Model Calculation of Positron States in Tungsten Containing Hydrogen and Helium

T. Troev\textsuperscript{a}, E. Popov, N. Nankov\textsuperscript{a} and T. Yoshiie\textsuperscript{b}

\textsuperscript{a}Institute for Nuclear Research and Nuclear Energy, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria

\textsuperscript{b}Research Reactor Institute, Kyoto University, Kumatori-Cho, Sennan-Gun, Osaka-Fu 590-0494, Japan

E-mail: troev@inrne.bas.bg

Abstract. Tungsten is a candidate material for plasma-facing first wall of a fusion power plant. Understanding of defects, tritium and helium behaviour in plasma facing materials [PFM] is an important issue for fusion reactor from viewpoints of its mechanical properties under neutron irradiation. Experiments with high-Z materials show that erosion of these materials under normal operation condition is considerably lower than the plasma induced erosion of low-Z materials like carbon or beryllium. Quantitative understanding of the experimental results for defects in tungsten needs a comprehensive theory of electron-positron interaction. The properties of defects in tungsten containing hydrogen or helium atoms have been investigated by model positron lifetime quantum-mechanical calculations. The electron wave functions have been obtained in the local density approximation LDA to the density functional theory DFT. On the bases of calculated results, the behaviour of vacancies, empty nano-voids and nano-voids with hydrogen and helium were discussed. It was established that hydrogen and helium in larger three-dimensional vacancy clusters in W change the annihilation characteristics dramatically. The hydrogen and helium atoms are trapped by lattice vacancies. These results provide physical insight for positron interactions in tungsten defects and can be used for prediction of hydrogen-H or helium-He\textsubscript{4} and (tritium-H\textsubscript{3}) generation for the design of fusion reactors.

1. Introduction

The positron is the antiparticle of the electron: it has the same mass as the electron but its charge is positive. Positrons are available \textit{e.g.} from radioactive sources such as the $^{22}$Na isotope. Positrons injected in matter quickly lose energy and live in thermal equilibrium for a short before annihilating with electrons at time-scale inversely proportional to the electron density. In a perfect crystal, the positron density is delocalized over the whole crystal where as in presence of vacancies, the repulsion from positive ion cores may cause positrons to be trapped in open volumes with lower electron density thus increasing the lifetime.
Positron lifetime spectroscopy is a powerful and sensitive technique for studying of defect concentrations as low as $10^{-6}$ in metals [1,2]. The method is based on the positron trapping at defects as shown in figure 1. The positron trapping in metals may be used for characterization of monovacancies, divacancies and vacancy-clusters (nano-voids). The annihilation characteristics of a positron trapped at a vacancy or empty nano-voids are different from those of positrons trapped at nanovoids containing hydrogen or helium. High amount of helium (~1000 appm He) can be generated in all materials proposed for fusion reactor first wall applications during the lifetime of a fusion reactor. Hydrogen or helium presences influence the behavior of defects in tungsten samples [3,4].

The interaction of positrons with defects containing hydrogen or helium illustrates interesting physical concepts concerning hydrogen and helium trapping by vacancy clusters. The micro-structural information is essential for understanding the helium mechanism in tungsten. The production of hydrogen or helium in the irradiated materials is dependent on the following nuclear reactions: (n, α) and (n, p).

$$^{1}\text{H}^2 + ^1\text{H}^3 \rightarrow ^{4}\text{He} + n + 17.6 \text{ MeV} \quad (1)$$

$$^{1}\text{H}^2 + ^1\text{H}^2 \rightarrow ^3\text{He} + n + 3.2 \text{ MeV} \quad (2)$$

$$^{1}\text{H}^2 + ^1\text{H}^2 \rightarrow ^3\text{He} + ^1\text{H} + 4.0 \text{ MeV} \quad (3)$$

