Journal of the Nigerian Association of Mathematical Physics
Volume **12 (May, 2008), 41 – 48**

Variation of positron annihilation rates in metals

O. M. Osiele
Department of Physics,
Federal University of Technology, Akure, Nigeria.

Abstract

The local density approximation was used to calculate positron annihilation rates in several metals. The calculated positron annihilation rates in metals were compared with experimental values. Study of the calculated and experimental positron annihilation rates in metals down the groups and along the periods of the periodic table shows that positron annihilation rates in metals decreases down the group for alkaline and earth-alkaline metals while it fluctuates down other groups. Along each period, positron annihilation rates in metals are least in alkaline metals. Positron annihilation rates in metals increases from the left of the period, and at about the centre of the period, it fluctuates and decreases towards the end of the period. The study also revealed that positron annihilation rates in metals are affected directly by the atomic concentration of the metals and is independent of atomic number. The variation of positron annihilation rates in metals with atomic numbers of the metals obtained in this work is in good agreement with experimental observation.

Keywords: Positrons, annihilation rates, metals and periodic table.

1.0 Introduction

Positron annihilation techniques have been developed into an invaluable tool for the study of problems in condensed matter and material physics, for probing the atoms and electronic structures of solids, determination and studying defects in solids [1-4]. Positron annihilation rate is one of the methods used to study positron annihilation spectroscopy in solids [5]. Theoretical calculations of positron states and their annihilation characteristics play an increasing important role in the interpretation of the experiments employing positron annihilation spectroscopic techniques. The annihilation characteristics commonly measured are the positron annihilation rate (the inverse of the lifetime), which provides information about defects in materials and is used to study defects, defect volumes, defect concentration and traps in solids [6-9]. The angular correlation of annihilation radiation spectra, which gives the momentum distribution of the annihilating electron-positron pairs, can be used to study electronic structure and surface structure of material [10-12]. Positrons annihilation rates indirectly probe the atomic and electronic structure of solids. When positrons are introduced into a defect-free specimen, the positrons spend all their time diffusing through the lattice. The annihilation process may be thought of as a chemical reaction with a rate proportional to the local density [13].

In order to understand positron annihilation process, knowledge of how electron-positron interaction changes the electronic structure of the solid is very important. The attraction leads to a pile up of screening electron cloud around the positron. For a delocalised positron in a metal, the interaction with the valence electron can be modelled successfully using the results for a uniform electron gas. This means that

the screening has a short range and the positron does not affect the average electron density. Consequently, the screening in the metal host can be well estimated in the local density such that the electron pile up, when the positron is instantaneously at a given point is like a homogeneous electron gas with a density equal to the unperturbed electron density at that point [14].

Both empirical and theoretical expressions have been used to calculate positron annihilation rates in solids. Brandt and Reinheimer, [15] gave an empirical relationship for calculating positron annihilation rates in solids. The results obtained with the empirical relation fitted experimental values. The independent particle model annihilation rates were not in satisfactory agreement with experimental values because of the neglect of the strong electron-positron correlation that enhances the effective electron density at the site of the positron. Other models like that due to Sterne and Kaiser, [16] the perturbed hypernetted chain approximation [17,18] gave annihilation rates that were generally lower than experimental values because of the inexact account of electron-electron correlation or electron-positron correlation.

As a result of the success of the local density approximation in calculating metallic properties, it was suggested that the local density approximation could be used to calculate positron annihilation rates in solids [19, 20]. Jensen, [19] applied the local density approximation to calculate positron lifetime in some metals. The results he obtained were shorter than experimental values. Puska, [20] improved the work of Jensen, [19] by using the enhancement factor of Boronski and Nieminen, [21] to obtain positron lifetimes that were in better agreement with experimental values.

The Local density approximation is successful in predicting metallic properties; hence, it becomes necessary to use the local density approximation to calculate positron annihilation rates in metals in order to investigate its success in predicting positron annihilation rates in metals. Also, there is the need to investigate how positron annihilation rates in metals varies down the groups and along the periods of the periodic table and investigate some properties of metals that may affect positron annihilation rates in metals.

