

# The influence of hydrogen concentration on positron lifetime and electrical resistivity in vanadium-hydrogen systems

Ryszard Pietrzak,  
Roman Szatanik

**Abstract.** Positron lifetime spectra and electrical resistivity of the vanadium-hydrogen systems with hydrogen concentration ranging from 0 to 0.29 at.H/at.V have been investigated. The range of hydrogen concentrations under investigation included the single  $\alpha$  phase and a mixture of the  $\alpha$  and  $\beta$  phases of V-H system. The registered positron lifetime spectra were analysed by decomposition into two components. A distinct change in the annihilation parameters has been found after exceeding the boundary concentration of hydrogen in vanadium corresponding to the phase transition  $\alpha \rightarrow (\alpha + \beta)$ . Correlation of changes in the parameters of the positron lifetime spectrum and in the electrical resistivity resulting from the changes in hydrogen concentration, has been revealed.

**Key words:** positron lifetime • resistivity • V-H system • annihilation parameters

## Introduction

For many years, the phenomenon of positron annihilation has been recognized as a method for investigations of the electronic structure as well as a very sensitive technique to study the formation and kinetics of defects in solids. The first investigations of positron annihilation in metal-hydrogen systems were carried out with the use of the method of angular correlation of annihilation quanta and their interpretation concerned the problem of the state of ionization of hydrogen absorbed in the metal. The investigations proved that for the systems: Pd-H, Ta-H, Zr-H, Ti-H, Nb-H, Ce-H the FWHM (full width at half maximum) of the angular correlations curves is greater than that for pure metals. The results were interpreted for the benefit of the so-called proton model, in which it is assumed that hydrogen, introduced into these metals, delivers its electron to the conduction band, and locates itself in interstitial holes as a proton repelling positrons from its neighborhood. On the other hand, decrease of the FWHM of the angular correlations curves, observed for La-H and Ca-H systems, was interpreted to the benefit of the anion model, which assumes that hydrogen, being in the crystalline lattice, connects an electron from  $s$  band of the metal and becomes a negative ion. However, the experimental results as well as the theoretical investigations conducted with reference to the electron structure proved that such a simple interpretation of results obtained by means of the method of angular correlation of annihilation quanta is wrong.

Similarly, understanding of the effect of crystal lattice defects on the phenomenon of positron an-

R. Pietrzak, R. Szatanik<sup>✉</sup>  
Institute of Physics,  
Opole University,  
48 Oleska Str., 45-052 Opole, Poland,  
Tel.: +48 77 452 7250, Fax: +48 77 452 7290,  
E-mail: szata@uni.opole.pl

Received: 8 June 2009  
Accepted: 28 September 2009

nihilation in hydrogen-metal systems brought about another possibility of interpretation of the changes in the angular correlations curves due to penetration of hydrogen into metal [10]. For investigations of the kinetics of formation various types of defects and their mutual interaction, two other annihilation techniques: investigations of Doppler-broadening of the annihilation line and measurements of the positron lifetime spectra are particularly useful. The first of them was applied to study the vanadium-hydrogen system and the investigation revealed, among others, that hydrogen in vanadium forms new defects, i.e. vacancies, dislocations and voids. Creation of these defects has been confirmed by the dependence of the so-called parameter  $S$ , defined as ratio of the central part to the total area under the annihilation line, on the temperature and hydrogen concentration. As it was proved in [2–4], hydrogen locates very easily in this type of defects or in their close vicinity.

On the other hand, changes in the electron structure of V-H system can be investigated by means of the above-mentioned techniques only at low hydrogen concentrations or at high temperatures. Increase in the hydrogen concentration in vanadium does not only change its electron and defect structures, but also leads to the appearance of areas of hydride phase, in which parameters of the crystalline structure are different, and the hydrogen atoms are chemically bonded with metal atoms.