Helium-3 and helium-4 are non-radioactive light isotopes of helium. The nucleus of helium-3 atom consists of two protons and one neutron, in contrast to two neutrons in ordinary helium. $^3\text{He}$ is a fermion while $^4\text{He}$ is a boson. The properties and behavior of $^3\text{He}$ could not be explained by the chemistry of helium, but it is explained by quantum mechanics. In addition to the fusion reactions, the reactions with neutrons are important in order to breed tritium in plasma machine. Neutron irradiation creates atomic displacements and generates helium or hydrogen in samples by atomic transmutations. Identification and behavior of defects in tungsten is important because they greatly affect its mechanical and electronic properties. The present investigation has focused on the model calculations of positron lifetime of defects in bcc structure of tungsten containing hydrogen or helium. Tungsten is considered as plasma facing materials as a first wall coating for Demo-related blankets and as amour.
material for gas-cooled divertors. Helium created by nuclear reaction during neutron irradiation of tungsten becomes stabilized in vacancies and changes the mechanical properties of tungsten. The retention of hydrogen or helium in the W first wall could be determined by hydrogen–defect and helium–defect interaction. At elevated temperatures, point defects by mutual recombination gather into clusters and grow into the nano-voids. Tungsten and tungsten alloys are among the structural materials to operate at high temperatures in high irradiation damage environments. Tungsten (4f145d46s2) has bcc lattice. The interactions between hydrogen and defects in metals like Be, W, V [6] plays an important role in various areas of technology of plasma machines and in future thermonuclear reactor ITER [7]. The importance of hydrogen or helium concentrations with respect to fusion reactor more systematic studies on the nano-voids containing hydrogen and helium are needed on advanced reactor materials like W, Be, V, Fe. The major difficulties in investigating intrinsic defect properties in tungsten after neutron irradiation originate from the hydrogen or helium interactions with vacancies and vacancies clusters. Hydrogen concentration as low as 10^{-5} atomic fractions causes serious mechanical changes [8]. Degradation of the mechanical properties increases with increasing of hydrogen or helium contents. Interstitial hydrogen has a high mobility in the metals [9,10]. The solubility of hydrogen in metals is usually small and it is known to increase in the presence of nano-voids. This is due to the trapping of hydrogen at these defects. The positron density distribution in a pure vacancy and vacancy-hydrogen or vacancy-helium complexes is very different [11].

The present paper deals with model calculations of the positron lifetime parameters for defects in tungsten containing hydrogen or helium and distribution of the hydrogen and helium in nano-voids. The purpose of the study is to obtain absolute values of positron lifetime parameters. Experimental methods for investigating the properties of helium and hydrogen in tungsten are field ion microscopy (FIM), TEM transmission electron microscopy (TEM), positron annihilation (PA), perturbed $\gamma\gamma$ angular correlations (PAC), electron energy loss spectroscopy (EELS), thermal desorption (THDS), nuclear scattering methods (NSC). Direct experimental information on single hydrogen or helium atoms and nano-voids containing hydrogen or helium in tungsten lattice, could be obtain only by PA, FIM and PAC. The determination of positron lifetimes for various defects in tungsten containing hydrogen or helium has not been completely performed yet both in the experiments and in the model calculations. In this respect, the main emphasis has been put on the investigation of empty nano-voids and nano-voids with hydrogen or helium and their behavior at different gas atoms concentrations. As pointed out in paper [12] the large nano-void can be considered as an internal surface. It was found that helium bubbles had large binding energies with vacancies. In the computer calculations, a cell with 2000 atoms is typically sufficient to obtain accurate results for positron lifetime and positron ground energy for a large nano-void.

2. Positron lifetime computation method

The positron lifetime and the momentum density depend on the site where the annihilation takes place. If the positron is trapped by a vacancy-type defect in a solid its lifetime increases from that of a delocalized positron due to the reduced electron density. These changes in the positron annihilation characteristics make the positron annihilation spectroscopy powerful to study the electronic and ionic structures and the associated processes of defects in solids. The goal of our work has also been to support the experimental positron research by theoretical calculations of positron annihilation characteristics. We have developed models (within the density functional theory) to describe positron states and annihilations in solids. Calculations were done in presence of different kinds of defects. In Born-Oppenheimer approximation, electrons follow adiabatically the movements of the ions. The calculation of positron states in solids has been done by the solution of Schrödinger equation for a system containing interacting electrons and ions. The time scale of electrons is several orders of magnitude smaller than the ionic time scale and therefore it can be assumed that the electrons adapt to the current ionic positions. The Born-Oppenheimer approximation allows the ionic positions to be treated as a set of parameters. The Kohn-Sham method [13] of density functional theory [DFT] considers the problem of many interacting electrons into problem of solving one-particle Schrödinger
equations. This simplification makes large-scale first-principle electronic structure calculations possible by local density approximation [LDA] [13]. The Kohn-Sham equation is an effective single-particle Schrödinger equation that has exactly the same form as the Schrödinger equation for the non-interacting electrons in an external potential. The electron density the effective potential and the corresponding Hamiltonian should be calculated until the total energy does not change more than a present limit. Plane-waves are used as basis functions. Plane-waves form a complete set that is simple and unbiased. The plane-waves do not depend on the ionic positions.

