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Positron lifetime calculation of the elements of the periodic table

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Abstract. Theoretical positron lifetime values have been calculated systematically for most of the elements of the Periodic Table. Self-consistent and non-self-consistent schemes have been used for the calculation of the electronic structure in the solid, as well as different parameterizations for the positron enhancement factor and correlation energy. The results obtained have been studied and compared with experimental data, confirming the theoretical trends. As it is known, positron lifetimes in bulk show a periodic behaviour with atomic number. These calculations also confirm that monovacancy lifetimes follow the same behaviour. From this fact a strong relation between the atomic volume and the positron lifetime has been set. The effects of enhancement factors used in calculations have been commented. Finally, we have analysed the effects that f and d electrons cause in positron lifetimes.

1. Introduction

The classification of the elements has been one of the major achievements in the history of Science. This classification was originally derived from empirical experimental results, because the concept of atomic number was unknown to Mendeleev [1]. Since then, the resulting periodic order has been most strikingly reflected in a quantitative manner by most of the physical properties of the elements. A proof of this fact is that about 700 forms of the Periodic Table have been proposed (classified into 146 different types or subtypes) [2, 3].

Positron-Annihilation Spectroscopy (PAS) is a powerful and versatile tool for the study of the microscopic structure of materials [4-7]. Using PAS, detailed experimental information about electronic and atomic structure from the region of the material sampled by the positrons is obtained. PAS measurements for material characterization generally use three techniques: positron lifetime spectroscopy, Doppler broadening analysis and angular correlation measurements. Positron lifetime measurements give information about electron density at the annihilation place. On the other hand, Doppler broadening and angular correlation measurements give information about electron momentum distribution. So, the electronic configuration of the material studied is reflected in the positron annihilation parameters. For example, in Doppler broadening experiments, the high-momentum part is used to distinguish different non-adjacent elements in the Periodic Table [8, 9].

As the annihilation properties of the positron are related to the electronic structure, they also show a periodic behaviour. In 1963, Rodda and Stewart [10] studied the behaviour of the experimental positron lifetime of rare-earth metals and compared it with the radius of the sphere, whose volume is equal to the volume per conduction electron, r'_s (correcting the value by excluding the volume of the ion). However, MacKenzie et al. set a stronger relation in 1975 [11]. They collected experimental bulk lifetimes of many elements and reported their "systematic dependence on atomic number". Also that year, Brandt et al. [12] calculated the lifetime of some elements. They explained that the periodic behaviour of positron lifetime "is linked *prima facie* to the virtual excitation of coupled valence-electron-plasma and single-particle modes in the collective response of the metal electrons to screen the positron charge". Later, in 1976, Welch and Lynn studied the variations of the experimental mean lifetime versus the atomic number, and stated that it "is strikingly similar to that of the atomic volume" [13]. In 1991 Puska found that the trends observed in bulk lifetimes along the 3d, 4d and 5d rows of the Periodic Table are very similar to the behaviour of the Wigner-Seitz radii [14]. However, this periodicity is not only reflected in the positron lifetime. Doppler broadening experiments [9, 15] and positron affinity of elemental metals [16] also show periodic behaviour.

In this work, a systematic Density Functional Theory (DFT) calculation of positron lifetimes has been performed for bulk and monovacancies of most of the elements of the Periodic Table. The main factors influencing bulk and vacancy positron lifetimes for elemental solids have been well understood for more than 30 years. So, our main aim is to show the periodic trends appearing in bulk and monovacancy positron lifetimes. The effort made to calculate and compile systematically the annihilation parameters is important to go deeply into the study of the calculation methods, improving the theoretical background required for a good interpretation of the experimental data. The organization of this paper is as follows: the computational method is explained in section 2; section 3 contains the results of the calculations, the correlation between lifetimes, and the periodic properties of the elements, information about the enhancement factors used in the calculations and the analysis of the effects of f and d electrons; and finally, the conclusions of the work are presented in section 4.

2. Computational method

The calculation of positron properties in solids can be traced back to the late sixties and early seventies (see for instance [17-20]) and since then numerical simulations have become a well developed technique (see the reviews [4, 6] and the recently published paper [21]). Positron states must be calculated self-consistently within the two-component DFT for positron and electron densities. However, the conventional way to treat positron states in solids simplifies the two-component DFT. Within the conventional scheme, an unperturbed electronic ground state for the system is constructed. Then, the positron distribution is calculated by assuming the electron density remains rigid, and by accounting for the electron-positron correlation in terms of a correlation (screening) potential dependent on the electron density. In the case of delocalized positron states, the positron density is vanishingly small at every point of the lattice, and it does not influence the electronic

structure. As a result, for bulk positron states the conventional scheme runs very well. In the case of a positron localized at a lattice defect, the situation is more complicated because the positron attracts electrons, and the average electron density increases near the defect (positron). However, in most applications for positron states at defects, the conventional scheme works very well too. Indeed, the two-component DFT calculations performed by Nieminen et al. [22] and Boronski and Nieminen [23] support the use of the conventional scheme, since the annihilation rates are very close to those obtained with the conventional scheme. This similarity of results between the conventional scheme and the two-component DFT calculation is due to the fact that the larger short-range enhancement compensates the smaller electron density at the positron.

Therefore, in the present work we have used the conventional way of calculation. Firstly, we have solved the electron density of the perfect or defected solid, then we have calculated the positron wave function, and finally, we have determined the positron annihilation rate. We have used a supercell method to compute the electronic densities following (a) the atomic superposition approximation (AT-SUP) developed by Puska and Nieminen [24] and (b) the tight binding version of the Linear Muffin-Tin Orbital method within the Atomic-Spheres Approximation (LMTO-ASA) [25, 26].

(a) AT-SUP method

The AT-SUP approximation of Puska and Nieminen is a simple method that makes use of non-self-consistent unrelaxed electronic densities. It gives satisfactory values of positron lifetimes in metals and semiconductors [24, 27, 28, 29]. The good agreement between the experimental and theoretical lifetimes is mainly due to the fact that the positron annihilation rate is obtained as an integral over the product of positron and electron densities. The positron density relaxes following the electron charge transfer, keeping the value of the positron-electron overlap integral constant. For this reason, positron lifetime calculations are not too sensitive to self-consistency.

In the AT-SUP approximation the electron density $n_-(\mathbf{r})$ of the solid is constructed by superimposing individual atomic charge densities:

$$n_-(\mathbf{r}) = \sum_i n_-^{at}\left(\left|\mathbf{r} - \mathbf{R}_i\right|\right) \tag{1}$$

where n_-^{at} is the free-atom electron density and $\mathbf{R}_i$ runs over the occupied atomic sites. For the crystalline Coulomb potential $V_c(\mathbf{r})$ the same procedure has been used:

$$V_c(\mathbf{r}) = \sum_i V_{at}\left(\left|\mathbf{r} - \mathbf{R}_i\right|\right) \tag{2}$$

where V_{at} is the atomic Coulomb potential due to the electron density and the nucleus. Densities and potentials of the atomic ground-state electronic configuration are obtained self-consistently within the DFT.

