Sov. Phys. JETP*, **20**, 440 (1965).

(7) W. BRANDT, L. EDER and L. LUNDQUIST: *Phys. Rev.*, **142**, 165 (1966).

In a previous paper (⁸) we have established the possibility of making a systematic investigation of positron-decay features in metal hydrides with sufficient accuracy.

In the present paper we give the experimental results about positron lifetimes and intensities of the various decay components in alkali metal and alkaline earth hydrides which are commercially available. A physical decay model is also proposed which is in qualitative agreement with experimental data available at present time.

2. - Experimental method.

Our delayed coincidence system consisted basically of a time-to-pulse-height converter Ortec Model 405 together with a conventional fast-slow system. In order to eliminate pile-up effects, the inhibit pulses of two pile-up detector circuits were put in anticoincidence with signals to be analysed. The γ -rays were detected by two NE 102 plastic scintillators, optically coupled to Philips XP 1021 photomultipliers. With narrow energy selection windows set near the Compton edges of the ^{22}Na spectrum, the full width at half maximum (FWHM) of the prompt resolution curve taken with the γ -rays emitted by ^{60}Co was $3.7 \cdot 10^{-10}$ s. The slope simulated by the resolution curve was $0.82 \cdot 10^{-10}$ s. These values were determined under typical experimental conditions. The peak-to-background ratio was $10^4:1$ for the activities of the sources used in our experiments. To reduce the effects of drift, which was mainly due to the multichannel analyser, data were taken alternately from prompt (^{60}Co) and delayed sources. We have not considered data accumulated between two prompt resolution curves whose centroids drifted more than $0.30 \cdot 10^{-10}$ s. Moreover all spectra were analysed by the slope method using a maximum likelihood procedure, in which allowance was made for finite time resolution, background and finite width of pulse-height analyser channels. Time calibration was made by means of fixed coaxial delay lines: they were inserted immediately before the stop input of the time-to-pulse-height converter, and subsequently we measured the centroid shifts of the prompt curves so obtained.

A few microcuries of $^{22}\text{NaCl}$ solution were evaporated on a 1 mg/cm^2 mica foil sandwiched between the specimens under investigation. The fraction K of the positrons annihilating in the supporting foil was evaluated by taking advantage of results obtained recently by BERTOLACCINI and ZAPPA (⁹).

(⁸) A. GAINOTTI, C. GHEZZI, M. MANFREDI and L. ZECCHINA: *Phys. Lett.*, **25 A**, 316 (1967).

(⁹) M. BERTOLACCINI and L. ZAPPA: *Nuovo Cimento*, **52 B**, 487 (1967).

In their paper they give directly this fraction as a function of the foil thickness and of the mean atomic number of the specimen. The values of K relative to our measurements are contained in few 10^{-2} : this is due to the low mean atomic number of the specimens under investigation. By knowing K and by taking a spectrum in a mica sample it has been possible to subtract correctly from every spectrum the contribution of annihilations taking place in the supporting foil. In order to test our apparatus we have compared the results obtained in Au and in intrinsic Ge with those recently given in the literature. It was found that in these elements the main part of the positrons annihilates with a single lifetime. In Table I our lifetimes are compared with those given by WEISBERG and BERKO ⁽¹⁰⁾ for Ge and BERTOLACCINI and ZAPPA ⁽⁹⁾ for Au.

The agreement is satisfactory: slight discrepancies are contained in some percent.

TABLE I. - Mean lives of positrons in Ge and Au: comparison between our values and those in the literature. ($\tau \cdot 10^{10}$ s.)

	Our values	Literature
Ge	2.32 ± 0.08 (Int.)	2.26 ± 0.05 (Int.) 2.27 ± 0.07 (N doped)
Au	2.07 ± 0.08	1.91 ± 0.03 2.00 ± 0.05

Owing to the fact that metal hydrides react very strongly with water, the preparation of the specimens was carried out in inert atmosphere and all measurements were taken under vacuum. Multicrystalline analytical reagent-grade chemical specimens were used. It is known that, apart from «tails» of very low intensity, the decay features of the positrons are considerably insensitive to small quantities of impurities and are identical for powder and for single crystal specimens. These conclusions were evidenced for LiH in our previous paper ⁽⁸⁾.

3. - Results.

For all investigated compounds a complex annihilation spectrum was observed; at least two decay components I_1 and I_2 with comparable intensities

⁽¹⁰⁾ H. WEISBERG and S. BERKO: *Phys. Rev.*, **154**, 249 (1967).