In this work, positron annihilation rates in metals will be calculated using the local density approximation. The calculated annihilation rates will be compared with experimental values. Study of the calculated and experimental positron annihilation rates in metals down the groups and along the periods of the periodic table will be investigated to see if positron annihilation rates in metals exhibits any similarity with other chemical properties of metals and these will thereby increase our understanding of positron annihilation characteristics in metals.

2.0 Theory

The ground state energy E of a system of electrons and a positron in an external potential V_{ext} can be written in the two-component density functional theory as a functional of the electron density n_- and the positron density n_+ [5-8,21] as

$$E[n_-, n_+] = F[n_-] + F[n_-] + \int dr V_{ext}(r)[n_-(r) - n_+(r)] - \int dr \int dr' \frac{n_-(r) n_+(r)}{|r - r'|} + E_c^{e-p}[n_-, n_+] \quad (2.1)$$

where $F[n]$ is the one-component density functional for electrons and positrons and,

$$F[N] = T[n] + \frac{1}{2} \int dr \int dr' \frac{n(r) n(r')}{|r - r'|} + E_{xc}[n] \quad (2.2)$$

$T[n]$ is the kinetic energy of non-interacting electrons and positrons, while $E_{xc}[n]$ is the exchange correlation energy between indistinguishable particles. $E_c^{e\text{-}p}$ is the functional of the correlation energy of the electron-positron pair.

The ground state of electron and positron densities, which minimizes the energy functional, $E[n_-, n_+]$ is calculated with a generalized Kohn-Sham method [8, 21]. It is necessary to solve the following system of one-particle Schrödinger equations for electrons and positrons

$$-\frac{1}{2}\nabla^2\psi_i^-(r)+\left[\frac{\delta E_{xc}[n_-]}{\delta n_-[r]}-\phi_c(r)+\frac{\delta E_c^{e-p}[n_+,n_-]}{\delta n_-[r]}\right]\psi_i^-(r)=\varepsilon_i^-\psi_i^-(r)$$

$$-\frac{1}{2}\nabla^2\psi_i^+(r)+\left[\frac{\delta E_{xc}[n_+]}{\delta n_+[r]}-\phi_c(r)+\frac{\delta E_c^{e-p}[n_+,n_-]}{\delta n_+[r]}\right]\psi_i^+(r)=\varepsilon_i^+\psi_i^+(r) \quad (2.3)$$

where
$$\phi_c=\int dr'\frac{n_o(r')-n_-(r')+n_o(r')}{|r-r'|} \quad (2.4)$$

is the total Coulomb potential and $n_0(r)$ is the positive charge density which arises from the external potential V_{ext}. The electron and positron densities are obtained by summing over all occupied states

$$n_-(r)=\sum_{\varepsilon_i=\varepsilon_p}|\psi_i^-(r)|^2,\quad n_+(r)=\sum_{i=1}^{N_0}|\psi_i^+(r)|^2 \quad (2.5)$$

where N_0 is the total number of positrons E_F is the Fermi energy of the electrons ψ_i^+ and ψ_i^- are the positron and electron wave functions, ε_i^+ and ε_i^- are the energy eigenfunctions of the positron and electron respectively. Equations (2.1) to (2.5) are solved self-consistently and simultaneously for the electron and positron states and their respective densities using an iterative method to obtain the positron and electron densities.

When a positron is introduced into a metal, the rate at which it annihilates with the surrounding electrons is given [5] as
$$\lambda=\pi r_0^2 c\int n^-(r)n^+(r)dr \quad (2.6)$$

where r_0 is the classical radius of the atom, $n^-(r)$ and $n^+(r)$ are the respective electron and positron densities at a position r, and c is the speed of light in vacuum. The conventional way of calculating positron annihilation rates in metals is based on the local density approximation formula [8]

$$\lambda=\pi r_0^2 c\int n^-(r)n^+g(r_s,0)dr \quad (2.7)$$

where $g(r_s,0)$ is the enhancement factor or the correlation function which takes into account the electron-positron interaction and is a manifestation of the electron-positron correlation. According to many-body calculations, in the local density approximation, the enhancement factor or correlation function is given [12, 22] as

$$g(r_s,0)=1+1\cdot 23r_s-0\cdot 0742r_s^2+\frac{r_s^3}{6} \quad (2.8)$$

In this work, electron and positron densities in metals were calculated by solving equations (2.1) to (2.5) simultaneously and self-consistently using an iterative scheme. Using the calculated electron and positron densities, positron annihilation rates in metals were calculated based on the local density approximation using equations (2.8) and (2.7).