We do not know any analyses of positron lifetime spectra in vanadium-hydrogen systems as far as phase transitions are concerned. It is well known that lattice vacancies play an important role in activating phase transition of order-disorder, and the process of structural ordering is controlled by their diffusion. Increase in the hydrogen concentration in vanadium results in the appearance of disordered areas, and after reaching some critical concentration (at a given temperature) – in the formation of ordered phase. Mantl and Triftshauer [7] found an increase in the intensity of the defect component  $I_V$  in the positron lifetime spectrum along with a rise in the hydrogen concentration in disordered phases and its decrease during the transition into the ordered state.

The main goal of the present work is to determine and analyze the positron lifetime spectra in the V-H system, with hydrogen concentrations ranging from 0 to 0.29 at.H/at.V. At room temperature, this range of concentrations includes phase  $\alpha$  and a mixture of  $\alpha$  and  $\beta$  phases. According to the phase diagram (Fig. 1) [1], at room temperature, the  $\alpha$  phase (solid solution of hydrogen in the bcc vanadium lattice) is stable up to the concentration of  $C_H \sim 0.022$  at.H/at.V. In this phase, hydrogen is randomly distributed in T-type interstices (tetrahedral sites). The energy of trapping the hydrogen atoms at these sites amounts to 375 meV. Above this concentration, up to about 0.45 at.H/at.V, the system is a mixture of phases  $\alpha$  and  $\beta$ , with a growing share of the latter. Phase  $\beta$  forms, as a result of cooperative influence of the metal lattice on hydrogen atoms, shifting them to the O-type interstices (octahedral sites) in the  $O_z$  direction with simultaneous distortion of the elementary cell. This results in the formation of a bct structure ( $c/a > 1.1$ ), in which hydrogen atoms are randomly distributed

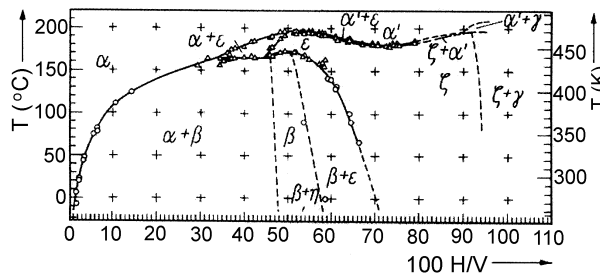


Fig. 1. Phase diagram of the V-H system [1].

distributed in T-type interstices. On the other hand, in  $V_2H$  and  $V_3H$  hydrides, hydrogen is distributed in the lattice in an ordered way.

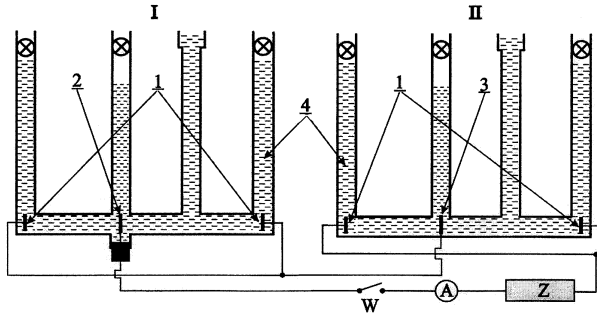
The changes in the electrical resistivity of vanadium due to the electrolytic hydrogenation have been investigated, too. Mantl and Triftshauer [7], reported on a similarity of changes in the electric resistance and the so-called lineshape parameter of the Doppler-broadening line during annealing of electron-irradiated copper. Application of both, the positron lifetime and electrical resistivity, techniques may be very helpful in interpretation of the obtained results and understanding the processes occurring during the electrolytic hydrogenation of vanadium.

