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Modelling of free positron states in TiH_x

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Abstract. Electron energy structure, positron spectrum and positron characteristics of α-Ti and α-$TiH_{0.125}$ were calculated. Self-consistent calculations of the band structure were performed by the linear muffin-tin orbital method in the atomic sphere approximation. Modelling has been made on low content of hydrogen into α-Ti with expanded close-packed hexagonal cell inclusive 8 titanium atoms. Variation of sphere radiuses permitted to consider anisotropy and spherical symmetry of potential. Positron potential and positron wave function were calculated on a base of self-consistent electron density. Then positron probability of existence into TiH_x lattice and lifetime were founded. Theoretical calculation indicated a satisfactory agreement of positron characteristics absolute values with the experimental data is achieved but the tendency of values with hydrogen defects increasing is not. The reason of divergence is discussed. On the basis of experimental data and theoretical calculations it was shown that different hydrogen atom states demonstrate the different influence in the lifetime spectra.

1. Introduction

Metals are the most important structural material. In many branch there is actual thread of hydrogen corrosion of metals. Well operation of oil and gas, operation of equipment in chemical and nuclear industry are the most risk because hydrogen and hydrogen containing medium makes up a large share of the working environment. Modification of the physical and mechanical properties of metals and alloy materials by hydrogen is significant problem. The used materials must combine the resistance to high stresses with acceptable high temperature deformation. However hydrogen influence on it strength characteristics depends from material analysis. At the same time visible surface change could be unobserved. But sample even having super difficult configuration requires precise diagnostic which would not destroy construction of sample.

Nondestructive and contactless methods, possibility to measure parameters of samples under different temperatures coupled with fast response to local change of electron density defines positron diagnostics as one of the unique method among traditional analysis of structure of matter. For metals and allows positron annihilation technique reveals the electron momentum distribution and Fermi level energy that largely determines their mechanical, electrical and magnetic properties [1]. Moreover positron spectroscopy is sensitive to define structure, cause and concentration of spots and extended defects, to investigate the disrupt blanket on metals, alloys, semiconductors and ionic crystals [2]. In that case positron annihilation method is useful as for nature and concentration of impurities analysis as for study of electron structure modification because of any factors. Now it is the defect spectroscopy tool. In [3, 4] the annihilation of positrons has been studied by *angular* distribution on

annihilation photons method (ADAP) and lifetime has been measured in metal hydrides. In [5] hydrogen influence on the dynamic of defect formation (crater and crack) in α-titanium has been investigated by sight with scanning microscopy and with average positron lifetime measurement.

Ab initio electron-positron structure and positron characteristics were calculated mainly for metals and alloys which has simple crystal structure. More compound one require improved calculation methods of electron density which is the basis for construction of the positron spectrum. Even less there are first principle calculation of hydrogen-containing compounds. In [6] electron and positron characteristics of tungsten changing with impact of hydrogen and helium were calculated by augmented plane wave method. Quasi-free positron lifetime *ab initio* for titanium hydride (TiH_2) was obtained by [7]. In this work we study influence of the atomic hydrogen on electron structure of titanium and its positron characteristics. Absorbing hydrogen at the standard pressure α-Ti crystal lattice extends, ratio c/a of the hexagonal closely packed (HCP) lattice parameter decreases. Dilution of hydrogen in metal shows uneven distribution from surface to volume. That explains differing degree of destruction of α-Ti on a surface and in a volume. Thus, after 360 minutes electrolytic hydrogenation of titanium samples "the traces of destruction" in the form of increased dislocation concentration were emerged [5]. However the whole crystal fracture within atomic hydrogen $11 \cdot 10^{-5}$ат% H was not observed.

In this paper we calculate electron structure, positron spectrum and positron characteristics of α-Ti and α-$TiH_{0.125}$ and compare them with experimental one. Comparing calculated electron structure results with different models crystal potential of pure titanium and titanium with a hydrogen impurity we try to make more exact the positron annihilation characteristics. An attempt to interpret the thermalized positron behavior in crystal by *ab initio* method was made.