I_1 and I_2 were separated. A typical example was KH whose spectrum is illustrated in Fig. 1: the two lifetimes are clearly separated. In several cases (CaH_2 , SrH_2 , BaH_2 and LiH) a third component I_3 with lifetime of some 10^{-9} s and very feeble intensity is found. In Fig. 2 the long «tail» in the SrH_2 spectrum is well in evidence. No comments are made in this paper about this component because we have already pointed out that values of I_3 and I_3 are not reproducible, for example in LiH (*).

All results are summarized in Table II.

It has been impossible to investigate RbH and CsH because they are not commercially available with a sufficient degree of purity. For each compound several specimens have been investigated: apart for the I_3 component in LiH , we have not found lack of reproducibility. In every case values reported in the Table are the arithmetic mean values among all measurements and there was no measurement leading to a result which is not included within the errors given in the Table.

In the last column the molecular densities of various compounds are reported.

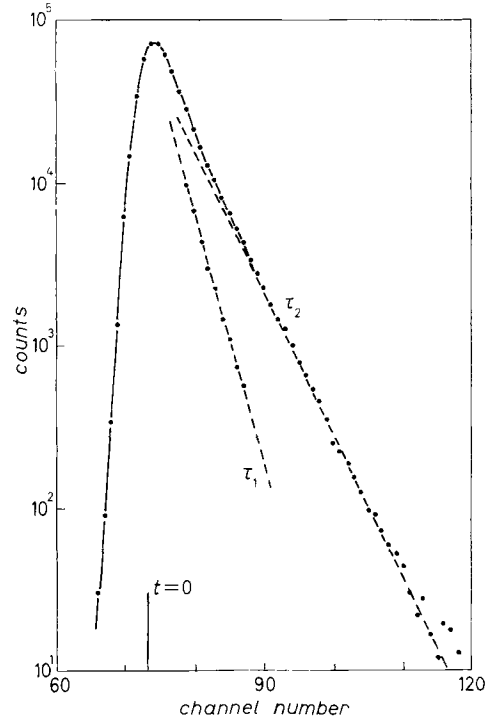


Fig. 1. — Delayed-coincidence spectrum for KH. 1 channel = $1.06 \cdot 10^{-10}$ s, $\tau_1 = 2.94 \cdot 10^{-10}$ s, $\tau_2 = 5.22 \cdot 10^{-10}$ s.

TABLE II. — Mean lives and intensities of positrons in metal hydrides. In the last column the molecular densities of various compounds are reported.

	$\tau_1 \cdot 10^{10}$ s	I_1 (%)	$\tau_2 \cdot 10^{10}$ s	I_2 (%)	$\tau_3 \cdot 10^9$ s	I_3 (%)	$n \cdot 10^{-22}$
LiH	1.75 ± 0.10	28 ± 5	3.20 ± 0.15	65 ± 10	$0.74 \div 1.45$	$2 \div 8$	5.88
NaH	2.44 ± 0.15	21 ± 5	4.13 ± 0.20	54 ± 5			3.41
KH	2.81 ± 0.13	33 ± 2	5.29 ± 0.15	56 ± 2			2.14
MgH_2	2.54 ± 0.15	68 ± 5	4.90 ± 0.20	17 ± 3			3.24
CaH_2	2.52 ± 0.20	73 ± 5	6.14 ± 0.25	11 ± 2	4.74 ± 0.10	1.2 ± 0.4	2.72
SrH_2	2.89 ± 0.15	52 ± 6	6.78 ± 0.20	33 ± 5	5.31 ± 0.25	5.6 ± 1.0	2.19
BaH_2	3.19 ± 0.10	81 ± 4	7.85 ± 0.40	10 ± 1	4.32 ± 0.20	2.4 ± 0.3	1.79
TiH_2	1.40 ± 0.15	52 ± 5	3.37 ± 0.10	31 ± 5			4.58
ZrH_2	1.80 ± 0.15	57 ± 8	3.71 ± 0.20	37 ± 5			3.65

The numbers of molecules for cm^3 are evaluated from X-ray data ⁽¹¹⁾ and are found consistent with values obtained by means of pycnometric determinations when these are available. The lifetimes τ_1 and τ_2 for alkali-metal and alkaline-earth hydrides are found to vary in a regular way with molecular