### Preparation of the samples

The investigated samples with dimensions of  $10 \times 10 \times 0.5$  mm<sup>3</sup> were prepared from a vanadium foil of 99.98% purity. The surface of samples was cleaned with methanol. Next, the samples were tempered for 8 h in vacuum ( $p < 10^{-5}$  torr) at 1123 K and then slowly cooled to room temperature during 12 h. The samples prepared in this way still contain a certain number of over-the-equilibrium defects which appear during the production of the foil (solidification and cold-rolling). This was confirmed by subsequent annihilation research. The hydrogen penetrating into such sample fills up not only the tetrahedral sites, but also the over-the-equilibrium defects. The number of the defects filled with hydrogen atoms depends on the concentration of hydrogen in the sample [2, 3].

After tempering and cooling, the samples were hydrogenated electrolytically in a Hoffmann apparatus. The hydrogenation procedure will be described in the next paragraph. The higher and higher concentration of hydrogen in the samples was obtained through their additional hydrogenation until they reached the required concentration. The density of the hydrogenation current in 0.1 N water solution of  $H_2SO_4$  amounted to  $2 \times 10^4$  A/m<sup>2</sup>. The method used for determining hydrogen concentration in the samples can be found in [8]. After each hydrogenation, but before measurement of positrons lifetimes, the samples were seasoned at room temperature for 5 days. This is an ample time to level the hydrogen concentration within the whole volume of the samples (the time of diffusion annealing, counted from the formula  $d^2/D$ , where  $d$  – thickness of the sample, and  $D$  – diffusion coefficient, is only 50 s). The maximum concentration of hydrogen in the sample, possible to obtain under these conditions, is 0.29 at.H/at.V.

The positrons lifetimes in the hydrogenated samples were measured using a fast-slow spectrometer with the



**Fig. 2.** Experimental setup for the sample hydrogenation: I – Hoffmann apparatus with a sample; II – reference Hoffmann apparatus; 1 – Pt anodes; 2 – investigated sample as the cathode; 3 – Pt cathode; 4 – electrolyte; Z – DC feeder; W – switch; A – amperometer.

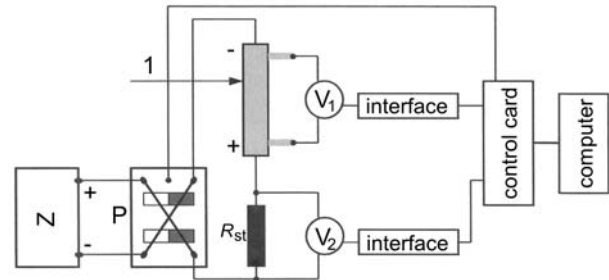
resolution of 240 ps, equipped with BaF<sub>2</sub> scintillators. The measurements were taken in the “sandwich” geometry: the <sup>22</sup>Na positron source was placed between two vanadium samples hydrogenated up to the same concentration. The total number of counts in each of the registered positron lifetime spectra was greater than 10<sup>6</sup>, and the share of annihilation in the source remained within 4–6%.

### Hydrogenation of the samples

Hydrogenation of the samples up to the required hydrogen concentration was carried out in a Hoffmann apparatus of our own construction (Fig. 2), connected in series with a reference conventional Hoffmann apparatus, necessary for determination of hydrogen content in the hydrogenated sample. In the first apparatus, the cathode was the hydrogenated sample, whereas in the reference apparatus the cathode was a platinum sheet, which does not absorb the hydrogen. The anodes, in both apparatus, were flat platinum sheets. Both the apparatus were filled with 0.1 N water solution of sulphuric acid. In order to ensure uniform hydrogenation of both surfaces of the examined samples, each apparatus contained two anodes. The sizes of the platinum anodes were much larger than those of the cathodes, what ensured an uniform distribution of concentration over the whole surface of the samples. In the apparatus with the investigated sample as the cathode, the hydrogen produced by the electrolysis was partly absorbed in the sample, the remaining part was evolved over the free surface of the electrolyte. In the reference apparatus hydrogen was not absorbed by the platinum cathode and the whole of it was evolved over the electrolyte.