The electron dynamics in tungsten is modeled 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 ground state properties of the interacting electron gas were determined by the electron density. First-principles calculations can also be used to provide reliable predictions of interstitial properties that can be used in molecular dynamics [MD] and kinetic Monte Carlo [kMC] studies of point defect evolution in irradiated materials [14]. The positron trapping is reflected by a lowered annihilation rate, due to the lower electron density. The model consisted of several thousands of W atoms in a bcc lattice. We have considered 2000 particles in a cubic cell with periodic boundary conditions. The time step was 0.0025 ps, the equilibration process was 5 ps and the calculation of positron lifetimes was made after another 40 ps. The number of electrons in tungsten is large so the calculation could 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. In order to understand the effect of hydrogen or helium decoration of vacancies on the positron lifetime, DFT calculations have been carried out as a function of the vacancy-cluster size in tungsten and vacancy-clusters in tungsten containing hydrogen or helium. The DF calculations for tungsten have been done with linear combination of Gaussian-type orbitals (LCGTO) based on the Kohn-Sham local-density approximation (LDA) and Honenberg-Kohn [15] DF formalism in which the ground state property is a function of the electron density in position space [13,15]. The lattice distance for tungsten is 3.163 Å [5.98 au] while the distance between the bulks nearest-neighbors is 2.74Å [5.18 au]. The basis sets LCGTO are presented in Ref. [16,17]. The hydrogen and helium electrons are considered as valence electrons. The coordinate \( z = 0 \) corresponds to the starting point of the positron penetration through the (111) face of the tungsten bcc structure for vacancy clusters in tungsten and for clusters containing hydrogen or helium. The ratio of hydrogen and helium atoms versus vacancy atoms in nano-voids has been varied. The positions of the atoms were allowed to relax to a minimum energy configuration. Lattice relaxations have been taken into account. The lattice relaxation around a vacancy results in about 9 % reduction of the effective vacancy volume, which decreases the positron lifetime at a vacancy. In the DF, formalism [13,15] 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:

\[
\left\{ -\nabla^2 + V_{\text{eff}}[n(r),r] \right\} \psi_i(r) = \varepsilon_i \psi_i(r),
\]

where \( \varepsilon_i \) and \( \psi_i \) are the eigenvalues and wave function, respectively. Equation 4 is the effective single-particle Schrödinger equation that has exactly the same form as the Schrödinger equation for the non-interacting electrons in an external potential; \( n(r) \) is the electron density at the position \( r \).

\[
n(r) = \sum_i |\psi_i(r)|^2,
\]

The effective potential is:

\[
V_{\text{eff}}[n(r),r] = \phi(r) + V_{\text{xc}}[n(r)],
\]

We consider that the density \( n(r) \) and the potential \( V_{\text{eff}}(n,r) \) have the periodicity of the tungsten lattice. At first approximation the energy of the tungsten atom, at side \( r \) is assumed the same as if the tungsten atom is placed into a uniform electron gas at that density. In regions far from the nucleus, the
valence electrons are most important [18]. \( V_{\text{eff}} \) is experienced by the electrons and \( \phi(r) \) is the electrostatic potential derived from Poisson’s equation.