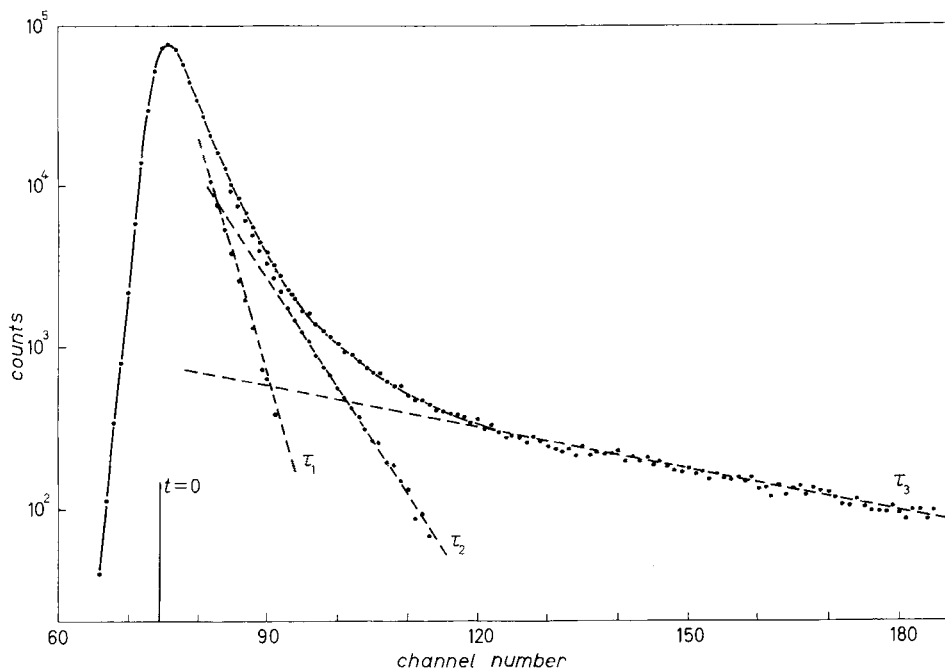


Fig. 2. - Delayed-coincidence spectrum for SrH_2 . 1 channel = $1.06 \cdot 10^{-10}$ s, $\tau_1 = 3.03 \cdot 10^{-10}$ s, $\tau_2 = 6.91 \cdot 10^{-10}$ s, $\tau_3 = 5.31 \cdot 10^{-9}$ s.

densities. This is better illustrated in Fig. 3 for alkali metal hydrides and in Fig. 4 for alkaline-earth hydrides where we plotted the annihilation rates Γ_1 and Γ_2 (the reciprocals of τ_1 and τ_2) against molecular densities.

It is difficult from these graphs to draw definite conclusions about the dependence of Γ_1 and Γ_2 from n , but in a crude approximation we may say that the annihilation rates linearly increase with molecular densities. Also we have extrapolated to very low densities, and particularly to $n = 0$, this linear behaviour. Values at $n = 0$ are clearly finite values and correspond to

⁽¹¹⁾ G. LIBOWITZ: *The Solid-State Chemistry of Binary Metal Hydrides* (New York, 1965).

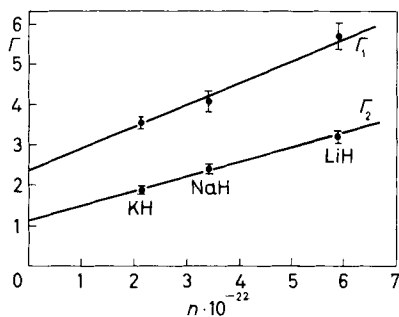


Fig. 3. - Plot of the annihilation rates Γ_1 and Γ_2 against molecular density n for alkali metal hydrides.

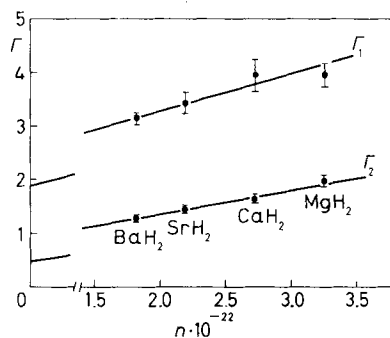


Fig. 4. - Plot of the annihilation rates Γ_1 and Γ_2 against molecular density n for alkaline-earth hydrides.

lifetimes of $(4.26 \pm 0.20) \cdot 10^{-10}$ s and $(8.70 \pm 0.6) \cdot 10^{-10}$ s for monovalent hydrides and to $(5.20 \pm 0.30) \cdot 10^{-10}$ s and $(2.15 \pm 0.35) \cdot 10^{-9}$ s for divalent hydrides.