The potential felt by the positron in the solid, $V_+(\mathbf{r})$, is obtained by adding to the Coulomb potential, $V_c(\mathbf{r})$, the positron-electron correlation energy, $V_{corr}(n_-(\mathbf{r}))$:

$$V_+(\mathbf{r}) = V_c(\mathbf{r}) + V_{corr}(n_-(\mathbf{r})) \tag{3}$$

where $n_-(r)$ is the electron density. The space is discretized in a three-dimensional mesh that forms an orthorhombic Bravais lattice, where the potential is projected. The discretized Schrödinger equation is solved iteratively at the mesh points by using a numerical relaxation method [30] to obtain the positron wave-function and its energy eigenvalue. Depending on the structure of the element, the density of the cubic mesh varies between 1 and 3 points per atomic unit in each direction. We have checked in some elements that this difference of density of the mesh does not affect the lifetimes.

(b) LMTO-ASA method

LMTO-ASA is a method that makes use of self-consistent electronic densities. It gives satisfactory values of positron lifetimes in metals and semiconductors [14, 28, 29]. In LMTO-ASA calculations the electron density and Coulomb potential are determined self-consistently within spheres centred around nuclei and interstitial sites (when the atomic packing is not dense) of the structure. The spheres fill the whole lattice space and the atomic ones have equal radii. The potential and the charge densities are assumed spherically symmetric inside each sphere. The potential felt by a positron is constructed according to equation (3), and the positron state is solved by using the same methods as used for electron states in the LMTO-ASA. From now on, all the references made to this method will be labelled as LMTO.

The f electrons are a strongly correlated system. However, we have treated the 4f electrons of the lanthanides and the 5f electrons of the actinides as band electrons, and the 4f electrons of the actinides as core like states.

Once we have calculated the electron and positron densities, the positron annihilation rate, the inverse of the positron lifetime, is obtained from the overlap of positron and electron densities as:

$$\lambda = \pi r_o^2 c \int \mathrm{d}\mathbf{r} n_+(\mathbf{r}) n_-(\mathbf{r}) \gamma(\mathbf{r}) \tag{4}$$

where r_o is the classical electron radius, c is the speed of light in the vacuum, $n_+(\mathbf{r})$ is the positron density and $\gamma(\mathbf{r})$ is the so-called enhancement factor. $V_{corr}(\mathbf{r})$ and $\gamma(\mathbf{r})$ have been taken into account by using two different schemes:

1.- within the Local Density Approximation. For the correlation energy the interpolation formula by Boroński and Nieminen [23] based on the results by Arponen and Pajanne [31] is used; and for the enhancement factor the widely used form [23] based on Lantto´s [32] hypernetted chain approximation calculations:

$$\gamma_{BN}(r_s) = 1 + 1.23 r_s + 0.8295 r_s^{3/2} - 1.26 r_s^2 + 0.3286 r_s^{5/2} + \frac{1}{6}\left(1 - \frac{1}{\varepsilon_\infty}\right) r_s^3, \quad (5)$$

where ε_∞ is the high-frequency dielectric constant of the material and r_s is the radius of a sphere whose volume is equal to the volume per conduction electron. This last parameter is related to the electron density, $n_-(\mathbf{r})$, by:

$$r_s = \left(\frac{3}{4\pi n_-}\right)^{1/3}. \quad (6)$$

Results obtained with this scheme are labelled with BN.

2.- within the Generalized Gradient Approximation (GGA). The correlation energy and the enhancement factor due to Barbiellini et al. [28, 33] are used, both based on the results by Arponen and Pajanne [31]. In this scheme the enhancement factor is given by:

$$\gamma_{GGA} = 1 + (\gamma_{LDA} - 1) e^{-\alpha\varepsilon}, \quad (7)$$

where γ_{LDA} is:

$$\gamma_{LDA}(r_s) = 1 + 1.23 r_s - 0.0742 r_s^2 + \frac{1}{6} r_s^3, \quad (8)$$

and α is an adjustable parameter and ε is obtained from this expression:

$$\varepsilon = \frac{|\nabla n_-|^2}{(n_- q_{TF})^2} = \frac{|\nabla \ln n_-|^2}{{q_{TF}}^2}, \quad (9)$$

with $(q_{TF})^{-1}$ the local Thomas-Fermi screening length. ε is a parameter proportional to the lowest–order gradient correction to the correlation hole density in the Local Density Approximation. The results obtained with these two schemes will be labelled LDA and GGA.

The α parameter is determined so that the calculated and experimental lifetimes agree as well as possible for a large number of different types of solids. Barbiellini et al. [28, 33] found that α = 0.22 value gives

lifetimes in good agreement with experiments for different types of electronic environments, including simple metals (Na and K of 1st group), transition metals (Fe, 8th group; Ni, 10th group; Cu, 11th group; Al, 13th group), group-IV semiconductors (Si and Ge) and III-V and II-V compound semiconductors (GaAs, InP and CdTe). $\alpha = 0$ gives the Local Density Approximation limit of this enhancement factor, that is to say γ_{LDA}. As it was pointed before [28, 34], the lifetimes calculated by using γ_{LDA} are always much shorter than those calculated with γ_{BN} and γ_{GGA}, and the experimental ones.

The positron lifetime calculations have been performed for most of the elements of the Periodic Table. The unit cell of the crystalline structure has been used as supercell for bulk calculations. In vacancy calculations one atom is removed from the supercell to produce a vacancy. If the supercell is large enough, the vacancy does not interact with its periodic image and the system describes quite well an isolated vacancy. However, in practice, the supercell size cannot be made arbitrarily large. The size of the supercells in AT-SUP method has been increased till convergence. The maximum number of atoms per supercell used to reach convergence has been: 511 atoms (orthorhonbic structure), 511 atoms (diamond structure), 499 atoms (tetragonal structure), 463 atoms (cubic structure), 255 atoms (FCC structure), 249 atoms (hexagonal structure), 383 atoms (rhombohedric structure) and 127 atoms (BCC structure). Self-consistent calculations within the LMTO method for monovacancies are much more computationally demanding than the ones performed with the AT-SUP method, particularly for large supercells. Moreover, for large supercells, calculations performed employing the Γ point for the positron density or the lowest lying band in the Brillouin zone give identical values for the monovacancy positron lifetime [29]. Therefore, for the calculations within the LMTO method for monovacancies we have integrated over the lowest positron band in the Brillouin zone, because it gives faster convergence in the supercell approach [29]. The maximum number of atoms used within the LMTO has been: 127 atoms (hexagonal structure), 124 atoms (BCC structure), 107 atoms (rhombohedric structure), 63 atoms (FCC structure), 53 atoms (tetragonal structure), 53 atoms (diamond structure), 31 atoms (orthorhonbic structure) and 28 atoms (cubic structure).

For the monovacancy supercells no relaxation in the atomic positions have been performed, this means that the ions neighbouring the vacancy are not allowed to relax from their ideal lattice positions. It is known that an accurate calculation of the monovacancy lifetime needs atomic relaxation. In insulators and semiconductors the atomic relaxation may be important, and can change with the charge state of the defect and with the localization of the positron [35, 36], but it is not large in metals [37-39]. However, the study of the effects of these relaxations goes beyond the aims of this work.