### Measurements of the electric resistance

The measurements of the electric resistance of the investigated samples were performed with the use of a measuring apparatus, whose scheme is shown in Fig. 3. Direct current of  $I = 0.5$  A from a stabilizing feeder was passed through the sample. In order to eliminate errors resulting from the appearance of the so-called “parasite” contact potentials between the sample and measurement electrodes, measurements of voltage  $U$ , on the ends of the sample, and voltage  $U_{st}$ , on the standard resistor  $R_{st}$ ,



**Fig. 3.** Block scheme of resistivity measurement device: Z – DC feeder; P – electronic switch; 1 – investigated sample;  $R_{st}$  – standard resistor;  $V_1$ ,  $V_2$  – microvoltmeters.

were taken many times at alternating directions of the current. The direction of the current was changed with the use of an electronic computer-controlled switch. Voltages  $U$  and  $U_{st}$  were measured by means of a digital voltmeter with an accuracy of up to 0.001mV. Since the intensity of the current passing through the sample and the standard resistor is

$$(1) \quad I = U_{st} / R_{st}$$

the resistance of the investigated sample is equal to

$$(2) \quad R = R_{st} \cdot (U / U_{st})$$

The values of voltages  $U$  and  $U_{st}$  were registered by a computer which then calculated the resistance  $R$ . The resistivity of the investigated sample was calculated from the second Ohm’s law:

$$(3) \quad \rho = R \cdot (S_{cs} / l)$$

where  $S_{cs}$  is the area of the surface of the cross-section of the sample,  $l$  is the real length of the sample corresponding to the given external stress. In the calculations of the resistivity of the samples, neither changes in their thickness nor those in the width accompanying uniaxial stretching, were taken into consideration. The error of the calculated value of the resistivity, resulting from this simplification, is negligibly small.

### Results of the investigation and their interpretation

As it was mentioned before, the paper presents the results of our investigations of the positron lifetime spectra and electrical resistivity of vanadium and vanadium-hydrogen systems, with hydrogen concentrations ranging from 0.011 to 0.29 at.H/at.V.

According to Matthiessen’s rule, the resistivity  $\rho$  of V-H system, is a sum of the resistivities resulting from scattering of current carriers on: phonons of host metal –  $\rho_0$ , interstitial H atoms –  $\rho_H$ , and defects appearing during the electrolytic hydrogenation –  $\rho_d$ , i.e.:

$$(4) \quad \rho = \rho_0 + \rho_H + \rho_d$$

Let us assume that the resistivity  $\rho_H$  is directly proportional to the concentration of interstitial hydrogen:  $\rho_H = kC_H$ , and the resistivity  $\rho_d$  is directly proportional to the concentration of defects:  $\rho_d = aC_d$ . Let us accept, additionally, that within certain range of hydrogen con-

centrations in the sample, the concentration of newly formed defects  $C_d$  is proportional to the concentration of hydrogen:  $C_d = bC_H$ , ( $k, a, b$  – proportionality coefficients). Then:

$$(5) \quad \rho = \rho_0 + (k + ab)C_H$$

and the expression describing the relative change in resistivity as a function of the hydrogen concentration  $C_H$  takes the form:

$$(6) \quad \frac{\Delta\rho}{\rho_0} = \left( \frac{k + ab}{\rho_0} \right) C_H + 1$$

Thus, when the expression  $[(k + ab) / \rho_0]$  does not depend on the concentration of hydrogen, one can expect a linear dependence of relative changes in the resistivity on  $C_H$ . Yet, when one of the mechanisms of electron scattering is changed, the slope of the graph of the dependence  $(\Delta\rho / \rho_0) = f(C_H)$  must be changed, too. As it will be seen in the figures presented further in the paper, within the investigated range of hydrogen concentrations in vanadium one can distinguish four ranges with different slopes of the dependence  $(\Delta\rho / \rho_0) = f(C_H)$ , and within these ranges of hydrogen concentrations, different kinetics of changes in annihilation parameters can be observed as well.

