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Positron lifetime calculations of defects in vanadium containing hydrogen

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Abstract

Positron lifetime quantum-mechanical calculations were carried out for the investigation of defects in vanadium containing hydrogen atoms. The convergence of electronic structure calculations for supercell size is studied for vacancies, vacancy-clusters (nano-voids) and vacancy-clusters containing hydrogen. The electron wave functions have been obtained in the local density approximation (LDA) to the density functional theory (DFT). On the basis of the calculated results, the behaviours of empty nano-voids and nano-voids with hydrogen are discussed. It is found that hydrogen in larger three-dimensional vacancy-clusters change the annihilation characteristics drastically. The hydrogen atoms are trapped by lattice vacancies. These results provide physical insight for positron interactions with defects in vanadium and can be used for the prediction of hydrogen generation useful for the design of a fusion reactor.

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Keywords: Positron lifetime; Model calculations; LDA; Vacancies; Nano-voids; Hydrogen

1. Introduction

The specific focus of this paper is on the model calculations of the positron lifetime of defects in vanadium containing hydrogen. By positron lifetime model calculations of vanadium we reproduce the structure and energies of point defects that are present in a damaged lattice. Positron lifetime spectroscopy is a powerful and sensitive technique for studying defects concentrations as low as 10^{-6} in metals [1,2]. The method is based on positron trapping at open volume defects and it may be used for the characterization of mono-vacancies, di-vacancies and vacancy-clusters. The annihilation characteristics of a positron trapped at a vacancy or empty nano-voids are different from those of positrons trapped at nano-voids containing hydrogen. This fact shows that the presence of hydrogen influences the behaviour of defects in samples. The interaction of positrons with defects containing hydrogen illustrates interesting physical concepts concerning hydrogen trapping by vacancy-clusters. Neutron irradiation creates atomic displacements and generates helium or hydrogen in samples by atomic transmutations. The production of hydrogen in irradiated vanadium is dependent on the (n, p) nuclear reaction. An unavoidable by-product of spallation reactions is the formation of large amounts of hydrogen in the target material. The retention of hydrogen in the first wall of a fusion reactor, determined by hydrogen-defect interaction, influences plasma parameters. At elevated temperatures, point defects (by mutual recombination) gather to clusters and grow to nano-voids. Vanadium ($3d^3 4s^2$) has a bcc lattice. Vanadium and vanadium alloys are among the structural materials to operate at high temperatures in high irradiation damage environments [3,4]. The properties of point defects in 14 MeV neutron irradiated vanadium and vanadium alloys have been the subject

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of papers [4,5]. The importance of hydrogen concentrations with respect to a fusion reactor requires more systematic studies of nano-voids containing hydrogen in advanced reactor materials like V, Cr, Mo, W, Fe. The major difficulties in investigating intrinsic defect properties in vanadium after neutron irradiation originate from the hydrogen interactions with vacancies and vacancy-clusters. Hydrogen concentration in materials as low as 10^{-5} atomic fraction causes serious mechanical changes [6]. Degradation of the mechanical properties increases with increasing hydrogen content. Interstitial hydrogen has high mobility in metals [7,8]. The solubility of hydrogen in metals is usually small. It is known that the accumulation of hydrogen increases in the presence of nano-voids. This is due to the trapping of hydrogen at these defects. The positron density profiles in a pure vacancy and vacancy–hydrogen complexes in metals are very different [9]. For the present paper, positron lifetime parameters for defects in vanadium containing hydrogen and the distribution of hydrogen in void complexes have been calculated based on a quantum-mechanical plane-wave pseudo-potential model. The determination of positron lifetimes for various defects in vanadium has not yet been completely performed either in experiments or in model calculations. The main emphasis has been put on the investigation of empty nano-voids, and nano-voids with hydrogen, and their behaviour at different hydrogen concentrations. The aim of the computer model calculations for vanadium is to obtain the electron and positron wave functions and the corresponding eigenvalues of energy. In this work, by using quantum-mechanical electronic-structure calculations based on the DFT the positron lifetime characteristics have been applied to clarify the behaviour of vacancy-type defects containing hydrogen atoms in vanadium. As pointed out in paper [10] a large void can be considered as an internal surface. For the largest defects a system of 800 atoms is typically sufficient to obtain accurate results. Calculations with more than 2000 atoms were identical to within 0.01 eV.

2. DFT positron lifetime computation method

In the computer simulations, atoms are represented as point-like centers. The electron dynamics in vanadium are modelled by a set of parameters and analytical functions, which in DFT depend on the mutual positions of the atoms in the calculated configuration. The parameters give information about the energy and correlation forces acting between the particles. The positron trapping is reflected by a lowered annihilation rate, due to the lower electron density. We have considered 2000 particles in a cubic cell with periodic boundary conditions. The time step was 0.0025 ps, the duration of the equilibration process was 5 ps and the calculation of positron lifetimes was made after another 40 ps. The number of electrons in vanadium is so large that the calculation can be treated using statistical arguments. According to DFT the correct ground-state energy of an interacting electron gas in an external potential can be determined by minimizing the functional of the electron density. That is why we do not need the full wave function but only the electron density. First-principles calculations can also be used to provide reliable predictions of interstitial properties that can be used in molecular dynamics and kinetic Monte Carlo studies of point defect evolution in damage materials [11]. Modelling radiation damage takes into account, atomic level dynamics, defects and transport kinetics [12]. Based on DFT we performed positron lifetime calculations of vacancy-clusters, within the frame of the Kohn–Sham approach [13]. The positron–electron correlation effect is calculated based on two-component DFT within the LDA [2,14,15], which is reliable in reproducing positron annihilation characteristics for bulk materials and materials with defects. In order to understand the effect of hydrogen on vacancies in vanadium, the positron lifetime calculations have been carried out as a function of the vacancy-cluster size in vanadium and the size of vacancy-clusters in a vanadium lattice containing hydrogen. The computed data could be also used to interpret the available experimental positron annihilation spectroscopy results for the nano-void size in vanadium. The calculations for vanadium have been done with a linear combination of Gaussian-type orbitals (LCGTO) based on the Kohn–Sham (LDA) and Hohenberg–Kohn DFT in which the ground state property is a function of the electron density in position space [13,16]. The lattice constant for vanadium is 0.3027 nm. This parameter is an essential structural measure of vanadium. The basis sets LCGTO are presented in [17,18]. The hydrogen electron is considered as a valence electron. The coordinate $z = 0$ corresponds to the starting point of the positron penetration through the (1 1 1) face of the vanadium bcc structure for vacancy-clusters in vanadium, and for clusters containing hydrogen. In the model calculations, we consider that single hydrogen 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 hydrogen atoms versus number of vacancies in nano-voids has been varied. In the positron calculations the lattice relaxations have been taken into account. The atomic positions in the relaxed configuration were obtained by carrying out calculations at constant volume. By the gradient method we obtained the relaxed state of minimum energy in the defective vanadium lattice. The lattice relaxation around a vacancy results in about 9% reduction of the effective vacancy volume, which decreases the positron lifetime at a vacancy. The vacancies were introduced by a modification of the BUBSIMUL algorithm [19]. In the DFT [13,16] proposed by Hohenberg, Kohn and Sham, 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:

$$\{-\nabla^2 + V_{\text{eff}}[n(r), r]\}\varphi_i(r) = \varepsilon_i \varphi_i(r), \tag{1}$$

where ε_i and φ_i are the eigenvalues and wave functions, respectively; V_{eff} is the effective potential experienced by