2. Method of calculation

Band structure of metal hydrides was calculated by the self-consistent linear muffin-tin orbital method in the atomic sphere approximation (LMTO-ASA) adjusted for overlap. Ceperley and Alder approximation was used for the exchange-correlation potential [8]. The self-consistency procedure was applied at 90 k-pontes in the irreducible part of the Brillouin zone for HCP lattice. The self-consistency was regarded to have been achieved by the variation energy eigenvalues from iteration to iteration did not exceed 3 mRy and the presser which was calculated at each iteration by Pettifor formula [9] was less than 1 kbar. Wigner–Seitz (WZ) sphere radii were identical and equal to average WZ-radius. The projection of the expanded HCP cell on the XOY plate is in figure 1.

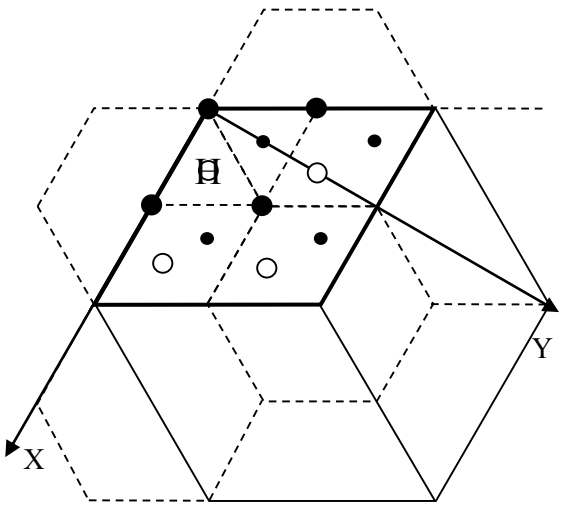

Figure 1. Project of expanded HCP cell to XOY.
● – Ti in z=0 plane,
• – Ti in z=c/2 plane,
○ – E in z= c/4 and z= 3c/4 planes,
H – H-defect in oct-pore (1/4;√3/12;c/4).

Crystal lattice was simulated by repeating hexagonal extended cells which contain 8 titanium atoms (lattice parameter of titanium: a=0.2952 x 2 nm, c=0.4684 nm [10]). Hydrogen atoms placed in octal pore with coordinate (1/4;√3/12;c/4). The others 7 octal pores were filled up empty spheres having zero electron density in order to consider the crystal potential anisotropy. The atoms positions of the expanded cell are in table 1.

Table 1. Coordinates of atoms in expanded cell per unit lattice parameter *a*.

atom	X	Y	Z
Ti	0.000000	0.000000	0.000000
	0.500000	0.000000	0.000000
	-0.25000	0.233020	0.000000
	0.250000	0.433020	0. 000000
	0.000000	0.288680	0.396828
	-0.25000	0.721680	0.396828
	0.250000	0.721680	0.396828
	0.500000	0.288680	0.396828
H	0.250000	0.144340	0.198414
Empty sphere (E)	0.750000	0.144340	0.198414
	0.000000	0.289000	0.198414
	0.500000	0.289000	0.198414
	0.250000	0.144340	0.595242
	0.750000	0.144340	0.595242
	0.000000	0.289000	0.595242
	0.250000	0.289000	0.595242

Used method of electron structure calculation demands to input addition empty spheres because LMTO assumes spherical symmetry of potential within the atomic spheres and zero potential out of spheres. That admission is not true for the most of crystals especially for dielectrics and semi-conductors. However, it could be corrected by putting the additional atomic spheres in void of cell which possess high symmetry enough. Thus we can solve some problems: to decrease the overlap, to increase spherical symmetry of potential, to decrease the volume between the spheres. The calculation of the hydrogenizes titanium in HCP lattice was carried out with two variants of atomic spheres radii which were equal to each other's ($R_{Ti}=R_H=R_E=2.4233$ a.u.) and increased titanium radius ($R_{Ti}=2.8000$ a.u., $R_H=R_E=1.8670$ a.u.).