The experimentally obtained positron annihilation spectra were analysed with the use of LT program [6], assuming the appearance of one, two and three components in the lifetimes spectrum. For all of the analysed spectra, the best fitting of experimental data ( $\chi^2$  test) was achieved when decomposing the spectrum into two components with two different mean values of positron lifetime ( $\tau_1$  and  $\tau_2$ ) and different relative intensities  $I_1$  and  $I_2$ , respectively.

The obtained results cannot, however, be interpreted in the frame of a simple two-state annihilation model which assumes annihilations from the free state and only in one type of defects. In such a model, the short-living component of the positron lifetime spectrum should apply a value lower than the positron lifetime in the free state. From the data presented in [10], it follows that for vanadium this value amounts to 138 ps, whereas the value of component  $\tau_1$  obtained in the present study is equal to 149 ps. The value of positrons lifetime in vacancies, as determined in [10] amounts to 191 ps, while the value of the second component of the positron lifetimes spectrum in vanadium ( $\tau_2$ ) determined by us is equal to 364 ps. This means that the experimentally determined component  $\tau_1$  is composed of two lifetimes: in the free state and in defects of small sizes of vacancy type, (dislocations or in new vacancies formed by hydrogen [5]) further referred to as Type I defects. On the other hand, component  $\tau_2$  should be interpreted as a positron lifetime in multivacancy clusters or on the boundaries of the phases  $\alpha$  and  $\beta$  (referred to as Type II defects). As it was proved in [9], the value of  $\tau_2$  rises along with increasing number of vacancies in the cluster, in which positrons annihilate.

The functional dependences of the relative changes in the electrical resistivity, selected annihilation parameters ( $\tau_1$  and  $\tau_2$ ) and intensity of long-lived component of positron lifetime spectrum ( $I_2$ ) on hydrogen concentration in vanadium are presented in Figs. 4, 5 and 6, re-

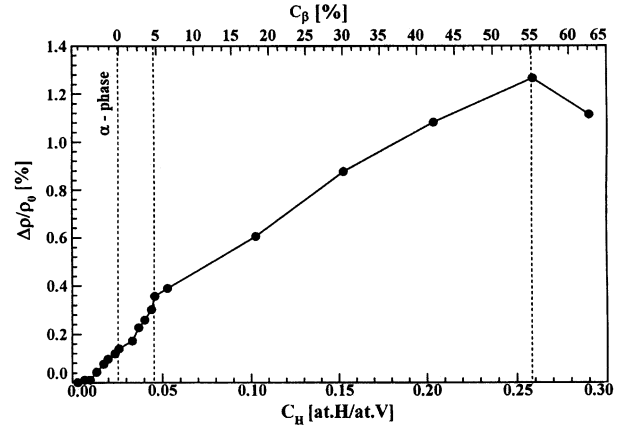


Fig. 4. Dependence of the relative changes in the electrical resistivity of V-H system on the hydrogen concentration.

spectively. A comparison of Figs. 4–6 indicates that the whole examined range of concentrations can be divided into 4 intervals with different trends in changes in the measured parameters. In the interval of concentrations ranging from 0 to 0.025 at.H/at.V (pure phase  $\alpha$ ), all of the determined annihilation parameters within the limits of error remain unchanged, while a small increase in the relative resistivity is observed.