4. - Discussion.

It is reasonable to assume that the annihilation process of the positron in ionic crystals mainly takes place with the electrons of the negative ions and more precisely, with the electrons in the valence band. This is suggested by simple considerations about Coulomb interaction and electronic polarizability, and is sufficiently confirmed by angular correlation (2) and lifetime (4,5) experiments in alkali halides. Similar conclusions can be drawn for metal hydrides by having in mind the angular correlation measurements (3) and the present experimental results. Some doubts may arise by observing that the low electronegativity difference between metal and hydrogen atoms seems to indicate a low degree of ionicity in the bond. The electronegativity difference varies from 1.0 (MgH₂) to 1.4 (CsH) in metal hydrides and from 1.5 (LiI) to 3.3 (CsF) in alkali halides. However it should be emphasized that the electronegativity difference is by no means a precise definition of the percentage of ionic character in a chemical bond. For example, according to PAULING (12), an electronegativity difference of 1.1 as in LiH, corresponds to 26 % ionic character for the chemical bond between lithium and hydrogen. However a different evaluation (13) of the relative partial charge in hydrogen atom gives -0.49

(12) L. PAULING: *The Nature of the Chemical Bond* (Ithaca, N. Y., 1960).

(13) R. T. SANDERSON: *Chemical Periodicity* (New York, 1964).

in units of electron charge. Finally recent diffraction investigations ⁽¹⁴⁾ and theoretical quantum mechanical calculations ⁽¹⁵⁾ indicate that the degree of electron transfer from lithium to hydrogen is in the range of 0.8 to 1 electrons, thus indicating a strong ionic bond.

GOL'DANSKII *et al.* ^(6,16) made a first attempt to explain the annihilation features of the positron in metal hydrides by supposing the positron interacting with a single H^- ion thus forming the system H^-e^+ . They considered the system in the free space and used the Hartree-Fock self-consistent method for calculating energy levels and electron and positron wave functions. They showed that the binding energy of the positron with H^- is equal to several eV for both the ground state and the first excited states, that is bound states are possible. Moreover they calculated the annihilation rates of the positron for different $(1s^2) nl$ configurations, and showed that the possibility of observing several annihilation rates coming from various excited states of the positron is indeed confirmed by the fact that the probability of capture of thermalized positrons is much larger for excited states than for the ground states, while the radiative transition rates between various levels are comparable with the annihilation rates.

In view of our results, the crude application of the Gol'danskii model to metal hydrides is not realistic:

1) The system H^-e^+ in the free space leads to lifetimes identical for all monovalent hydrides. This is clearly against the experimental results that Γ_1 and Γ_2 increase with molecular densities.

2) The size of the H^-e^+ bound system is considerably greater than the distance between nearest H-H neighbours in real lattices ^(6,16). This shows that the interactions with other neighbours H^- cannot be neglected.

3) Following FERREL ⁽¹⁾ we may suppose that the effect of the surrounding ions is to raise the positron energy by the Madelung term. If c is one-half the inter-atomic spacing and a the radius of the first Bohr orbit, the Madelung energy is $1.74(a/c)$ ryd for cubic crystals; this is of the same order as the binding energy to an isolated H^- ion, that is 4.57 eV for the ground state, and makes questionable if the binding to a single H^- ion is energetically favourable.

Only for sufficiently low values of n the minimum distance between H^- ions in the lattice becomes greater than the size of the H^-e^+ system. The Gol'danskii

⁽¹⁴⁾ R. S. CALDER, W. COCHRAN, D. GRIFFITHS and R. D. LOWDE: *Journ. Phys. Chem. Solids*, **23**, 621 (1962).

⁽¹⁵⁾ H. SHULL: *Journ. Appl. Phys.*, **33**, 292 (1962).

⁽¹⁶⁾ A. V. IVANOVNA and E. P. PROKOP'EV: *Sov. Phys. JETP*, **21**, 771 (1965).

model seems therefore realistic only in the limit of very low molecular densities and particularly for $n = 0$. The reciprocal of our extrapolated Γ_1 and Γ_2 values at $n = 0$ (see Fig. 3), that is $(4.26 \pm 0.20) \cdot 10^{-10}$ s and $(8.70 \pm 0.60) \cdot 10^{-10}$ s, should have the meaning of the lifetimes for the positron bound to a single H^- ion in the free space and should directly be compared with the lifetimes of $2.84 \cdot 10^{-10}$ s and $12.7 \cdot 10^{-10}$ s calculated in ref. (6,16). The disagreement is perhaps not serious if one has in mind that the calculated values are mean values over several excited positron levels.