3.0 Results and discussion

Figure 3.1 shows the variation of the calculated and experimental positron annihilation rates in metals with electron density parameter. As shown in Figure 3.1, in the high-density limit, ($r_s \le 3a.u.$), the calculated positron annihilation rates are not in good agreement with experimental values for some metals. But in the low-density limit, ($4 \le r_s \le 5a.u$), the calculated positron annihilation rates are in better agreement with experimental values. The results obtained in this work compares favourably well with the results obtained by other workers [11, 19] that used different methods. The difference between the calculated and the experimental positron annihilation rates in metals for metals in the high-density limit may be attributed to the none division of the enhancement factor into core and valence enhancement

factors, since the core enhancement factor is high for metals in the high-density limit and low for metals in the low-density limit [11, 19, 20, 23]. The calculated positron annihilation rates in metals for alkaline, earth-alkaline and simple metals are in better agreement with experimental values than those of the transition metals. This may be due to the fact that the former are closer approximation to homogeneous electron gas. The results obtained in this study is in better agreement with experimental values than the results obtained with the perturbed hypernetted chain approximation [17, 18], and the independent particle model, where the electron-positron enhancement factor or correlation function was neglected [24, 25]. The success of the local density approximation used in this calculation lies in its ability to include the core electrons density in the total density on the same basis as the conduction electrons [26, 27].

The group and periodic variation of calculated and experimental positron annihilation rates in metals is shown in Table 3.1. As shown in the Table 3.1, calculated and experimental positron annihilation rates in metals is least for Cs while the calculated annihilation rates in metals is highest for *V* and positrons has the highest experimental annihilation rates in Pb. In Table 3.1, positron annihilation

rates in metals decreases down groups one (alkaline metals) and two (earth-alkaline metals) and fluctuates down other groups. Along each period, positron annihilation rates in metals have the least annihilation rates in alkaline metals. Along the transition series, calculated positron annihilation rates in metals increases from the left, to about the centre of the period, where it fluctuates and decreases towards the end of the period. The experimental positron annihilation rates in metals show a similar behaviour although the experimental annihilation rates for some of the metals are not available for a generalized conclusion. The lack of a general trend in the positron annihilation rates in transition metals may be attributed to the unfilled electronic levels in the metals.

The positron annihilation rates in the rare-earth metals are generally not high and the calculated positron annihilation rates are in fairly good agreement with experimental values. The positron annihilation rates for the rare-earth metals lies between 3.31 and 4.27ns^{-1} and the positron annihilation rates in these metals do not follow a particular trend as it fluctuates from one metal to another. This fluctuation may be attributed to the filling of the 4*f*, 5*d* and 6s electronic levels along the period and the fluctuation of the electronic concentration of the metals.

The observed trend of positron annihilation rates in metals along groups and periods of the periodic table follows the same trend as the atomic concentration of the metals [28], which seems to suggest that positron annihilation rates in metals are affected by the atomic concentration of the metal. The variation of experimental positron annihilation rates in metals with atomic concentration in is shown in figure 3.2. Figure 3.2 reveals that positron annihilation rates are high in metals with high atomic concentrations and low in metals with low atomic concentrations. Statistically, a correlation coefficient of 0.75 was obtained between experimental positron annihilation rates in metals and atomic concentration of metals, which shows that positron annihilation rates in metals are affected directly by the atomic concentration of the metals.

