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Positron lifetime computations of defects in nickel containing hydrogen or helium

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Abstract

Positron lifetime of defects in nickel containing hydrogen or helium has been calculated, using Monte-Carlo, density-functional theory and local-density approximation. It is found that the values of positron lifetime in voids are lowered by the presence of hydrogen or helium. The calculations show a correlation between the microvoid size in nickel and the value of the positron lifetime. With the growth of the void size the difference in the positron lifetime for clusters containing hydrogen or helium becomes significant. Calculations show a saturation of the positron lifetime for microvoids containing more than 45 hydrogen atoms and around 30 helium atoms. A dependence between the positron lifetime and the ratio of hydrogen or helium atoms to the number of vacancies in nickel voids is established.

1. Introduction

The experimental and theoretical studies of gases in metals have become a subject of increasing interest in recent years [1]. This activity has been stimulated by the discovery that inert gases implanted into metals can precipitate in the solid phase. Hydrogen and helium play a particularly important role, when produced at the various species, causing drastic changes in materials structural properties, even at low concentrations. In nuclear technology the interaction of neutrons in structural materials leads to displacement damage and production of foreign elements [2,3]. The nuclear reactions (n,α), (n,p) and (n,γ) contribute to the displacement damage and two of them generate significant amount of helium and hydrogen. In the case of nickel the ^{59}Ni and ^{58}Ni isotopes contribution to hydrogen generation is important. Hydrogen enhances tritium inventory and perturbing fueling in fusion-energy devices. Concentrations of a few ppm hydrogen may cause severe changes in the ductility of the metals. Helium, being a closed shell atom, interacts repulsively with metal atoms and hence has a very low solubility. Helium in metals was studied also in connection with tritium, which decays into ^{3}He [3]. In the neutron spallation source a large amount of helium is created in materials by (p,α) reactions. Hydrogen and helium are effectively trapped at open-volume defects such as vacancies, dislocations and grain boundaries. Preferential clustering of helium and hydrogen around these defects, lead to the formation of helium and hydrogen bubbles, which results in the degradation of materials used in fission reactors. Positron lifetime spectroscopy (PLS) is effective, sensitive and valuable tool for investigation of the microviods in materials. It has been established that positrons are localized by defects such as vacancies, vacancy-clusters and dislocations [4]. Usually, for experimental purposes, hydrogen or helium can be introduced into nickel by neutron, proton irradiation or by implantation. The introduced H or He in the samples, in the majority of cases, are studied by transmission electron microscopy

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(TEM), PLS, small angle X-ray scattering (SAXS), neutron scattering or other techniques. In this work, by using quantum-mechanical electronic-structure calculations based on the density-functional theory (DFT), Monte-Carlo (MC) and positron lifetime characteristics have been applied to clarify the behavior of vacancy-type defects containing H or He in Ni. According to DFT the correct ground-state energy of an interacting electron gas in an external potential can be determined by minimizing a functional of the electron density. In order to understand the effect of helium and hydrogen decoration of vacancies on the positron lifetime, DFT calculations have been carried out as a function of the vacancy-cluster size in nickel and vacancy-clusters in nickel containing hydrogen or helium. Hydrogen is much more mobile than helium in nickel [5]. The computed positron lifetimes have been also used to interpret the available experimental positron annihilation spectroscopy results for the bubble size. To our knowledge, theoretical calculations of positron lifetimes for hydrogen in nickel vacancies have not been performed. Not many investigations of the electronic structure of metals containing hydrogen or helium were published in open literature.