It cannot be proved that the hydrogen absorbed by vanadium creates new defects in phase  $\alpha$ , e.g. vacancies with two hydrogen atoms – as it is claimed in [3] for phase  $\alpha$ , in the Nb-H system, although in

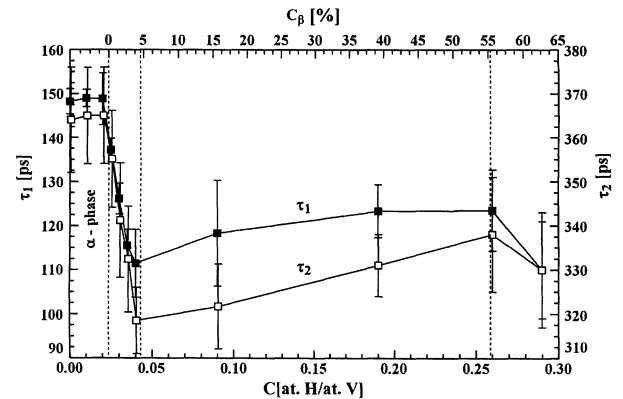


Fig. 5. Dependence of the lifetimes  $\tau_1$  and  $\tau_2$  on the hydrogen concentration in V-H system.

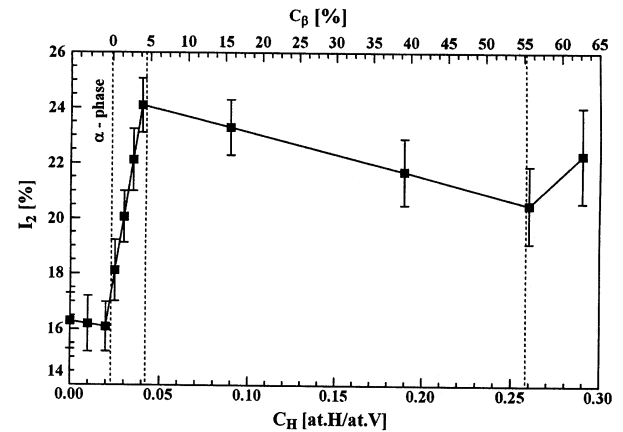


Fig. 6. Dependence of the intensity of the long-lived component of positron lifetime spectrum  $I_2$  on the hydrogen concentration in V-H system.

**Table 1.** Positron lifetime parameters for  $\alpha$  and  $\beta$  phases in the V-H system

Parameter	$\beta$ -phase	$\alpha$ -phase
$\tau_1$ (ps)	115	149
$\tau_2$ (ps)	355	366
$I_2$ (%)	17	16.5

many respects V and Nb have similar properties. Most probably instead of forming new defects, hydrogen occupies circumvacancy locations in the already existing over-the-equilibrium defects. It can be thought, that within this range of concentrations the defect structure of vanadium remains unchanged, and the observed increase in the electrical resistivity is induced by filling the electron holes in the conduction band of vanadium by electrons released by interstitial hydrogen.

An inspection of Figs. 4–6 shows, that new mechanisms of positrons trapping and electrons scattering appear as soon as the first regions of phase  $\beta$  are formed. Within the range of hydrogen concentrations from 0.025 to 0.04 at.H/at.V a distinct decrease in both the positron lifetimes (Fig. 5), as well as an increase in the intensity of component  $I_2$  of the spectrum (Fig. 6) is observed. It may be believed that this is connected with disintegration of Type II defects into smaller ones. Beyond concentration  $C_H > 0.04$  at.H/at.V one can observe linear changes in the annihilation parameters of the system in dependence on hydrogen concentration (and that of the amount of phase  $\beta$ ). Thus, the values of lifetimes  $\tau_1$  and  $\tau_2$  rise along with increase in the relative amount of phase  $\beta$ , whereas the value of  $I_2$  decreases. The approximation of the dependences  $\tau_1$ ,  $\tau_2$  and  $I_2$  to the concentration corresponding to the uniform phase  $\beta$  (i.e. 100% of  $\beta$  phase) yields values of these parameters presented in Table 1 (for comparison, the values of the same parameters in phase  $\alpha$  are also included in the table).