Some elements get a different crystal structure for different conditions of pressure and temperature. When an element has more than one possible structure, we have chosen the most common one in normal conditions. The rare gases are not solid in normal conditions, so we have studied the solid state at very low temperature. The crystal structure and the lattice parameters used in the calculations are shown in table 1, and have been taken from experimental data [40-42].

In BN calculations, the semiempirical correction based on high-frequency dielectric constant of equation 5 [43] is used for the elements of table 2, which shows experimental values of dielectric constants [41, 42, 44]. For several insulators (As, Cl, Br and I) we have not found any value for their dielectric constants in the literature. So, these insulators and rare gases have been treated as metals, using $\varepsilon_\infty = \infty$. In the rare gases a special treatment is needed; however, it goes beyond the aim of this work. In LDA and GGA frameworks, this correction is not necessary.

3. Results and discussion

3.1. Bulk and monovacancy lifetimes

The positron lifetime values calculated for the bulk state are given in table 3 and table 4. The values of table 3 correspond to calculations made within the AT-SUP method with BN and GGA approximations. The results obtained within the LMTO method with BN and GGA approximations are given in table 4.

On the other hand, the results of monovacancy lifetime calculations (BN and GGA) are shown in tables 5 and 6 for AT-SUP and LMTO methods, respectively. Table 6 do not present monovacancy lifetime of actinides due to convergence problems with the LMTO code. The bulk and monovacancy lifetime results are in agreement with previously reported values (Barbiellini et al. [28, 33]).

Table 7 shows the AT-SUP results of bulk and monovacancy lifetimes obtained within the LDA framework. As mentioned before, these values are shorter than BN and GGA ones, but show the same trend.

Finally, experimental positron lifetime values in bulk and monovacancy states (see [45] and the references therein) are given in table 8 for comparison with theoretical ones. Even though the first positron lifetime measurements were made more than 50 years ago [46-49], nowadays the experimental data does not reach to all elements of the Periodic Table. Moreover, there is much more data for bulk than for monovacancy lifetimes. In some elements, there is no experimental data, but in others the experimental data and the scattering among them is large. Therefore, the selection of the measurements is a difficult affair, and we have fixed some conditions to select data with a minimum of quality and coherence. The chosen conditions might not be the best ones; however, a selection has to be made. First of all, we have considered data from 1975 up to now. We have chosen this requirement because the POSITRONFIT program was developed around 1972 [50], and improved in 1974 [51], becoming a common, or even standard, tool for the positron community to analyze experimental spectra. Furthermore, we have chosen a maximum of 320 ps for the full width at half maximum of the resolution function. Finally, we have taken as the limit value for the error of the measurement ±5 ps in bulk lifetimes, and ±10 ps in monovacancy lifetimes. In the case the literature gives different lifetime values following the previous requirements, the average value has been calculated. It is expected that the systematic errors from various experiments would be cancelled. In order to fill the extremes of the Periodic Table, we have taken into account two experimental works in alkalines (Li, Na, K, Rb, Cs) [52] and ideal

gases (Ar, Xe) [53] that do not fit the previous requirements. However, these works have been used in previous reviews.

3.2. Positron lifetime among periodic properties

In order to present the expected periodic behaviour of the positron lifetime, figure 1 shows calculated bulk (circles) and monovacancy (squares) positron lifetimes versus atomic number. Plotted lifetimes have been calculated within the AT-SUP method using BN approximation for the enhancement factor and correlation energy. Experimental values of table 8 have not been plotted, but follow the same theoretical trends.

The atomic volume of the elements [54] has been plotted against atomic number in figure 1, too. The atomic volume (defined as the product of the atomic weight and the specific volume of an element at normal conditions) is a good magnitude to measure the size of one single atom in its own structure and is defined for all the elements in the same way. This is one of the main reasons why the atomic volume has been chosen, even though different magnitudes such as metallic radius, ionic radius, covalent radius ... have been defined for the quantification of the atomic size. However, from these last magnitudes it is not possible to obtain an accurate value for the volume. Besides, most of radii types are defined only for some kind of elements and not for all. The atomic volume, as other properties of the elements, has a strong relation with the arrangement of the electrons in atomic shells [55-59]. For this reason, the atomic volume is a periodic function of the atomic number, as it was formulated first by Lothar Meyer in 1870 (with reference to atomic weight, not to atomic number) [60].

The similarity between atomic volume curve and the two positron lifetime curves on figure 1 is very big. Different factors affect positron lifetimes, like many-body enhancements, the region occupied by the positron (which in the bulk is less than the atomic volume), and the electrons available for annihilation in that region. However, the three graphics show the same periodic behaviour, reproducing also many little details. Although the lifetime has been compared with other periodic properties like r_s parameter, Wigner-Seitz radii,... the relation with the atomic volume seems to be more fundamental. This work confirms previous statements [13], but also proves that the monovacancy lifetimes exhibit the same periodic behaviour. Despite the localization of the wave function, the positron lifetime in bulk (delocalized state) and at a monovacancy (localized state) are still related to a single atom's volume, and this is independent of the methods of calculation used in this work. When an atom is removed from perfect crystal structure, the remaining volume is mainly related to that atom. But removing more than one atom the remaining volume is more structure dependent [34].

The lifetimes of some elements (As, Br, Kr, I and Xe) do not follow the trends of atomic volume (see figure 1). This special behaviour will be analyzed in section 3.3.

The periodic behaviour of the positron lifetime found for AT-SUP method within BN approximation is also found using GGA and LDA frameworks, as well as in the calculations performed with the LMTO code by using BN and GGA approximations.

3.3. Enhancement factors

The enhancement factor is of crucial importance in positron lifetime calculations [61, 62, 63 and references therein]. For this reason, it is necessary to study the behaviour of enhancement factors used in these calculations.

As it has been pointed before, in figure 1 the lifetimes of some elements (As, Br, Kr, I and Xe) do not follow the periodic trends as it could be predicted from the atomic volume. In the case of insulators, a model based in atomic polarizabilities, estimated from the Clausius-Mossotti relation, has been used too [43], where the dielectric constant of the solid is also needed. For the rare gases a special framework is needed. However, in these calculations, some insulators (As, Cl, Br and I) and all the rare gases (Ne, Ar, Kr and Xe) have been considered as metals ($\varepsilon_\infty = \infty$). So the real lifetimes of BN approximation for these eight elements are really longer and closer to GGA values than the calculated ones (see tables from 3 to 6).

Boroński-Nieminen enhancement, γ_{BN} (eq. 5), is based on the many-body calculations performed by Lantto [32]. Stachowiak and Boroński reported that the calculations of Lantto start from a physically oversimplified trial function [64]. Fraser in her Ph.D. thesis failed to reproduce Lantto's results using a Quantum Monte Carlo approach [65]. However, Boroński reported that the lifetimes calculated based on Fraser's results are quite inaccurate, becoming even unreasonable for $r_s > 4$ [66].