2. Positron lifetime calculations

The computational bases for MC simulation of positron implantation in solids are the energy loss mechanisms for positrons within a given material. The knowledge of the stopping profile is necessary for detailed studies of positron diffusion and transport of thermal positrons. We use the method developed by Valkealahti and Nieminen [6,7] for MC simulations. The improved version for inelastic cross-sections, the full energy loss, angular dependencies of electron–hole pair as well as the plasmon excitations are presented in the work of Baker et al. [8]. We used the same approach as that in Ref. [8]. In addition, lattice structure effect was taken into account by a modification of atomic cross-sections. The output positron coordinates and energies from MC simulations serve as input data for the DFT program. The limit of the MC calculations is around 20 eV and depends strongly on the investigated materials. The aim of the electronic structure calculations is to obtain the electron and positron wave functions and the corresponding eigenvalues of energy. The density-functional (DF) calculations for Ni have been done with linear combination of Gaussian-type orbitals (LCGTO) based on the Kohn–Sham local-density approximation (LDA) and Honenberg–Khon DF formalism [9–11]. Model core potentials (MCP) for Ni atoms have also been used. This method has already been applied to determine the metal–atom distance in Ni and the most stable sites for H adsorption [12]. The core electrons are taken into account by using Huzinaga's model potential method [13]. Number of electrons explicitly used into calculations are 16 for ^{28}Ni. The basis sets LCGTO are presented in Ref. [14,15]. The hydrogen and helium electrons are considered as core electrons. The coordinate $z = 0$ corresponds to the starting point of the positron penetration through the (1 1 1) face of the Ni fcc structure for vacancy clusters in nickel and for clusters containing H or He. The lattice distance for Ni is 3.52 Å while the distance between the bulk nearest-neighbors is 2.49 Å. In the model calculations, the single H and He atoms are situated on a threefold site, which is located above the bulk tetrahedral interstitial site or above the octahedral interstitial site. The ratio of H or He atoms versus vacancy atoms in voids has been varied. Lattice relaxations have been taken into account. The positions of the atoms were allowed to relax to a minimum energy configuration. The vacancies were introduced by a modification of the BUBSIMUL algorithm [16]. In the Hamiltonian of the Schrödinger equation electron exchange correlation interactions is included in the Coulomb interaction. This properly dealt with the DF formalism [9,10] proposed by Hohenberg, Kohn and Sham, where the ground-state energy of an interacting electron gas is a function of the electron density $n(r)$. In the variational principle the electron wave function satisfies the following equations:

$$\begin{aligned} &\{-\nabla^2 + V_{\text{eff}}[n(r), r]\}\varphi_i(r) = \varepsilon_i \varphi_i(r), \\ &n(r) = \sum_i |\varphi_i(r)|^2, \\ &V_{\text{eff}}[n(r), r] = \phi(r) + V_{\text{xc}}[n(r)], \end{aligned} \tag{1}$$

where ε_i and φ_i are the eigenvalues and wave function, respectively, $n(r)$ is the electron density at the position r, V_{eff} is the effective potential experienced by the electron and $\phi(r)$ is the electrostatic potential derived from Poisson's equation.

$$\nabla^2 \phi = -4\pi[n(r) - n_{\text{ext}}(r)], \tag{2}$$

where $n_{\text{ext}}(r)$ is the positive-charge density distribution. $V_{\text{xc}}[n(r)]$ in Eq. (1) is the exchange correlation potential which is the derivative of the exchange correlation energy $E_{\text{xc}}[n(r)]$ with respect to the electron density $n(r)$. E_{xc} is the exchange and correlation energy of an interacting system with density $n(r)$. For an arbitrary electron density, it is difficult to calculate the precise form of $E_{\text{xc}}[n(r)]$. The exchange-correlation energy has been obtained by MC calculations. When the changes of $n(r)$ in the volume are small enough, we get a satisfactory result using the LDA [9,10,15]:

$$E_{\text{xc}}[n(r)] = \int n(r)\varepsilon_{\text{xc}}[n(r)]\,\mathrm{d}r, \tag{3}$$

where $\varepsilon_{xc}[n(r)]$ is the exchange correlation energy per particle in a homogeneous electron gas of density $n(r)$. The electronic structure of the point-like defect is obtained from the self-consistent solution of Eq. (1). The single-electron Schrödinger equation entering in the local spin density LSD method is solved in the framework of the LCGTO method [15]. The positron wave function of the defect system is obtained by a method similar to that for electrons, which satisfies the following Schrödinger equation:

$$\{-\nabla^2 + V_+[n(r), r]\}\varphi_+(r) = \varepsilon_+\varphi_+(r). \tag{4}$$