The positron states problem have been solved on basis of two-component density functional theory [11, 12]. Positron potential and positron wave function were calculated on a base of self-consistent electron density. It was considered the approach of low positron density, positron-electron correlation potential was depending on electron density only and was not perturbed by positron. Using this potential single-particle Schrödinger equation was solved by LMTO-ASA method and positron wave function was found. It was used calculating probability of positron distribution to atomic spheres, annihilation rate and lifetime.

3. Discussion of results

Electron band structure and lower positron band of $TiH_{0.125}$ with equaled atomic sphere radii are in figure 2. Filled levels of the valence band is here only. The presence of hydrogen defect leads to formation of the separated lower band. The Fermy energy is upper and the occupied part of the valence band is increased. There is the band gap. Band structure of α-Ti and $TiH_{0.125}$ is similar in every

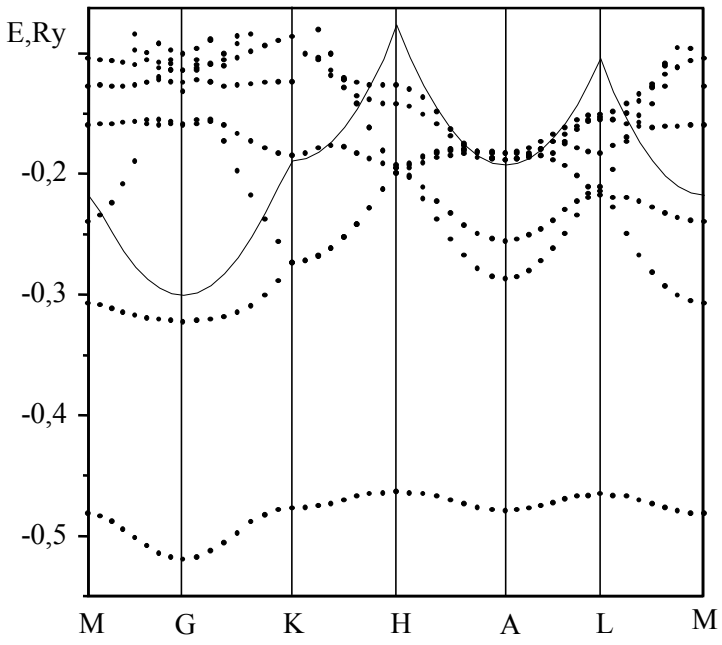

Figure 2. Electron structure (dashed lines) and the lowest energy positron band (solid line) of $TiH_{0.125}$..

respect of α-Zr and $ZrH_{1.5}$ [13]. But numerical and scale of characteristics differs.

The positron band is similar to the lowest valence electron band that agrees well with theoretical representation about quasi-free positron state in solid. Positron energies at G point are -0.200, -0.301 and -0.211 Ry for Ti, $TiH_{0.125}$ (equal atom spheres) and $TiH_{0.125}$(different atom spheres), respectively. Electron band structure and positron band peculiarity is kept when the ratio of the atomic spheres is changed. It should be noted that increasing of the atomic sphere titanium radius and decreasing of the hydrogen and empty spheres radii insignificantly reduces the atom spheres overlap. But the values of characteristics (bottom and width of the valence band, energy values of the symmetrical points) shifted by an amount greater than the accuracy of the calculation. Comparative energy data are in the table 2.

Table 2. Electron band structure values of pure and hydrogenize α-Ti. Fermy energy E_F (Ry), the occupied part of the conduction band E_F-Γ_1 (Ry), terms Γ_1 and Γ_4 (Ry).