Figures 3.3 shows the variation of the calculated positron annihilation rates in metals with atomic number *Z* while figure 3.4 shows the variation of experimental annihilation rates in metals with the atomic number *Z.* As shown in the figures 3.3 and 3.4, for $Z \leq 20$, there are few elements in this region and the positron annihilation rates in metals do not show any definite variation with atomic number. But for $21 \leq Z \leq 51$, positron annihilation rates in metals exhibits a kind of oscillatory behaviour. But for $Z > 51$, there is no definite variation of positron annihilation rates in metals with *Z*. The observed variation of positron annihilation rates in metals with atomic number *Z* shows that positron annihilation rates in metals may not be affected by the atomic number of the metals. The above variation of positron annihilation rates in metals with atomic number is in perfect agreement with the experimental observation of Mackenzie, [13] on the variation of the mean positron lifetimes with atomic number for annealed metal at room temperature.

4.0 Conclusion

The local density approximation gives positron annihilation rates in metals that are in good agreement with experimental values. Study of the experimental and calculated positron annihilation rates in metals down the groups and along the periods in the periodic table shows that positron annihilation rates decreases down the group for the alkaline and earth-alkaline metals, just as their atomic concentrations decreases down the group. While for other groups, it does not follow a particular trend. Along a period, positron annihilation rates increases from the left, at about the centre of the period, positron annihilation rates do not follow a particular trend and it decreases towards the end of the period. Positron annihilation rates in metals depend directly on the atomic concentration of the metals and are independent of the atomic number of the metals.

The results obtained in this work is in better agreement with experimental values than the results obtained by Jensen [19], who used the first principle theory based on local density approximation to calculate position lifetime in defect free twenty-nine simple and transition metals. The better agreement of the result obtained in this work with experimental values compared to the work of Jensen [19] may be due to the fact that Jensen calculated the Hartree potential using Lowdin alpha expansion, while the Hartree potential of the metals were calculated using the standard augmented plane wave method in this work.

Figure: 3:1: Variation of calculated and experimental positron annihilation rates in metals with electron gas parameter.

Li 3.48 3.44	Be 7.51 7.04													
Na 2.93 2.96	Mg 4.39 4.42											Al 6.37 6.13		
K 2.55 2.46	Ca 3.45 ------	Sc 3.40 4.35	Ti 7.24 6.80	V 9.67 7.69	Cr 7.65 8.33	Mn 6.03 ----	Fe 7.73 9.43	Co 6.37 8.45	Ni 6.37 9.56	Cu 6.12 9.09	Zn 5.35 6.76	Ga 5.81 5.10		
Rb 2.50 2.46	Sr 3.18 -----	Y 4.50 4.01	Zr 6.17 6.06	Nb 6.08 8.40	Mo 7.80 9.71	Tc 7.78 ----	Ru 6.78 -----	Rh 7.04 -----	Pd 5.13 10.42	Ag 5.09 7.63	Cd 4.55 5.71	In 5.03 5.04	Sn 3.76 4.99	Sb 4.69 3.78
Cs 2.37 2.39	Ba 3.02 ------	La 3.65 4.03	Hf 4.50 -----	Ta 4.83 8.93	W 6.52 -----	Re 6.42 ----	Os 6.59 -----	Ir 5.22 ----	Pt 6.74 10.10	Au 5.09 8.55	Hg 3.39 5.17	Ti 7.24 6.80	Pb 3.94 4.57	Bi 4.80 3.98
				Ce 3.75 4.17	Pr 3.76 4.27	Nd 3.76 4.27	Sm 3.82 4.13	Eu 3.31 3.57	Gd 3.80 4.08	Tb 3.91 4.10	Dy 3.91 4.24	Er 3.92 4.20	Yb 3.80 3.75	Lu 3.99 4.11

Table 3.1: Group and periodic variation of calculated and experimental [11,12] positron annihilation rates in metals.

Figure 3.2: Variation of calculated and experimental positron annihilation rates in metals with atomic concentration of metals.