The positron lifetime is obtained by the wave functions and energy eigenvalues of the electron and positron in the defect system. The annihilation rate λ or the lifetime τ of a positron in an inhomogeneous electron gas is:

$$\frac{1}{\tau} = \lambda = \int \mathrm{d}r|\varphi_+(r)|^2\Gamma[n(r)], \tag{5}$$

where $\Gamma[n(r)]$ is a function of the electron density. If the positron wave function is a planar wave function

$$\frac{1}{\tau} = \lambda = \Gamma[n_0]\int \mathrm{d}r|\varphi_+(r)|^2 = \Gamma(n_0). \tag{6}$$

Due to the limitation of computational time the electrons are separated into core and valence. This means that Γ is composed of two electron densities (for valence electrons and for core electrons)

$$\Gamma[n(r)] = \Gamma_V[n_v(r)] + \Gamma_{in}[n_{in}(r)], \tag{7}$$

where $n_v(r)$ is the valence electron density and $n_{in}(r)$ is the core electron density [17]. The valence electron's response to the positron can be treated by the same method as that of the free electron. Hence for the region where only the valence electrons exist, for example in a void, the constant density n_0 is replaced with the local density $n_{(r)}$ and the local rate of annihilation is calculated by the following expression:

$$\Gamma[n(r)] = \Gamma_V[n_v(r)] = 2 + 134n_v(r). \tag{8}$$

The calculations have been carried under computer CRAY using a modification of the DeMon program package.

3. Results and discussion

The positron lifetime calculations have been carried out on two kinds of model samples: nickel containing vacancy clusters and nickel with hydrogen or helium in vacancy clusters (nH–mV and nHe–mV, where n and m are the number of introduced H or He atoms and vacancies number, respectively). Positron lifetimes for nH–mV and nHe–mV clusters with different ratio ($n <> m$)

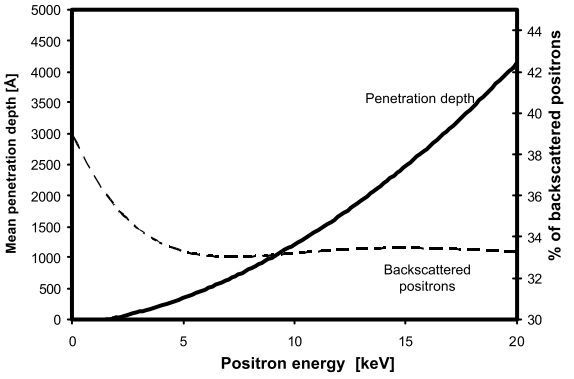

Fig. 1. Mean penetration depth and backscattering of the positrons in nickel as a function of positron energy. The symbols denote: full line (—) for mean penetration depth, dashed line (- - -) for backscattered positrons.

of the number of included atoms have been computed as a function of the number of vacancies. The MC computation results for the mean penetration depth and the backscattering of the positrons in Ni shown in Fig. 1 are in good agreement with experimental data [18]. The computed values show a polynomial increase of the mean penetration depth as a function of the positron energy. The penetration depth for positrons in Ni up to 4000 Å is well achievable. The MC simulations show that the fraction of backscattered positrons remains constant for higher energies. Probably this is due to the scattering of positrons in the surface layer. There is no observable difference between the backscattered fractions of positrons in nickel with vacancies and nickel voids containing H or He. MC calculations have been carried out up to 60 atom-vacancies cluster. The plot for backscattering of positrons from Ni with vacancies and Ni containing H or He in vacancy clusters are practically indistinguishable. We would like to note that results from this figure are valid for positron energies in the range of 20 keV to 20 eV. The density of electrons inside a vacancy is less than that in the interstitial region, the lifetime of trapped positron is larger than that of the positron annihilating in free state. The lifetime of trapped positron is sensitive to the defect size as well as to the ratio H or He-to-vacancies in void. In Fig. 2 are shown the isometric plot and the corresponding contour plot for the computed positron density distribution (PDD) in a Ni monovacancy and in nickel monovacancy with hydrogen. From PDD it is evident that positron is localized at the center of the monovacancy as shown in Fig. 2(a) and (b). For a vacancy decorated with a H or He atom (Fig. 2(c) and (d)) the isometric and contour plot of the computed PDD shows that a central hole appears in the PDD. This can be explained by the presence of the substitutional H or He atoms at the center of the void resulting in the exclusion of the positron from