Boroński-Nieminen parameterization, used in this work, agrees very well the positron enhancements calculated by Arponen and Pajanne [67], Gondzik and Stachowiak [68] and Rubaszek and Stachowiak [69] for $r_s \leq 8$ (see Fraser´s thesis [65], page 143). Indeed, Stachowiak and Boroński [64] pointed out that γ_{BN} is the best formula to fit the experimental lifetimes in metals. In bulk metals, r_s usually runs from 2 to 6 (in Cs it gets the maximum value, 5'6). However, the enhancement factor of Boroński-Nieminen approach has two important problems at low densities (see figure 1 in [28]):

a) The scaled proton limit rule [70] is violated for $r_s \geq 9$. This is the upper bound for all the enhancement factors.

b) For r_s greater than 6 the lifetimes obtained with γ_{BN} do not increase monotonically with r_s. For this reason, the lifetimes can not reach the 500 ps limit.

These two problems appear when the electronic density is low (semiconductors, insulators, rare gases, vacancies, voids,…). In the case of semiconductors and insulators, the problem has been tackled using semiempirical corrections introduced by Puska et al. [43]. Using this correction, calculated lifetimes in the BN approximation fit well the experimental ones, even when the densities are low.

In the case of γ_{LDA} (eq. 8), the enhancement factor has the same form as that used by Stachowiak and Lach [71]. γ_{LDA} has been obtained fitting the Arponen-Pajanne data points only up to $r_s = 5$ [28]. In Arponen-Pajanne data, the Friedel sum rule is violated for $r_s = 6$ and 8, and the scaled proton limit value is crossed at $r_s = 8$ [31]. As γ_{GGA} (eq. 7) is obtained from γ_{LDA}, the LDA and GGA enhancements are both not very reliable for

low electron densities, like BN enhancement. Calculations made in systems of low electron densities using GGA approximation with the universal value $\alpha = 0'22$ do not give reasonable lifetimes [63, 72]. For example, in order to get lifetime values near the experimental ones for C_{60}, it is necessary to fit the α parameter to a "suitable" value [72].

As a result of all of these problems in the enhancements, we have to be very careful with all of the calculated lifetimes near or longer than 400 ps. So, more theoretical work is needed for low density systems.

3.4. f and d electrons

Figure 2 represents the behaviour of positron lifetimes for bulk (circles) and monovacancy (squares) in elements from $_{57}$La to $_{80}$Hg of the 6th row of the Periodic Table. As f and d shells get filled between $_{57}$La and $_{80}$Hg, positron lifetimes of these elements can be used for studying the effects of f and d electrons in positron annihilation properties. The represented lifetimes are those obtained within the LMTO method using BN (empty symbols) and GGA (full symbols) approximations (see table 4 and 6). Experimental lifetimes from table 8 have been plotted as a reference. As it is known, GGA calculation method uses the gradient of electronic density. So, for an accurate calculation, it is necessary to use a self-consistent electronic density, enabling charge-transfer in the system. Therefore, in order to make a better comparison between BN and GGA calculation methods, we have represented LMTO results.

First of all, we must remark that figure 2 shows the same general behaviour for bulk and for monovacancy lifetimes. As electrons fill the d shell between $_{71}$Lu and $_{80}$Hg, the bulk and monovacancy lifetimes show the same parabolic behaviour. As d electrons start filling the shell, the lifetime reduces considerably, and, after reaching a minimum near the half-filled shell (d^6), it rises up again. This trend is explained simply with the behaviour of the atomic volume (see figure 1). This general dependence of positron lifetime with the outermost d electrons in bulk and monovacancies is independent of the row of the Periodic Table. The 4th row, from $_{21}$Sc to $_{30}$Zn elements, and the 5th row, from $_{39}$Y to $_{48}$Cd elements, show the same behaviour.

On the other hand, in lanthanides (from $_{57}$La to $_{70}$Yb) the positron lifetime remains nearly constant as 4f shell fills up ($\tau_{bulk} \approx 200$ ps and $\tau_{vacancy} \approx 315$ ps). The increasing number of the f inner electrons is responsible for the magnetic properties of lanthanides, and the outermost s-d electrons determine the bonding and other electronic properties [73-75]. So, the f inner electrons can not cause appreciable changes in positron lifetimes, since the positron wave-function is mainly located in the interstitial space. However, the lifetimes of $_{63}$Eu and $_{70}$Yb are larger than the other lanthanides, because they have a half-filled ($_{63}$Eu) or completely filled 4f shell ($_{70}$Yb). For this reason, Eu and Yb get a more closed electronic structure and show a particular behaviour in several properties (atomic volume, electronegativity, melting point, ionization potentials,...). It has to be remarked that in the case of actinides (from $_{90}$Th to $_{97}$Bk), the positron lifetime does not remain constant (see table 4). Indeed, it follows a parabolic behaviour (see figure 1) similar to the one found in d shells. This behaviour is in agreement with previous statements [76-78], which indicate that opposite to 4f electrons, 5f

electrons are relatively delocalized and can contribute to the bonding. This special electronic structure makes positron lifetime (and other physical properties) behaviour more complex.

However, there are some especial features superposed to these general trends. In bulk, for the first lanthanide elements (from $_{57}$La to $_{62}$Sm) GGA lifetimes are similar to BN ones. But, between $_{64}$Gd and $_{69}$Tm, GGA lifetime is a little bit larger than BN one, about 4 ps (see table 4). There are only three experimental bulk lifetimes from the literature. These experimental lifetimes are from different researcher groups and not from very recent measurements. So, it would be interesting to get new experimental data in the lanthanides.

In monovacancies, lifetimes of lanthanides have a particular behaviour (see figure 2). For most of the elements of the Periodic Table, GGA lifetimes are usually larger than BN ones (see table 6). Opposite to this general trend, the GGA lifetimes of lanthanides are shorter than BN ones, about 3-5 ps (see table 6). As it is known, the positron is much localized in a monovacancy and the probability of annihilating with inner electrons is much lower than in bulk. Taking into account that f electrons are inner electrons, they have not an appreciable effect in these lifetimes. So, the values of these lifetimes are due to the external electronic configuration, similar to the outer electronic configuration of $_{57}$La. As in bulk case, $_{63}$Eu and $_{70}$Yb are outside this trend, showing a special feature. It could be expected them to follow the same trend as the other lanthanides. However, they show the opposite, GGA lifetimes are longer than BN ones.

A lot of work has been made to understand the behaviour of d electrons [79, 34]. In the bulk case (see figure 2), for La, Ce and Lu the BN lifetimes are longer than the GGA ones. However, as electrons start to fill the d shell, the difference gets smaller. And from d^3 ($_{73}$Ta) to d^{10} ($_{80}$Hg) GGA lifetime is longer than BN one, increasing the difference as d orbitals are being occupied. The GGA correction to the Local Density Approximation is roughly proportional to the number of outermost d-electrons in the atom [34]. The four experimental lifetimes found in the literature fit very well GGA values in this region. Local Density Approximation calculations made with different parameterizations, BN (table 3) and LDA (table 7), show that the positron lifetimes for bulk transition metals are systematically too short in comparison with the experimental values, and GGA fits better experimental values.

In monovacancies the trend is similar to that of the bulk. BN lifetime is longer than GGA one for the first elements, from Lu (d^1) to Ta (d^3). At W (d^4) and Re (d^5) BN and GGA lifetimes are the same. And finally, from Os (d^6) to Hg (d^{10}) GGA lifetimes are longer than BN ones. So, the trend is the same, but in monovacancies more d electrons are needed for GGA lifetimes to get longer than BN ones. In monovacancies, the calculated lifetimes and the experimental ones show a larger difference than in the bulk case.