At higher values of molecular density, as we have already pointed out, the positron should interact with several H^- ions and one expects an increase of Γ_1 and Γ_2 with molecular density, according to the experimental result. Thus calculations like that of BRANDT *et al.* (?), involving the positron interacting with the whole crystal, should be more realistic even if they lead to a single lifetime: this difficulty could be removed by considering also excited positron bands and by ascribing the different rates Γ_1 and Γ_2 to annihilations from different positron bands.

Considerations like these can be applied to alkaline-earth hydrides with the only difference that annihilations from $H_2^- e^+$ bound system must be considered now in the low- n limit.

Finally we have measured positron lifetimes in two other divalent hydrides, *i.e.* TiH_2 and ZrH_2 ; the results are reported in the last two rows of Table II and we observe that positron lifetimes in such compounds are considerably (higher) than lifetimes in alkaline-earth hydrides. In other words, if we plot the annihilation rates Γ_1 and Γ_2 for TiH_2 and ZrH_2 against molecular densities we find points that lie considerably above the straight lines of Fig. 4. This is probably due to the nature of the chemical bonding of these compounds, which seems to consist of a mixture of ionic and metallic bonds. More precisely the agreement between measured inter-atomic distances and the sum of the ionic radii indicates ionic bond whereas the electrical conductivity of metallic type exhibited by these compounds indicates electrons in the conduction band (11). Probably it is the contribution of these highly polarizable conduction electrons to the annihilation process that causes the observed relevant decrease in positron lifetimes.

Some conclusions can be drawn from this paper. The observed positron lifetimes in metal hydrides together with considerations about the size of the $H^- e^+$ system advise against the crude application of the Gol'danskii model. This model seems realistic only in the limit of very low molecular densities, whereas it is a useful model for a tentative explanation of the multiplicity of the observed annihilation rates. It is to be noted here that molecular densities sufficiently low in order to ensure the reality of the application of the Gol'danskii model are not experimentally reproducible. In fact these values of n are characteristic of the gaseous phase, whereas metallic hydrides do not

exist in this phase, and in general the annihilation features of the positron in gaseous media are very different from what is observed in solids, because of positronium formation.

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We are grateful to Prof. R. FIESCHI for helpful discussions.

RIASSUNTO

Le vite medie dei positroni negli idruri metallici commercialmente disponibili sono state misurate mediante un sistema di coincidenza ritardata avente una risoluzione di 0.37 ns (FWHM). L'annichilamento è risultato essere complesso con due componenti di decadimento esponenziali aventi intensità paragonabili. Sia negli idruri dei metalli alcalini che in quelli dei metalli alcalino terrosi si è trovato che le probabilità di annichilimento Γ_1 e Γ_2 aumentano con le densità molecolari. I risultati sperimentali sono contrari alla applicazione del semplice modello di decadimento del positone legato ad un singolo ione H^- . Questo modello sembra plausibile solo nel limite di densità molecolari molto basse. Le vite medie dei positroni in TiH_2 e ZrH_2 sono risultate considerevolmente più brevi di quelle riscontrate negli idruri dei metalli alcalino terrosi: ciò è probabilmente dovuto al contributo degli elettroni di conduzione.

Времена жизни позитронов в металлических гидридах.

Резюме (*). — Были измерены кривые распада позитронов в имеющихся с продаже металлических гидридах, используя запаздывающую систему совпадений с 0.37 нсек (FWHM) мгновенным временным разрешением. Найдено подтверждение, что аннигиляция является сложной, с двумя экспоненциальными распадами, со сравнимыми интенсивностями. В щелочных металлических гидридах, подобных щелочно-земельным гидридам, получено, что скорости аннигиляции Γ_1 и Γ_2 увеличиваются с увеличением молекулярных плотностей. Экспериментальные результаты противоречат непосредственному применению простой модели распада, которая рассматривает позитрон, связанным с отдельным ионом H^- в решетке. Эта модель оказывается реалистичной только в пределе очень низких молекулярных плотностей. Получено, что времена жизни позитронов в TiH_2 и ZrH_2 значительно короче, чем времена жизни в двухвалентных щелочно-земельных гидридах, что, вероятно, обусловлено наличием сильно поляризуемых электронов в зоне проводимости.

(*) Переведено редакцией.