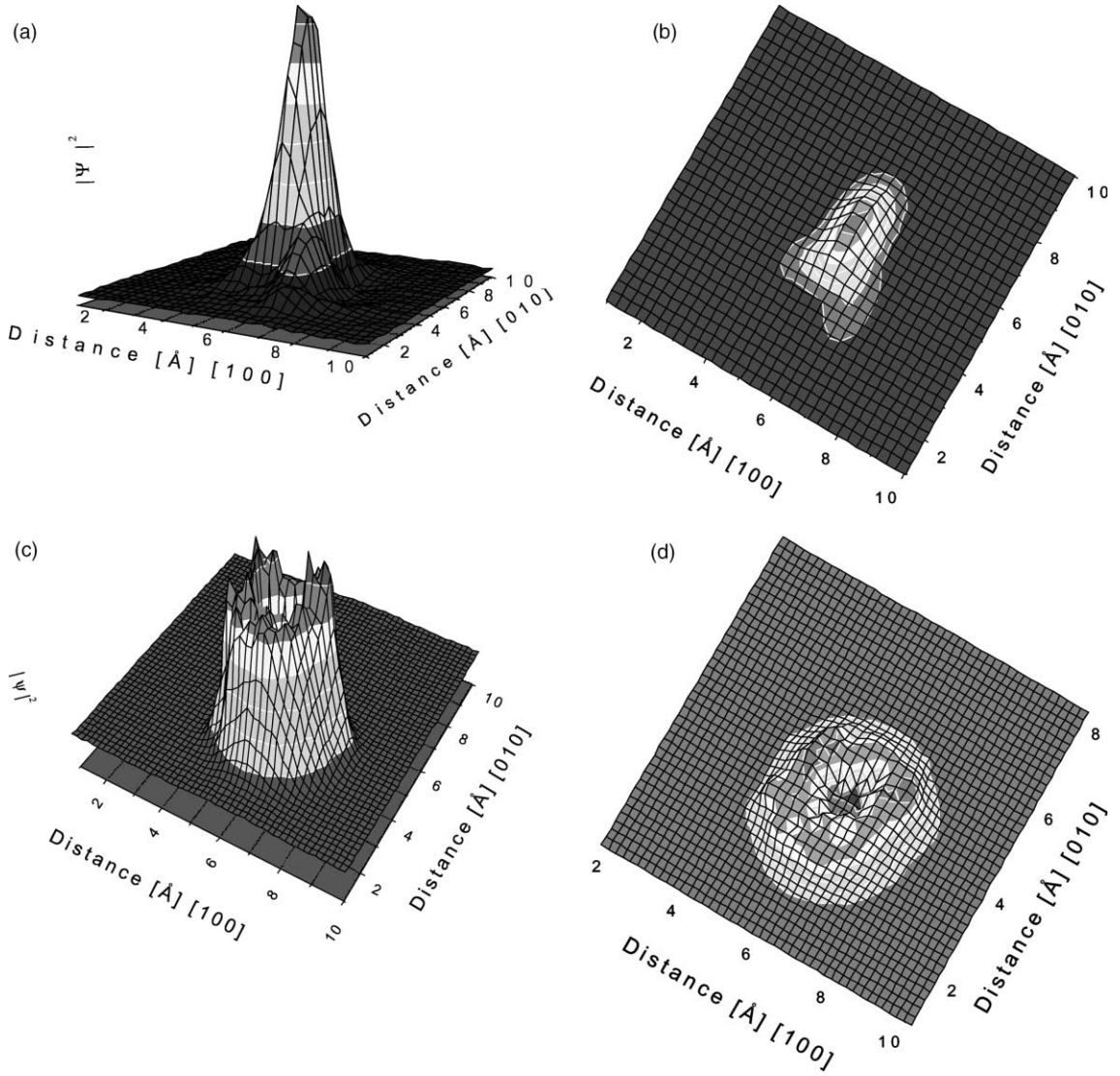

Fig. 2. (a) PDD: in nickel monovacancy – isometric plot; (b) PDD: in nickel monovacancy – contour plot; (c) PDD: in nickel monovacancy containing one hydrogen atom – isometric plot; (d) PDD: in nickel monovacancy containing one hydrogen atom – contour plot.

the center of the complex. The computed positron lifetime for a monovacancy in pure nickel is 175, 158 ps for 1H–1V and 115 ps for 1He–1V. The variation of the calculated positron lifetime τ as function of the cluster size is shown in Fig. 3. A correlation between the vacancy cluster size and positron lifetime is observed. Positron lifetime in nickel increases and tends to saturate around the values of 480 ps for empty microvoids. The values of the positron lifetimes calculated as a function of vacancy-cluster size are supported by the corresponding experimental values reported earlier in the literature [19]; both values are in good agreement. The saturation of positron lifetime corresponds to 40–45 vacancies in the cluster. The saturation typically occurs when the empty void radius reaches a value of about 10 Å. In