On the other hand, the rapid growth in the electrical resistance, accompanying the rise in the hydrogen concentration in vanadium is, most probably, connected with the rise in the probability of scattering of current carriers in the microvolumes containing phase  $\beta$ . Within the range of concentrations from 0.04 to 0.26 at.H/at.V one of the scattering mechanisms occurring at lower concentrations of phase  $\beta$  disappears, which manifests itself by lowering the slope of the  $(\Delta\rho/\rho_0) = f(C_H)$  dependence. We believe that new lattice defects cease to form.

Under the applied conditions of electrolytic hydrogenation, it was impossible to reach hydrogen concentrations higher than 0.29 at.H/at.V. At this concentration, the electric resistance, as well as all of the discussed annihilation parameters decrease their values. This is probably connected with a decrease in the concentration of defects or with different filling of them by hydrogen atoms. As suggested by Čížek *et al.* [2], in Nb hydrogen atoms may occupy two circumvacancy positions. Since V-H and Nb-H systems show many structural and electron-related similarities, such a possibility seems to be very probable for V-H systems, too. It is also probable that hydrogen begins to fill the octahedral holes.

## Conclusions

The results of the present study may be summarized as follows:

- changes in the annihilation parameters and in the electrical resistivity induced by a rise in the hydrogen concentration due to electrolytic hydrogenation of vanadium are mutually correlated;
- the registered spectra of positron lifetime can be decomposed into two components with good accuracy. The short-lived component ( $\tau_1$ ) could be ascribed to annihilation in the free state and in defects of small sizes, whereas component  $\tau_2$  is connected with annihilation of positrons in multivacancy clusters;
- within the limits of experimental error the annihilation parameters in the phase  $\alpha$  of the V-H system do not depend on hydrogen concentration, they change suddenly on passing to the mixed ( $\alpha + \beta$ ) phase region;
- in the two-phase region of low hydrogen concentration (up to 0.04 at.H/at.V) a rapid decrease in concentration of defects and a drop in the sizes of multivacancy clusters is observed;
- in the mixed ( $\alpha + \beta$ ) phase region, above the concentration of 0.04 at.H/at.V, the positrons lifetimes  $\tau_1$  and  $\tau_2$  increase, and the intensity of the long-lived component  $I_2$  decreases with increasing hydrogen concentration.

## References

1. Bambikidis G (ed) (1981) Metal hydrides. NATO ASI Series B, Physics, Vol. 76. Plenum Press, New York, p 5
2. Čížek J, Procházka I, Becvar F *et al.* (2004) Hydrogen-induced defects in bulk niobium. *Phys Rev B* 69:224106–224119
3. Čížek J, Procházka I, Brauer G *et al.* (2007) Hydrogen interaction with vacancies in electron irradiated niobium. *Acta Phys Pol A* 113:1293–1300
4. Hasegawa M, Koike S, Hirabayashi M, Asano H, Suzuki T (1979) Angular correlation of positron annihilation radiation from single crystals of vanadium-deuter alloys. *J Phys Soc Japan* 46:481–487
5. Hautojärvi P, Huomo H, Puska M, Vehanen A (1985) Vacancy recovery and vacancy-hydrogen interaction in niobium and tantalum studied by positrons. *Phys Rev B* 32:4326–4331
6. Kansy J (1996) Microcomputer program for analysis of positron annihilation lifetime spectra. *Nucl Instrum Methods A* 374:235–244
7. Mantl S, Trifthauser W (1975) Direct evidence for vacancy clustering in electron irradiated copper by positron annihilation. *Phys Rev Lett* 34:1554–1557
8. Pietrzak R, Frączek D, Szatanik R (2009) The influence of external uniaxial stretching on the electromigration and diffusion of hydrogen in iron. *J Phys Chem Solids* 70:588–594
9. Puska M, Nieminen R (1983) Defect spectroscopy with positrons: a general calculational method. *J Phys F: Metal Phys* 13:333–346
10. Seger A (1997) Challenges to positron and positronium physics by material science. *Mater Sci Forum* 1:1–34