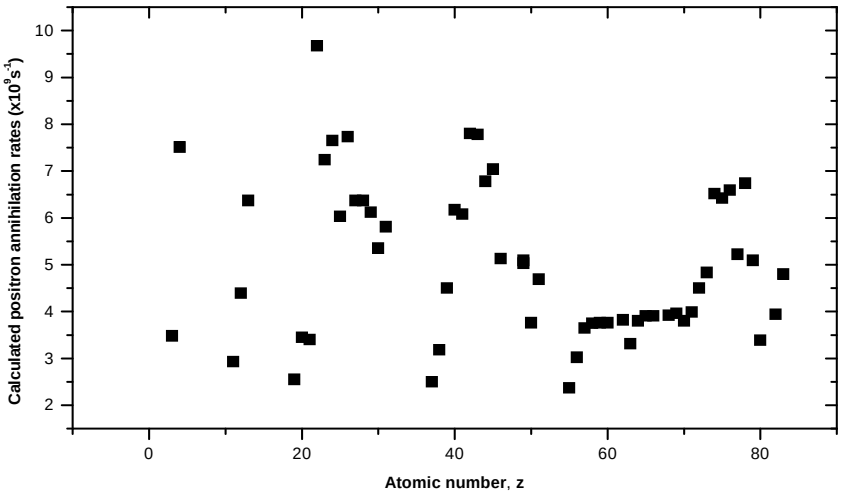

Figure 3.3: Variation of calculated positron annihilation rates in metals with atomic numbers.

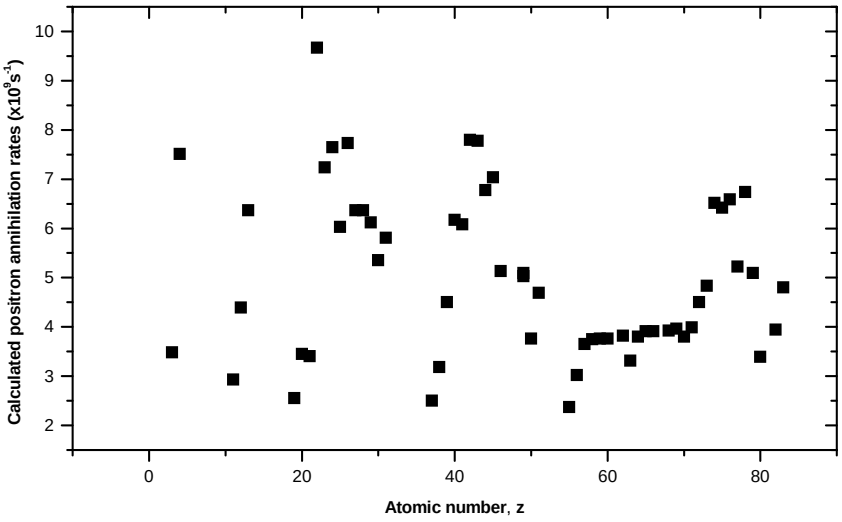

Figure 3.4: Variation of experimental positron annihilation rates in metals with atomic numbers.

References

[1] Seeger, A. and Britton, D. T. (1999), Slowing down and penetration of positrons in condensed matter. Applied Surface Science, Vol. 149, 287 - 288

[2] Barbiellini, B., Puska, M. J., Torsti, T. and Nieminen, R. M. (1985), Gradient correction for positron states in solids. Physical Review B, Vol. 50, No.11, 7341 - 7244.

[3] Gosh, V. J., Alatalo, M., Asoka-Kumar, P., Nielsen, B., Lynn, K. G., Kruseman, A. C. and Mijnarends, P. E., (2000), Calculation of the Doppler-broadening of the electron-positron annihilation radiation in defect-free bulk material. Physical Review B, Vol. 61, No. 15, 10092 - 1098.

[4] Pi, X.D., Coleman, P. G., Tseng, C. L., Burrows, C. P., Yavich, B. and Wang, W. N. (2002), Defects in GaN films studied by positron annihilation spectroscopy. Journal of Physics: Condensed Matter, Vol. 14: L234 – L248.

[5] Eldrup, M. (1995), Positron methods for the study of defects in bulk materials. Journal de Physique (iv), C-93 - C-109.

[6] Hidalgo, C., Linderoth, S. and Nieves, D. E. (1987), Positron trapping mechanism at dislocation in Zn. Physical Review B, Vol.36, No.13, 6740 - 6748.

[7] Nieminen, R. M., Laakkonen, J. Hautojarvi, P. and Vehanen, A., (1979). Tenperature dependence of positron trapping at voids in metals. Physical Review B, Vol. 19, No.13, 21456 - 21466.