the case of vacancy-cluster in nickel containing helium 1He–1V, the lifetime value is 116 ps taken into account relaxation of the lattice atoms around the defects. When the relaxation of lattice atoms is not included in the calculations positron lifetime is 115 ps. For hydrogen-vacancy complexes the computed lifetime is 112 ps without lattice relaxation and 158 ps with relaxation of lattice atoms close to the defect. In both cases the positron lifetimes are lower than that of the pure Ni vacancy. In the hydrogen case when relaxation is considered, the electron density distribution is spread not in

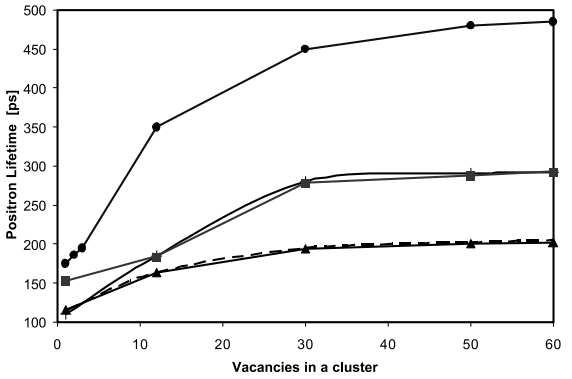

Fig. 3. Correlation between the positron lifetime and the number of vacancies in the void: The symbols denote: (●) for pure vacancy cluster in nickel; (■) voids containing H, lattice ralaxations are taken into account in the calculations; (+) voids containing H, lattice relaxations are not taken into account; (▲) voids containing He, lattice ralaxations are taken into account in the calculations; (- - -) voids containing He, lattice relaxations are not taken into account.