\[
V^2 \phi = -4\pi \left[ n(r) - n_{\text{ext}}(r) \right],
\]

where \( n_{\text{ext}}(r) \) is the positive-charge density distribution. \( V_{\text{xc}}[n(r)] \) in equation (6) 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 \( n(r) \). The magnitude of the correlation energy is important for lattice energy parameters [19]. When the changes of \( n(r) \) in the volume are small enough, we get a satisfactory result using the LDA [14,16]:

\[
E_{\text{xc}}[n(r)] = \int n(r)e_{\text{xc}}[n(r)]dr,
\]

where \( e_{\text{xc}}[n(r)] \) is the exchange correlation energy per particle in a homogeneous electron gas of density \( n(r) \). The exact form of \( E_{\text{xc}} \) is not known. The electronic structure of the point-like defect is obtained from the self-consistent solution of equation (4). The single-electron Schrödinger equation entering in the LDA is solved in the framework of the LCGTO method [16]. We calculate the density at the position of hydrogen or helium atoms in a lattice of tungsten atoms, whose electron density is known. We consider that the size of nano-void is large enough to include the density of many neighbors. The positron wave function of the defect system is obtained by a method similar to that for electrons established by Puska and Nieminen [20], which satisfies the Schrödinger equation. Kimball and Shortley [21] introduced a method where the wave electron function is obtained through an iterative relaxation scheme. To solve the Schrödinger equation the numerical method given by Kimball and Shortley [21] was used.

\[
\{-V^2 + V_{\text{eff}}[n(r),r]\}\psi_+(r) = e_+\psi_+(r).
\]

where \( \psi_+ \) is the positron wave function and \( V_{\text{eff}} \) is the effective positron potential.

The positron lifetime is obtained by the wave functions and energy eigenvalues of the electron and positron in the defect system. The positron annihilation rate \( \lambda \) or the lifetime \( \tau \) of a positron in an inhomogeneous electron gas is proportional to the electron density at the positron position.

\[
\frac{1}{\tau} = \lambda = \int dr |\psi_+(r)|^2 \Gamma[n(r)],
\]

where \( \Gamma[n(r)] \) is the local annihilation rate which is a function of electron density \( n(r) \) and including the enhancement. Due to the attraction between the electron and the positron the electron density around a positron will be enhanced. The electron density \( n(r) \) in the imperfect metal lattice is composed of free and core electrons, they are expected to react differently to the presence of positron; therefore the local annihilation rate \( \Gamma[n(r)] \) is divided into the following two parts. \( \Gamma \) is composed of two electron densities (for valence electrons and for core electrons)

\[
\Gamma[n(r)] = \Gamma_{v}[n_v(r)] + \Gamma_{in}[n_{in}(r)],
\]

3. Results and discussion

Calculations were done in presence of different defects, vacancies, vacancy-cluster and vacancy clusters containing hydrogen or helium.
In figure 2a,b are shown the isometric plot and corresponding contour plot of the calculated positron density distribution [PDD] in the tungsten mono-vacancy. The contour plot of the screening potential components in the [100] plane in tungsten shows that potential is spherical close to the atomic sites. In a perfect tungsten lattice, the positron density is delocalized over the whole lattice. The calculated positron lifetime of 108 ps corresponds to those at the matrix when no defects exist in the perfect tungsten lattice. The calculated value of the positron lifetime in pure tungsten is supported by the experimental value 105 ± 3 ps reported earlier in the literature [22] both values are in good agreement. The positron lifetime calculations have been performed in bcc tungsten lattice containing vacancies, empty nano-voids and nano-voids consisting from 1 to 6 vacancies with 1 to 10 hydrogen or helium atoms. The positron lifetimes in nano-voids have been computed as a function of the number of vacancies and number of included hydrogen (nH-mV) or helium (nHe-mV) atoms, where n and m are the number of introduced hydrogen or helium atoms and vacancies number, respectively. The lifetime of...
trapped positron is larger than that of the positron annihilating in the free state, because the density of electrons inside a vacancy is less than that in the interstitial region. The positron lifetime was calculated as 200 ps for monovacancy in tungsten. It is evident that positron is localized at the center of the monovacancy as shown in figure 2a,b. In figure 3a,b are shown the isometric plot and the contour plot of PDD for tungsten mono-vacancy with hydrogen 1V-1H. The procedure is similar to that in paper [20]. In figure 4 are shown the results of positron lifetime calculations for different number of vacancies in tungsten lattice. Our calculations show that positron in tungsten is bound to the open defects even it contains a hydrogen or helium atom. The lifetime of positrons annihilating in voids is longer than that for mono-vacancies and gives information for presence of vacancy-cluster with two or more vacancies. Positron lifetime in tungsten has a value of 437 ps for nano-voids containing 37 vacancies. The result shows a correlation between the size of nano-voids containing hydrogen or helium and computed positron lifetime. The longer lifetime corresponds to three-dimensional vacancy-clusters, namely, nano-voids, which are observed in bcc and fcc metal lattices, like V, Fe and Mo.