In lifetimes calculated within AT-SUP method, BN and GGA values follow the very same general trends. However, the differences between GGA and BN lifetimes are much greater, due to the lack of self-consistency of the electronic densities used in calculations.

4. Conclusions

The systematic calculations performed in this work set a theoretical support for understanding and interpreting different positron lifetime experiments. It has to be remarked that there are many firstly calculated elements among these lifetimes.

As a result of this positron lifetime calculations, a well-known trend for the bulk lifetimes has been systematically proved again, and the same trend has been established for the calculated monovacancy lifetimes too. In both cases, the correlation with atomic volume of the elements is direct, and it is demonstrated that the trends of atomic volumes can be extrapolated to positron lifetime values. However, a direct quantitative extrapolation on the absolute values can not be done in the whole Periodic Table due to the fact that positron lifetimes reach saturation at 500 ps. This fact deforms the trends compared to the atomic volume. So, it is concluded that the positron lifetime of bulk and vacancy is a periodic property of the elements.

Acknowledgment

The authors acknowledge N. de Diego and J. del Rio for some useful ideas for the work. We also want to thank J. M. Igartua for interesting discussion about structural data of some elements, and X. Artetxe for technical assistance.

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TABLE CAPTIONS

Table 1. Structural data of the elements. The crystal structures of the elements are named as: cubic (CUB), body-centered cubic (BCC), face-centered cubic (FCC), cubic diamond (DIAM), rhombohedral (RHOMB), tetragonal (TETRA), orthorhombic (ORTHOR), hexagonal close-packed (HEX) and double hexagonal close-packed (HEX/abac). (*) Manganese has a cubic complex structure (see Donohue [40]).

Table 2. High-frequency dielectric constant of some elements used in calculations.

Table 3. Calculated positron bulk lifetimes using AT-SUP method with BN and GGA parametrizations.

Table 4. Calculated positron bulk lifetimes using LMTO method with BN and GGA parametrizations.

Table 5. Calculated positron monovacancy lifetimes using AT-SUP method with BN and GGA parametrizations.

Table 6. Calculated positron monovacancy lifetimes using LMTO method with BN and GGA parametrizations.

Table 7. Calculated positron lifetimes using AT-SUP method with LDA parametrization for bulk and monovacancy states.

Table 8. Experimental positron lifetimes for bulk and monovacancy states.

TABLE 1

H																	**He**
Li BCC 3.49	**Be** HEX 2.29 3.59											**B**	**C** DIAM 3.57	**N**	**O**	**F**	**Ne** FCC 4.43
Na BCC 4.23	**Mg** HEX 3.21 5.21											**Al** FCC 4.05	**Si** DIAM 5.43	**P** ORTHOR 3.32 10.52 4.39	**S**	**Cl** ORTHOR 6.24 4.48 8.26	**Ar** FCC 5.31
K BCC 5.23	**Ca** FCC 5.58	**Sc** HEX 3.31 5.28	**Ti** HEX 2.95 4.68	**V** BCC 3.03	**Cr** BCC 2.88	**Mn** CUB (*) 8.91	**α-Fe** BCC 2.87	**α-Co** HEX 2.51 4.07	**Ni** FCC 3.52	**Cu** FCC 3.61	**Zn** HEX 2.66 4.94	**Ga** ORTHOR 4.52 7.66 4.53	**Ge** DIAM 5.66	**As** RHOMB 3.76 10.55	**Se** HEX 4.36 4.95	**Br** ORTHOR 6.67 4.48 8.72	**Kr** FCC 5.64
Rb BCC 5.59	**Sr** FCC 6.08	**Y** HEX 3.65 5.73	**Zr** HEX 3.23 5.15	**Nb** BCC 3.30	**Mo** BCC 3.15	**Tc** HEX 2.74 4.40	**Ru** HEX 2.70 4.28	**Rh** FCC 3.80	**Pd** FCC 3.89	**Ag** FCC 4.09	**Cd** HEX 2.98 5.62	**In** TETRA 3.25 4.95	**β-Sn** TETRA 5.83 3.18	**Sb** RHOMB 4.31 11.27	**Te** HEX 4.45 5.92	**I** ORTHOR 7.27 4.80 9.80	**Xe** FCC 6.13
Cs BCC 6.05	**Ba** BCC 5.02	**La** HEX 3.75 6.07	**Hf** HEX 3.20 5.06	**Ta** BCC 3.31	**W** BCC 3.16	**Re** HEX 2.76 4.46	**Os** HEX 2.74 4.33	**Ir** FCC 3.84	**Pt** FCC 3.92	**Au** FCC 4.08	**β-Hg** TETRA 4.00 2.83	**Tl** HEX 3.46 5.53	**Pb** FCC 4.95	**Bi** RHOMB 4.55 11.86	**Po** CUB 3.35	**At**	**Rn**
Fr	**Ra** BCC 5.15	**Ac** FCC 5.31															

	γ-Ce FCC 5.16	**Pr** HEX/abac 3.67 11.83	**Nd** HEX 3.66 5.91	**Pm** HEX/abac 3.65 11.65	**Sm** RHOMB 3.63 26.22	**Eu** BCC 4.61	**Gd** HEX 3.64 5.78	**Tb** HEX 3.60 5.69	**Dy** HEX 3.59 5.65	**Ho** HEX 3.58 5.62	**Er** HEX 3.56 5.59	**Tm** HEX 3.54 5.56	**Yb** FCC 5.49	**Lu** HEX 3.51 5.56
	Th FCC 5.08	**Pa** TETRA 3.93 3.24	**U** ORTHOR 2.85 5.87 4.96	**Np** ORTHOR 4.72 4.89 6.66	**Pu** FCC 4.64	**Am** HEX/abac 3.47 11.24	**Cm** HEX/abac 3.50 11.33	**Bk** FCC 5.00	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**

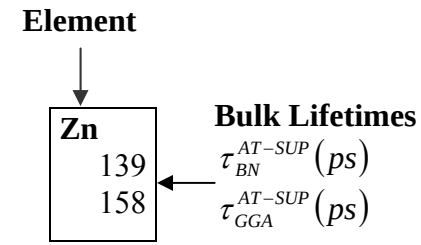
Element

Crystal Structure → ORTHOR **U** 2.85 5.87 4.96 ← *a* (Å), *b* (Å), *c* (Å)