the center of the hole but at the vacancy border, while PDD is predominantly at the center of the vacancy. This explains the computed longer positron lifetime value. The similarity of the computed positron lifetimes for H and He trapped in a monovacancy without lattice relaxation might be due to the difference of one electron in the electron structure of H and He atoms. We wish to point out that in the present work relaxation calculations for lattice atoms have been performed to obtain the energetically most 'stable' configuration. At the beginning of the computation the inclusion atoms are located at the center of the created vacancy complexes nH/1V nHe/1V. The relaxation of the complex is computed, while coordinates of the lattice 'border' atoms are not fixed-similar to the procedure in paper [20]. Since H atom can 'diffuse' between Ni atoms, we restricted the diffusion process. A correlation between the size of clusters containing hydrogen or helium and computed positron lifetime is observed in Fig. 3. This correlation is not valid for void size greater than 45 vacancies in a cluster and around 30 hydrogen or helium atoms in vacancies cluster. With the growth of the number of vacancies the difference in the positron lifetime for H and He decorated vacancies becomes more significant due to the increasing number of electrons taking part in the cluster complex. We should notice that the computed positron lifetimes are sensitive to the lattice relaxation only for hydrogen vacancy clusters containing up to 12 vacancies. For clusters containing He no significant differences for positron lifetimes are observed. For all considered cases the saturation of the positron lifetime for vacancy clusters with H or He is around 30 vacancies in the void. In the case of He inclusion the comparison of calculations with experimental data [5] shows a good agreement and we can conclude that the computer model is working quite well. These results are valid for clusters containing hydrogen nH–mV or helium nHe–mV with fixed ratio of $n = m$ equal to unity. It is interesting to compute data for the case of multiple atom (H or He) decoration of a monovacancy and the multiple vacancies i.e. the ratio nH/mV and nHe/mV is varied only by the inclusion of the substituted atoms (n is varied, m = constant). The existence of such complex is known from computed binding energies and thermal He desorption spectroscopy (THDS) experiments [21,22]. Since the behavior of the positron-lifetime for a pure vacancy in nickel and for the substitutional atoms $n\mathrm{H}/\mathrm{He}/m\mathrm{V} = 1$ has been obtained, the annihilation parameters were computed for a monovacancy decorated by 1–6 H or He atoms (i.e. for 6 H atoms $6n/1m = 6$). It is interesting to note that our results show a sensitivity of the positron lifetime to the relative position of the atoms decorating the vacancies and hence to the configuration of the cluster. Calculations show that there is a formation of H–H bond. We consider that H atom tends to associate with another H or becomes interstitial atom. The computed positron lifetimes for corresponding clusters containing hydrogen or helium are shown in Fig. 4. The results indicate the influence of the added multiple H or He in the voids on the positron lifetime. The computed lifetimes from introduction of H atoms in nickel voids show constant decrease and saturation around 105 ps. There is a sharp decrease of the positron lifetime for unrelaxed clusters containing hydrogen. Results of positron lifetime for relaxed and unrelaxed voids containing helium are similar. In jellium-model [23] where the configuration of the defect complex is 'ignored', the calculated positron lifetime shows a monotonous decrease with addition of the substitutional atoms. The difference in the shape of the lifetime plot, shown in Fig. 4, between clusters

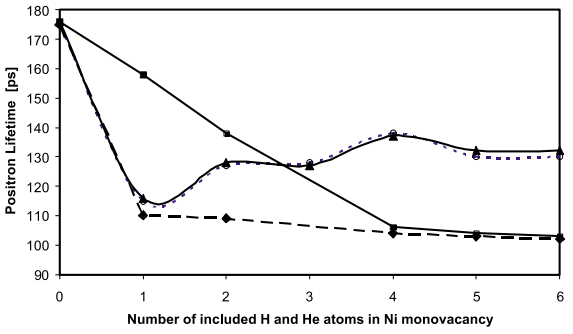

Fig. 4. Calculated positron lifetime as a function of number of hydrogen or helium atoms in nickel monovacancy. (–◆–) for H; (■) for H atoms relaxation taken into account; (- - -) for He; (▲) for He relaxaction taken into account.

containing hydrogen or helium is significant. In contrast with voids containing H there is no trend to associate for the He inclusion in the void. An increase in the positron lifetime is calculated after the second He atom has been added. Saturation for computed lifetime occurs around the value of 132 ps for clusters containing He. The present computational results show the sensitivity of the positron annihilation parameters to the inclusions of hydrogen or helium in the nickel atom structure. A decrease of positron lifetime is observed when hydrogen or helium atoms are included in the range of 12–30 nickel vacancies. In Fig. 5 is shown the ratio nH/12V and nHe/12V. For ratio greater than unity positron lifetime tends to saturate. The positron lifetime decreases monotonously depending on the H or He introduction in the vacancy-cluster in nickel. The calculated results show that in both cases there are two different linear dependences of the positron lifetime associated to the ratio of n (gas atoms)/m (vacancy atoms) = 1. The electron density of vacancy cluster remains lower than that of pure Ni sample and the values of the positron lifetimes are higher than that of nickel without vacancies. The results in Fig. 5, show that increasing of helium atoms in 12 vacancy cluster is more remarkable compared to the influence of hydrogen atoms on positron lifetime spectra. This is due to the increasing of binding energy of helium to vacancies in the range of 5–12 atoms [22]. The computed positron lifetime saturation for 12 vacancies cluster in Ni containing H or He is around 150 ps. In Fig. 6 the positron lifetime dependence on number of hydrogen or helium atoms in 30 vacancies cluster is presented. Increasing of hydrogen or helium concentration in vacancy cluster leads to decrease of positron lifetime. Drastic changes in the positron lifetime are obtained for variation of the number of hydrogen and helium atoms in the range from 10 to 25 atoms. This result can be explained by increasing of electrons in the cluster due to introduction of hydrogen or helium atoms. The calculated saturated lifetime values are about