α-TiH_x	α-TiH	α-$TiH_{0.125}$	
	R_{Ti} =3.0532 a.u.	R_{Ti}=R_H=R_E=2.4233 a.u.	R_{Ti}=2.8000 a.u.; R_H= R_E=1.8670 a.u.
E_F (Ry)	-0.0526	0.0680	0.0046
E_F-Γ_1 (Ry)	0.4744	0.5978	0.6393
Γ_1 (Ry)	-0.5270	-0.5198	-0.6347
Γ_4 (Ry)	-0.2680	-0.3006	-0.2112

The calculated positron characteristics and experimental the first component of positron lifetime is in table 3. The calculated value of thermalized positron lifetime agrees with the experimental one. However, the calculated trend of lifetime decrease with defects increase in α-titanium disagrees with the experiment [14]. In this connection the band structure and positron lifetime was calculated with

corrected potential. Titanium radius of the atomic sphere was enlarged and hydrogen radii of the atomic spheres were diminished. The radii change significantly affected on the charge redistribution in atoms. The charge increased in titanium spheres and decreased in defect sphere and void (table 3). As a result probability of positron distribution in titanium sphere and annihilation increased from there. It was caused lessening of positron lifetime in the hydrogenated titanium. The other reason of disagreement of the experimental trend with theory would be swelling of titanium sample at its hydrogenation which was obtained by experiment. It could not be considered by theory.

Table 3. Positron lifetime τ(ps), probability of positron distribution W (%) to atomic spheres (S), electron charge Q (el.) in atomic spheres and probability of electron-positron annihilation ω (%).

	α-Ti	α-$TiH_{0.125}$			α-$TiH_{0.125}$			SIC-$TiH_{1.0}$		
τ(ps) [14]	150	154 ($TiH_{0.01}$)								
τ(ps)	158.1	154.5			149.8			163.5		
atom spheres radii (a.u.)	3.0532	$R_{Ti}=R_H=R_E=2.4233$			$R_{Ti}=2.800$ $R_H=R_E=1.867$			$R_{Ti}=R_H=R_E=2.0656$		
sphere	Ti	Ti	H	E	Ti	H	E	Ti	H	E
W (%)	100	32.25	4.90	62.85	59.87	1.93	38.20	10.05	23.72	66.23
ω(%)	100	42.19	5.35	52.46	64.79	2.24	32.97	16.68	27.97	55.35
Q (el/at)	22	20.47	2.48	1.48	21.28	1.35	0.75	19.68	1.64	0.84

In order to take account of the volume cell increasing by hydrogenation electron structure and positron lifetime were calculated for $TiH_{1.0}$ in cubic phase and lattice parameter a=0.4397 nm. Elementary cubic cell with 16 atoms per cell was designed like HCP and discussed in [7]. The calculation showed that positron redistributed into hydrogen trap a lot, although charge of hydrogen sphere changes lightly.

Note that experimental positron lifetimes of the first and the second components showed the slight increase of the first component τ_1 together with decrease of the corresponding intensity I_1. It could be explained that density of free electrons is not changed a lot by hydrogenation. For the hydrogen charged samples the second component decreases together with increase of the corresponding intensity compared with the original titanium samples: τ_2=369 ps, 362 ps, 321 ps, 331 ps for 0 min, 60 min, 120 min, 360 min hydrogen charged titanium, respectively [14]. It could be explained that positron annihilation increases from region of the vacancy-type defects which are trapping hydrogen atoms. In that case electron density of vacancy defect increases. It have to lead to the lifetime decreasing of positron trapped by the defects.

4. Conclusion

Thus, in the present work the detail investigations of electron band structure of α-Ti and hydrogen charged titanium α-TiH_x to x=1 were performed. The positron states and annihilation characteristics were calculated in frames of LMTO-ASA method, which allows us to analyze the contributions of the different electron states in electron-positron annihilation process in titanium samples as well. There is the satisfactory agreement with experimentally measured the delocalized positron lifetime, but not the tendency. It can be connected with either experiment or calculation method precision. To analysis the localized positron it is necessary to use the method which allows to model the soft core.

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