TABLE 2

Element	ε_∞
C	5.62
Si	11.9
P	6.1
Ge	16.0
Se	13.98
Sn	23.8
Te	29.5

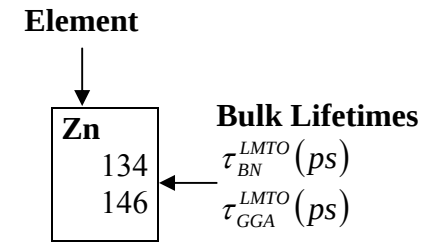
TABLE 3



H — —																	**He** — —
Li 301 285	**Be** 137 129											**B** — —	**C** 93 93	**N** — —	**O** — —	**F** — —	**Ne** 237 566
Na 322 342	**Mg** 233 226											**Al** 168 160	**Si** 218 207	**P** 230 226	**S** — —	**Cl** 248 352	**Ar** 271 483
K 367 402	**Ca** 288 281	**Sc** 197 199	**Ti** 147 153	**V** 116 124	**Cr** 104 118	**Mn** 106 115	**α-Fe** 102 112	**α-Co** 97 108	**Ni** 96 108	**Cu** 108 130	**Zn** 139 158	**Ga** 190 202	**Ge** 222 228	**As** 184 195	**Se** 286 355	**Br** 245 322	**Kr** 281 459
Rb 376 420	**Sr** 309 305	**Y** 217 215	**Zr** 160 162	**Nb** 126 134	**Mo** 109 118	**Tc** 98 105	**Ru** 94 106	**Rh** 97 110	**Pd** 107 130	**Ag** 125 150	**Cd** 159 184	**In** 183 201	**β-Sn** 193 201	**Sb** 213 227	**Te** 289 345	**I** 262 325	**Xe** 297 444
Cs 387 437	**Ba** 305 303	**La** 209 209	**Hf** 150 156	**Ta** 119 125	**W** 102 108	**Re** 94 101	**Os** 89 96	**Ir** 90 98	**Pt** 99 116	**Au** 112 131	**β-Hg** 154 184	**Tl** 185 214	**Pb** 190 214	**Bi** 230 257	**Po** 231 262	**At** — —	**Rn** — —
Fr — —	**Ra** 307 308	**Ac** 199 197															

γ-Ce 204 210	**Pr** 207 213	**Nd** 207 214	**Pm** 206 214	**Sm** 206 214	**Eu** 273 278	**Gd** 204 207	**Tb** 204 214	**Dy** 204 214	**Ho** 204 215	**Er** 202 214	**Tm** 201 213	**Yb** 256 265	**Lu** 196 202
Th 173 171	**Pa** 139 142	**U** 117 121	**Np** 119 125	**Pu** 145 155	**Am** 171 182	**Cm** 172 180	**Bk** 176 181	**Cf** — —	**Es** — —	**Fm** — —	**Md** — —	**No** — —	**Lr** — —

TABLE 4



H — —																	**He** — —
Li 301 281	**Be** 137 128											**B** — —	**C** 99 97	**N** — —	**O** — —	**F** — —	**Ne** 206 534
Na 324 334	**Mg** 232 216											**Al** 165 153	**Si** 222 211	**P** 237 223	**S** — —	**Cl** 250 275	**Ar** 268 435
K 368 391	**Ca** 290 279	**Sc** 196 193	**Ti** 144 146	**V** 114 119	**Cr** 99 105	**Mn** 102 109	**α-Fe** 101 110	**α-Co** 96 107	**Ni** 96 108	**Cu** 105 118	**Zn** 134 146	**Ga** 165 167	**Ge** 223 228	**As** 181 188	**Se** 281 313	**Br** 248 270	**Kr** 289 448
Rb 377 408	**Sr** 311 300	**Y** 215 208	**Zr** 156 154	**Nb** 120 122	**Mo** 103 106	**Tc** 94 99	**Ru** 89 95	**Rh** 92 100	**Pd** 102 113	**Ag** 122 137	**Cd** 154 167	**In** 181 190	**β-Sn** 182 179	**Sb** 208 211	**Te** 286 307	**I** 260 268	**Xe** 299 416
Cs 387 426	**Ba** 307 304	**La** 208 207	**Hf** 146 146	**Ta** 115 117	**W** 98 100	**Re** 90 93	**Os** 85 89	**Ir** 86 92	**Pt** 93 101	**Au** 108 119	**β-Hg** 146 161	**Tl** 183 203	**Pb** 188 197	**Bi** 224 233	**Po** 214 216	**At** — —	**Rn** — —
Fr — —	**Ra** 308 309	**Ac** 195 192															

γ-Ce 197 196	**Pr** 200 200	**Nd** 202 202	**Pm** 201 202	**Sm** 200 203	**Eu** 271 266	**Gd** 205 209	**Tb** 201 205	**Dy** 200 205	**Ho** 200 206	**Er** 199 205	**Tm** 198 203	**Yb** 254 253	**Lu** 193 192
Th 170 167	**Pa** 125 125	**U** 107 108	**Np** 116 117	**Pu** 137 141	**Am** 164 171	**Cm** 171 180	**Bk** 181 193	**Cf** — —	**Es** — —	**Fm** — —	**Md** — —	**No** — —	**Lr** — —

TABLE 5

Element

Monovacancy Lifetimes

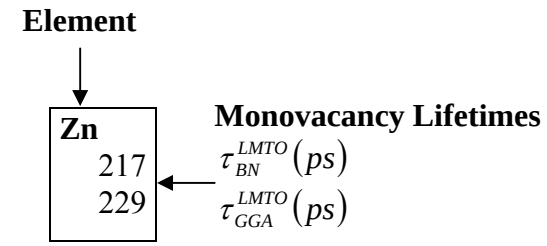
$\tau_{BN}^{AT-SUP}(ps)$

$\tau_{GGA}^{AT-SUP}(ps)$

H																	**He**
—																	—
—																	—
Li	**Be**											**B**	**C**	**N**	**O**	**F**	**Ne**
338	180											—	110	—	—	—	239
315	165											—	109	—	—	—	562
Na	**Mg**											**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
362	299											244	252	251	—	249	274
384	292											231	241	245	—	353	483
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**α-Fe**	**α-Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
411	366	291	236	198	180	198	177	168	166	169	196	239	254	236	297	251	287
452	367	281	228	194	188	199	183	177	177	200	224	255	263	255	359	324	458
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**β-Sn**	**Sb**	**Te**	**I**	**Xe**
419	387	319	262	222	200	185	177	178	173	200	231	273	277	275	329	290	320
475	398	311	254	224	206	186	191	198	220	245	276	303	294	303	353	329	444
Cs	**Ba**	**La**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**β-Hg**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
429	392	322	254	217	194	183	175	175	177	191	218	268	277	288	293	—	—
496	399	310	252	217	197	188	184	189	191	233	270	325	329	335	345	—	—
Fr	**Ra**	**Ac**															
—	394	317															
—	415	306															

γ-Ce	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
316	318	318	316	314	366	312	311	310	309	307	305	346	300
302	306	306	307	307	378	309	307	307	307	307	306	364	301
Th	**Pa**	**U**	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**
292	250	218	203	259	285	287	290	—	—	—	—	—	—
284	238	208	199	255	287	289	299	—	—	—	—	—	—