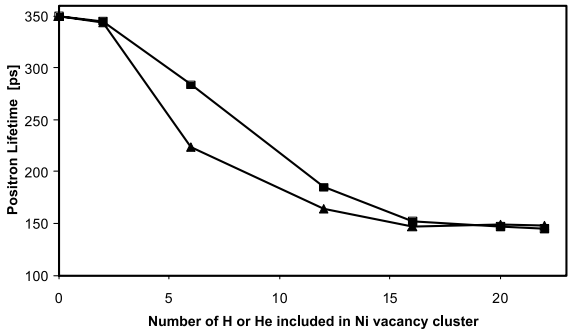

Fig. 5. Correlation between the positron lifetime and the number of H or He atoms in voids containing 12 vacancies; (■) for H; (▲) for He.

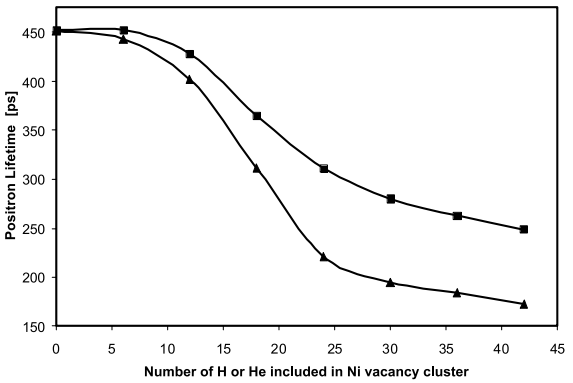

Fig. 6. Correlation between the positron lifetime and the number of H or He atoms in voids containing 30 vacancies; (■) for H; (▲) for He.

160 ps for helium and around 250 ps for hydrogen. For clusters containing 30 vacancies the results are similar to the ones calculated for cluster containing 12 vacancies, the differences are in the values of the positron lifetime.

4. Conclusions

In this study the emphasis has been put on the application of DFT calculations of positron lifetime parameters for vacancy clusters, containing hydrogen or helium in nickel and the influence of gases on the evolution of defects. It is found that the values of positron lifetime of voids in nickel are lowered by the presence of hydrogen or helium, due to the increasing of electron density and binding energies of vacancies to hydrogen or helium void complexes. The similarity of the computed positron lifetimes for hydrogen and helium trapped in a monovacancy without lattice relaxation is due to the electron difference of hydrogen and helium atoms. Helium atoms are bound most strongly to large voids, but helium has little additional effect than hydrogen on positron lifetime spectra of large voids containing more than 12 vacancies. A correlation is established between the vacancy cluster size in nickel and the computed positron lifetime. With the growth of the cluster size the difference in the lifetime for clusters containing hydrogen or helium becomes significant. The calculations show that the positron lifetime is sensitive to relative position of the gas atoms decorating the vacancies e.g. to the configuration of the complex. It was found a saturation of the positron lifetime for vacancy cluster containing more than 45 hydrogen atoms and around 30 helium atoms. A dependence was established, between the lifetime and the ratio of hydrogen or helium atoms to the number of vacancies. Although the present results are restricted to voids containing hydrogen or helium in nickel the calculations can be extended to other gases.

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