[8] Puska, M. J. and Nieminen, R. M. (1994), Theory of positrons in solid surfaces. Reviews of Modern Physics, Vol.66, No.3, 841- 897.

[9] Kawasuso, A., Redmann, F., Krause-Rehberg, R. Yoshikawa, M., Kojima, K. and Itoh, H. (2001), Positron annihilation due to silicon vacancies in 3C and 6H SiC epitaxial layers induced by 1 MeV electron irradiation. Physical Status Solidi (B): Vol. 101, R8 – R10.

[10] Manuel, A. A., Oberli, L., Singh, A,. K., Jarlborg, J., Peter, M., Minnarends, P. E., Rabou, L. P. L., Hyodo, T. and Stewart, A. T. (1993), The electronic structure of alkali metals: Experiment and theory. Journal of Physics: Condensed Matter Vol.5, 8703- 8709.

[11] Daniuk, S. Sob, M. and Rubaszek, A. (1991), Theoretical calculation of positron annihilation with rare-gas core electrons in simple and transition metals. Physical Review B, Vol. 43, No. 4, 2580 - 2593.

[12] LiMing, W., Panda, B. K., Fung, S. and Beling, C. D. (1997), Calculation of the momentum distributions of positrons annihilation radiation in Ge. Journal of Physics: Condensed Matter, Vol. 9, 8147 - 8154.

[13] Mackenzie, I. K. (1983), Experimental methods of annihilation time and energy spectroscopy. Positron Solid State Physics edited by Brandt, W. North-Holland Publishing Company Amsterdam. 196 – 201.

[14] Puska, M. J. (1987), Theoretical aspects of positrons in imperfect solids. Physical Status Solidi (A), Vol.102, 11-15.
[15] Brandt, W. and Reinheimer, J. (1971), Impurity screening in amorphous semiconductor. Physics Letters, Vol. 35A, No 2, 109 – 110.
[16] Sterne, P. A. and Kaiser, J. H. (1991), First principle calculation of positron lifetimes in solids. Physical Review B, Vol. 43, No.17, 13892 – 13898.
[17] Stachowiak, H. (1990), Electron-positron interaction in jellium. Physical Review B, Vol. 41, No. 18, 12522 - 12535.
[18] Stachowiak, H. and Lach, J. (1993), Positron annihilation characteristics in an electron gas from low to high densities. Physical Review B, Vol.48 No.3, 9828 – 9830.
[19] Jensen, K. O. (1989), Local density calculation of positron annihilation in metals. Journal of Physics: Condensed Matter, Vol.1, 10595 - 10601.
[20] Puska, M. J. (1991), Ab-initio calculation of positron annihilation rates in solids. Journal of Condensed Matter 3, 3455 - 3469.
[21] Boronski, E. and Nieminen, R. M. (1986). Electron-positron density functional theory. Physical Review B, Vol. 34, No.6, 3820 - 3831.
[22] Barbiellini, B., Hakala, M., Puska, M. J. and Nieminen, R. M., (1997), Correlation effects for electron-positron momentum density in solids. Physical Review B, Vol.56, No.12, 7136 - 7141.
[23] Rubaszek, A. and Szotek. Z and Temmerman, W. M. (2001), Non-local effects in the electron-positron interaction in metals. Physical Review B, Vol. 63, 16511-1 – 165115-13.
[24] Kahana, S. (1963), Positron annihilation in metals. Physical Review, Vol.29, No. 4, 1622 –1628.
[25] Ferrell, R. A. (1958), Theory of positron annihilation. Reviews of Modern Physics Vol.28 No.3, 315 - 327.
[26] Arponen, J. and Pajanne, E. (1985), Electron-positron interaction in Positron Annihilation edited by Jain, P. C., Singru, R. M. and Gopinathan, K. P. World Scientific Co. Singapore. P. 21 - 32.
[27] Welch, D. O.and Lynn, K. G. (1976), Systematic variation of the mean positron lifetime and Gaussian fraction in annealed metals and semiconductors. Physics Status Solidi (B) 77, 227 –285.
[28] Kittel, C. (1976), Introduction to solid state physics, Fifth edition, John Wiley and Sons Inc, New York. P.32.