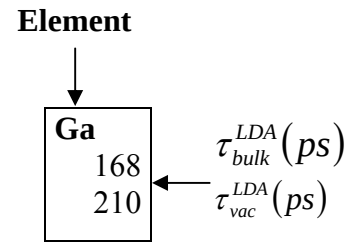
TABLE 6



H — —																	**He** — —
Li 330 308	**Be** 183 161											**B** — —	**C** 118 114	**N** — —	**O** — —	**F** — —	**Ne** 244 556
Na 363 377	**Mg** 308 292											**Al** 250 237	**Si** 262 245	**P** 275 260	**S** — —	**Cl** 280 321	**Ar** 290 456
K 409 446	**Ca** 374 364	**Sc** 298 282	**Ti** 242 234	**V** 203 200	**Cr** 184 184	**Mn** 194 196	**α-Fe** 181 188	**α-Co** 172 182	**Ni** 169 182	**Cu** 178 194	**Zn** 217 229	**Ga** 238 240	**Ge** 265 266	**As** 253 267	**Se** 326 392	**Br** 300 337	**Kr** 323 482
Rb 415 466	**Sr** 388 393	**Y** 324 311	**Zr** 269 258	**Nb** 226 220	**Mo** 205 204	**Tc** 191 191	**Ru** 183 187	**Rh** 185 194	**Pd** 192 209	**Ag** 212 236	**Cd** 251 273	**In** 278 298	**β-Sn** 280 283	**Sb** 290 307	**Te** 350 400	**I** 329 370	**Xe** 353 473
Cs 423 499	**Ba** 395 395	**La** 328 321	**Hf** 261 253	**Ta** 224 219	**W** 203 203	**Re** 191 191	**Os** 184 188	**Ir** 185 193	**Pt** 192 206	**Au** 206 228	**β-Hg** 234 264	**Tl** 278 320	**Pb** 293 324	**Bi** 299 318	**Po** 312 346	**At** — —	**Rn** — —
Fr — —	**Ra** 393 426	**Ac** 324 324															

γ-Ce 315 312	**Pr** 317 312	**Nd** 317 312	**Pm** 315 311	**Sm** 314 311	**Eu** 362 373	**Gd** 316 314	**Tb** 312 308	**Dy** 311 308	**Ho** 311 307	**Er** 309 305	**Tm** 307 304	**Yb** 350 355	**Lu** 305 297

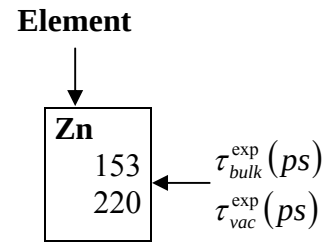
TABLE 7



H — —																	**He** — —
Li 261 294	**Be** 123 158											**B** — —	**C** 84 98	**N** — —	**O** — —	**F** — —	**Ne** 222 223
Na 286 326	**Mg** 203 260											**Al** 148 212	**Si** 184 210	**P** 188 205	**S** — —	**Cl** 221 223	**Ar** 246 250
K 332 387	**Ca** 249 326	**Sc** 173 253	**Ti** 132 206	**V** 106 174	**Cr** 96 160	**Mn** 98 175	**α-Fe** 94 157	**α-Co** 90 150	**Ni** 90 149	**Cu** 100 153	**Zn** 125 177	**Ga** 168 210	**Ge** 190 216	**As** 163 208	**Se** 244 257	**Br** 218 223	**Kr** 253 260
Rb 343 401	**Sr** 269 350	**Y** 189 278	**Zr** 142 228	**Nb** 114 195	**Mo** 100 176	**Tc** 91 163	**Ru** 88 158	**Rh** 90 159	**Pd** 99 157	**Ag** 115 180	**Cd** 143 205	**In** 162 241	**β-Sn** 171 243	**Sb** 187 242	**Te** 250 289	**I** 231 260	**Xe** 267 294
Cs 356 420	**Ba** 265 355	**La** 183 281	**Hf** 135 221	**Ta** 109 191	**W** 94 172	**Re** 88 162	**Os** 83 156	**Ir** 84 157	**Pt** 92 160	**Au** 103 172	**β-Hg** 139 196	**Tl** 165 239	**Pb** 169 247	**Bi** 202 256	**Po** 204 261	**At** — —	**Rn** — —
Fr — —	**Ra** 267 360	**Ac** 174 276															

Ce 179 275	**Pr** 182 277	**Nd** 182 277	**Pm** 181 275	**Sm** 181 274	**Eu** 238 327	**Gd** 179 273	**Tb** 180 272	**Dy** 179 271	**Ho** 179 270	**Er** 178 268	**Tm** 177 267	**Yb** 223 308	**Lu** 172 262
Th 153 254	**Pa** 125 217	**U** 107 190	**Np** 109 178	**Pu** 131 225	**Am** 152 249	**Cm** 153 251	**Bk** 156 254	**Cf** — —	**Es** — —	**Fm** — —	**Md** — —	**No** — —	**Lr** — —

TABLE 8



H — —																	**He** — —
Li 291 —	**Be** 137 —											**B** — —	**C** 107 —	**N** — —	**O** — —	**F** — —	**Ne** — —
Na 338 —	**Mg** 225 254											**Al** 165 244	**Si** 219 272	**P**	**S** — —	**Cl**	**Ar** 430 —
K 397 —	**Ca**	**Sc** 230 —	**Ti** 150 222	**V** 124 191	**Cr** 120 150	**Mn**	**α-Fe** 111 175	**α-Co** 119 —	**Ni** 109 180	**Cu** 120 180	**Zn** 153 220	**Ga** 198 —	**Ge** 228 279	**As**	**Se** 335 —	**Br**	**Kr**
Rb 406 —	**Sr**	**Y** 249 —	**Zr** 164 252	**Nb** 120 210	**Mo** 106 170	**Tc**	**Ru**	**Rh**	**Pd** 98 —	**Ag** 130 208	**Cd** 184 252	**In** 196 270	**β-Sn** 200 242	**Sb** 214 275	**Te**	**I**	**Xe** 400 —
Cs 418 —	**Ba**	**La** 241 —	**Hf**	**Ta** 120 203	**W** 105 195	**Re**	**Os**	**Ir**	**Pt** 99 168	**Au** 116 205	**β-Hg**	**Tl** 226 258	**Pb** 204 294	**Bi** 240 325	**Po**	**At** — —	**Rn** — —
Fr — —	**Ra**	**Ac**															

γ-Ce	**Pr**	**Nd**	**Pm**	**Sm** 199 —	**Eu**	**Gd** 230 —	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**

FIGURE CAPTIONS

Figure 1. Atomic volume (filled circles) and positron lifetimes plotted against atomic number. Positron lifetimes are calculated in bulk (circles) and monovacancy (squares) states within the AT-SUP method using BN approximation.

Figure 2. Bulk (circles) and monovacancy (squares) positron lifetimes of elements from La to Hg (6th row of the Periodic Table) versus atomic number. Lifetimes have been calculated within the LMTO using BN (open symbols) and GGA (filled symbols) approximations.