![Figure 4: Correlation between positron lifetime and the number of vacancies in the nano-void](image)

![Figure 5: Correlation between positron lifetime and nano-void containing equal number of gases atoms and vacancies.](image)
In figure 5 are shown the calculated results for vacancies containing equal number of hydrogen or helium atoms. It is seen that positron lifetime increased with the included number of hydrogen or helium atoms. Helium is mobile in tungsten below room temperature. Above 10 Å helium atoms are very stable up to temperature closed to the melting temperature of sample. Helium is practically insoluble in tungsten. Our results show that helium atoms are trapped to vacancies. A significant amount of hydrogen or helium remains in nH-mV or nHe- mV nano-voids, but these nano-voids are small and they could not be observed by TEM. The computed positron lifetime for nano-voids containing (1V + nH, 2V + nH, 6V + nH) different number of hydrogen atoms in tungsten are shown in figure 6. The obtained results present the influence of the hydrogen atoms on vacancies in the nano-voids.

![Figure 6: Correlation between positron lifetime and the number of hydrogen atoms in nano-void containing 1V+nH, 2V+nH, 6V+nH](image)

![Figure 7: Calculated positron lifetime in nano-void containing 1V, 2V, 6V, and various He atoms.](image)
Binding of hydrogen and helium atoms with vacancies in tungsten decrease positron lifetime because the introduced electron density by hydrogen or helium atoms led to increasing of the valence electron density. The positron lifetime decreases from 200 ps to 162 ps when hydrogen is bound with the vacancy (1V + 1H). It is seen that the values of calculated positron lifetimes decrease with increase of the number of hydrogen atoms. Positron lifetime decreases as 162 ps, 156 ps, 148 ps, 143 ps and 130 ps for a (1V + 1H, 1V + 2H, 1V + 3H, 1V + 4H and 1V + 6H), respectively. In figure 6, the computed value of PLT decreases with increase of hydrogen atom concentration and reaches a value of 130 ps for 1V + 6H atoms. The decrease in positron lifetime suggests an increase in hydrogen density inside of the nano-voids. The comparing of the positron lifetime for vacancy with hydrogen to vacancy in pure tungsten shows that the calculated values of the lifetimes differ. This result for first time indicates that the presence of single H atom bound with mono-vacancy affect the process of vacancies in tungsten. It is interesting to note that our results show a sensitivity of cluster for 2V containing nH atoms. The computed lifetimes for 2V + nH atoms show decrease of positron lifetime with increasing of hydrogen atoms in tungsten nano-voids. In figure 6 is observed dependence of the 6V + mH atoms from the hydrogen in the vacancy cluster in tungsten sample. Positron lifetime for vacancy-cluster 6V + 10H atoms in tungsten is 188 ps. The computer results or 1V + mH, 2V + mH and 6V + mH clearly show that increasing of hydrogen concentration in vacancy cluster leads to decrease of positron lifetime. In figure 7 are shown the results for nano-voids containing (1V + nHe, 2V + nHe, 6V + nHe) helium atoms in tungsten. The results show that binding of helium atoms with vacancies decrease positron lifetime. The obtain correlation between positron lifetime and nano-void size for first time demonstrates that positron lifetime is very sensitive method for determination of helium concentration in tungsten.

The calculated positron lifetime for various defects and voids containing hydrogen and helium in tungsten can be summarized as shown in figure 8. It is observed that with increase of nano-void size and number of hydrogen atoms positron lifetime has a higher values. We consider that positron wave function is localized at the inner space of the nano-void. When the nano-void contains hydrogen atoms, the positron wave function is localized not at the center of the nano-voids, which gives a lifetime of order 132 ps for 2V + 10H and 6V + 10H 188 ps, respectively. It is clear that PLT depends on behavior of H or He filled vacancies in these simulations.

It is observed that with increase of nano-void size and number of helium atoms positron lifetime has a higher values. We consider that positron wave function is localized at the inner space of the nano-void. When the nano-void contains helium atoms the positron wave function is localized not at the center of the nano-voids, which gives a lifetime of order [132 ps for 2V + 10H and 6V + 10H 188 ps], respectively.
Table 8. Calculated values of positron lifetime for various defects in W: mono-vacancy, divacancy, empty nano-voids, nano-voids containing hydrogen atoms.

| Matrix | τ (ps) |
|--------|--------|
|        | 108    |
|        | 130 1V+8H |
|        | 156 1V+2H |
|        | 162 1V+1H |
|        | 183 2V+2H |
|        | 206 2V+H   |
|        | 221 3V+6H   |
|        | 233 3V+4H   |
|        | 237 3V+2H   |
|        | 249 4V+4H   |
|        | 269 5V      |
|        | 330 9V      |

![Figure 8. Calculated values of positron lifetime for various defects in W: mono-vacancy, divacancy, empty nano-voids, nano-voids containing hydrogen atoms.](image)

4. Conclusion

This study is the first positron lifetime quantum-mechanical calculations of nano-voids and nano-voids containing hydrogen or helium in tungsten. The positron lifetime correlates with the magnitude of electron density. The study sheds light on the nano-defects formation and their evaluation in tungsten containing hydrogen or helium. It was found that a positron is bound to a metal mono-vacancy even if it contains a hydrogen or helium atoms. The model calculated positron lifetimes of nano-void containing gases atoms are shorter than in the empty void of the same size. The vacancy-clusters without hydrogen or helium are active positron traps, if once they are bound with hydrogen, they become less effective in the trapping of positrons. These results provide physical insight for positron interaction in tungsten defects and can be used for prediction of hydrogen as well as tritium-H$_3$ or helium-He$_4$ generation for the design of fusion reactors.

Acknowledgement: The EURATOM/INRNE Fusion Association supports this work.

References

[1] Schultz P J and Lynn K G 1988 Rev Modern Phys. 60 71
[2] Puska M J and Nieminen R M 1994 Rev. Modern Phys. 66 841
[3] Katayama K, Imaoka K, Okamura T and Nishikawa M 2007 Fusion Engineering and Design 82 1645–50
[4] Lee H T, Haasz A A, Davis J W and Macaulay-Newcombe R G 2007 JNM 360 196–207
[5] Xu Q, Yoshiie T and Huang H C, 2003 NIM B 206 123–126
[6] Troev T, Nancov N, Petrov L and Popov E, 2008 Repport Letters Physics 1 746892
[7] Garner F A et al. 2001 J. Nucl. Mater. 296 66–82
[8] Thompson A W and Bernstein I M 1986 Effect of hydrogen behavior of materials (AIME, New York)
[9] Sakamoto Y 2000 Hydrogen in Metals System, Solid State Phenomena 73-75 137–206
[10] Ishizaki T, Xu Q, Yoshiie T, Nagata S, Troev T, 2002 J. Nucl. Mat. 307–311 961
[11] Shivachev B L, Troev T and Yoshiie T 2002 *J. Nucl. Mater.* **306** 105
[12] Puska M J 1991 *J. Phys. Condens. Matter* **3** 3455
[13] Kohn W, Sham L J 1965 *Phys. Rev.* **A 140** 1133
[14] Domain C and Becquart C S 2001 *Phys. Rev.* **B 65** 024103
[15] Hohenberg P, Kohn W 1964 *Phys. Rev.* **B 136** 864
[16] Chiarello G, Andzelm J, Fournier R, Russo N, Salahub D R 1988 *Surf. Sci.* **202** L621
[17] Vosko H, Wilk L, Nussair M 1980 *Can. J. Phys.* **58** 1200
[18] Jansen H J F and Freeman A J 1984 *Phys. Rev.* **B 30** 561
[19] Wigner E, 1934 *Phys. Rev.* **46** 1002
[20] Puska M J, Nieminen R M 1983 *J. Phys.* **F 13** 333
[21] Kimball G E and Shortley G H 1934 *Phys. Rev.* **45** 815
[22] Ziegler R and Schaefer H E 1987 *Mater. Sci. Forum* **15-18** 145