FIGURE 1

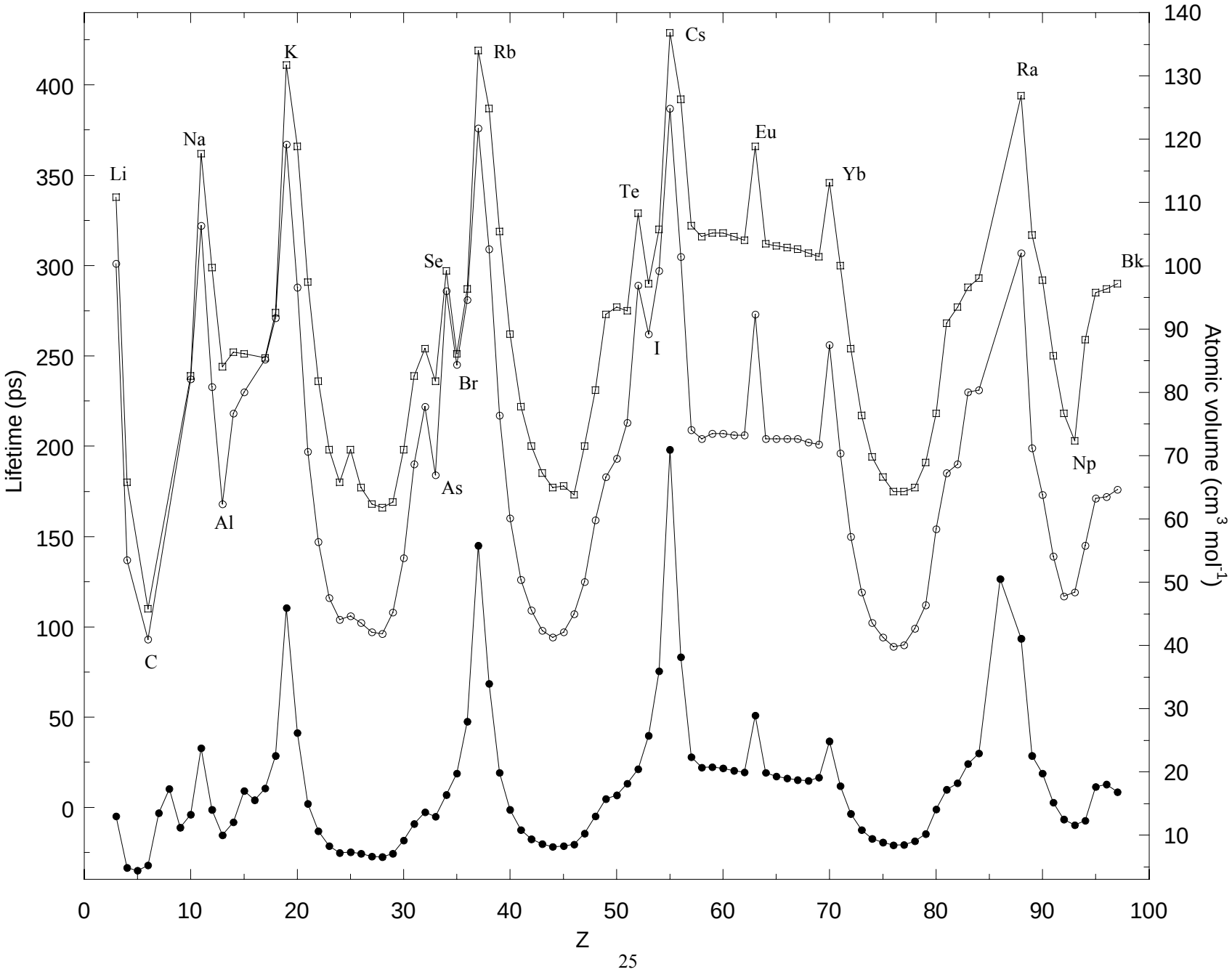
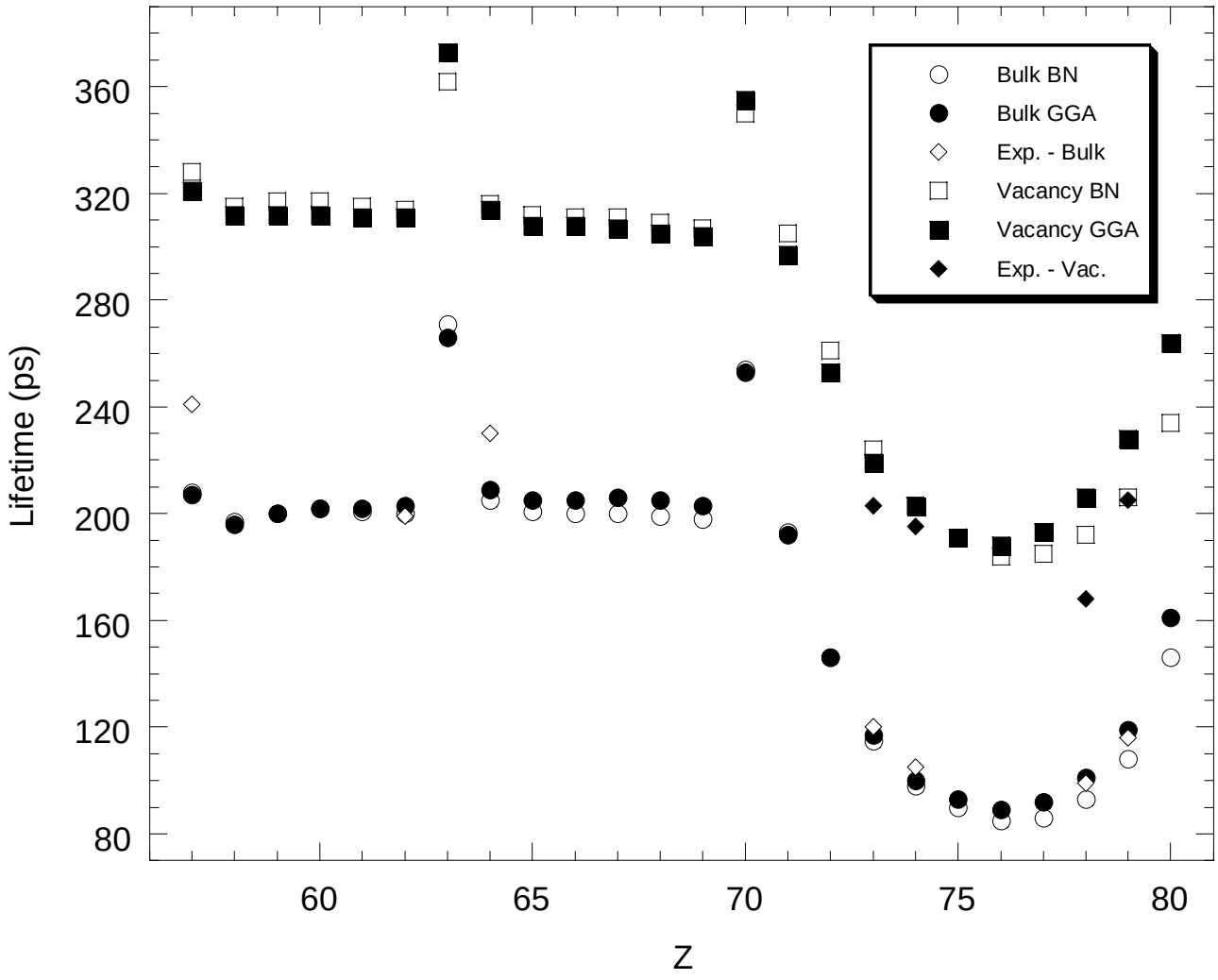

Lifetime (ps)
Atomic volume (cm^3 mol^{-1})
Z
Li
C
Na
Al
K
Se
As
Rb
Br
Te
I
Cs
Eu
Yb
Ra
Np
Bk

FIGURE 2


Bulk BN
Bulk GGA
Exp. - Bulk
Vacancy BN
Vacancy GGA
Exp. - Vac.
Lifetime (ps)
360
320
280
240
200
160
120
80
60
65
70
75
80
Z