

Monte Carlo calculation of carbon atom displacement damage in C60 fullerene bulk materials irradiated with gamma rays

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Abstract

The displacement per carbon atom cross-sections behaviors with the secondary electron and positron kinetic energy for spherical fullerene C60 molecules are calculated. To this end, the McKinley-Feshbach approach and the Kinchin-Pease approximation were taken into account, using two different displacement threshold energies. The total displacements per atom number indirectly generated by photons in bulk samples composed of C60 fullerenes are also calculated. Furthermore, the behaviors of secondary particles contributions with the used displacement threshold energies and incident photon energies are determined. The in-depth distribution of electron and positron contributions and their relationship with the total displacements number are presented and discussed. It was finally concluded that the contribution of positrons to the total atom displacements number is very significant in processes involving the interaction of gamma quanta with energy up to 100 MeV in C60 fullerenes bulk samples.

Key words: fullerenes, atomic displacements, cross sections, radiation effects, Monte Carlo method, gamma radiation

Cálculo por Monte Carlo del daño por desplazamientos de los átomos de carbono en materiales masivos basados en fullerenos C60 irradiados con rayos gamma

Resumen

Teniendo en cuenta las aproximaciones de *McKinley-Feshbach* y *Kinchin-Pease* se calcularon los comportamientos de las secciones eficaces de desplazamientos de los átomos de carbono en moléculas esféricas de fullereno C60, en función de la energía cinética de los electrones y positrones secundarios para dos valores de energía umbral de desplazamiento. También se calcularon el número total de desplazamientos atómicos generados de manera indirecta por los fotones en las muestras masivas de fullerenos C60 estudiadas. Además, se estudió el comportamiento de las contribuciones electrónicas y positrónicas, determinando sus dependencias con las energías de desplazamiento utilizadas y la energía de los fotones incidentes. Se presentan y debaten la distribución en profundidad de las contribuciones de los electrones y positrones, así como la relación entre ellos y el número total de desplazamientos. El aporte de la contribución de los positrones al número total de desplazamientos atómicos generados durante el proceso de interacción de los cuantos gamma de energías hasta 100 MeV con muestras masivas de fullerenos C60 se discutió, concluyéndose que este resulta muy significativo.

Palabras clave: radiación gamma, desplazamientos atómicos, secciones eficaces, efectos de las radiaciones, método de Monte Carlo, radiación gamma

Introduction

The carbon-based nanostructured materials are in a privileged position within the scope of scientists and engineers around the world as a result of its unusual properties and almost unlimited current and future applications in practically all areas of science and technology [1-4].

One of these surprising materials is the so-called buckminsterfullerene, or simply buckyball, which consists in a roughly spherical cage of 60 carbon atoms arranged in interlocking hexagons and pentagons (C60). Since its discovery in 1985 [5], C60 had captured a great attention as consequence of their unique chemical and physical properties. C60 fullerenes are potentially useful in several

applications, such as hydrogen storage for fuel cells, classical and painted-on solar cells, development of lubricants for friction reductions to decrease energy consumption, nonlinear optics, photonics and molecular electronics, biological and medical applications, etc. [6-8].

In the development process of many of these applications, chemical groups must be attached to a fullerene carbon atom, a procedure called functionalization, modifying C60 properties. This functionalization process is supported by different techniques, one of which is gamma-ray irradiation [9,10], required to facilitate the generation of free bonds to which the chemical interesting groups are linked. This method, together with some of previous cited applications, involves radiation aggressive environments. This makes strategically important to evaluate the effect that may cause gamma rays on the C60 structure and properties from the radiation damage view point.

The aim of this paper is to calculate the displacements per carbon atoms cross-section dependence on the secondary electron and positron energies in C60 fullerenes, using a classical formalism and the displacement threshold energies reported in literature. Also the authors determine the in-depth distribution of the displacements per atom (dpa) number, which are generated when gamma rays of selected energies interact with bulk C60 materials (BC60M).

There is very limited information about this paper in scientific literature [11-13], and the analysis of the positrons contribution to the atom displacement cross-section in C60 and to the atom displacements number in BC60M is always excluded.

Materials and Methods

One of the basic parameters on studying radiation damage in crystals is the displacement threshold energy (E_d), which is defined as the kinetic energy a Primary Knock-on Atom (PKA) must have to leave its equilibrium site on the structure. E_d for C60 appears reported in the literature with a lot of dispersion, not existing consensus in an exact value, fundamentally because E_d has a strong angular dependence. In this work we will use two of the average values reported, both calculated by means of molecular dynamics methods: $E_d = 15$ eV [14] and $E_d = 29.1$ eV [15].

The total displacements per atom cross-section, σ_{dpa} , is defined by equation (1).

$$\sigma_{dpa}(E) = \sigma_{PKA}(E) \cdot v(T), \quad (1)$$

where E is the particle kinetic energy, T is the atom recoil kinetic energy, $\sigma_{PKA}(E)$ is the PKA cross-section, and $v(T)$ is the damage function.

As known, σ_{dpa} is a hypothetical area which describes the likelihood of structural atom being displaced by a particle, and then this parameter may be associated with the sensitivity of the target material to be damaged by the incident radiation.

The PKA cross-section is obtained from the McKinley-Feshbach approximation [16], extended to include the positrons case [17]:

$$\sigma_{PKA}(E) = \frac{\pi r_0^2 Z^2}{\beta^4 \gamma^2} \cdot \left\{ \tau - 1 - \beta^2 \ln(\tau) \pm \pi \alpha \beta \cdot [2\sqrt{\tau} - \ln(\tau) - 2] \right\}, \quad (2)$$

with Z being the atomic number, r_0 is the electron classic radius, $\alpha = Z/137$, β is the ratio of the electron velocity to the velocity of light, $\gamma^2 = 1/(1 - \beta^2)$, $\tau = T_{max}/E_d$, being

$$T_{max} = \frac{2E(E + 2mc^2)}{Mc^2}, \quad (3)$$

the maximum kinetic energy of the corresponding recoil atom with mass M . The sign of term $\pi \alpha \beta$ in (2) is positive for electrons and negative for positrons.

The damage function $v(T)$ in eq. (1) allows including the atom displacement cascades phenomenon in the calculation, which was expressed according to the Kinchin-Pease model [18]:

$$v(T) = \begin{cases} 0, & T < E_d \\ 1, & E_d \leq T \leq 2E_d \\ \frac{T}{2E_d}, & T > E_d \end{cases}, \quad (4)$$

To evaluate this function the average atom recoil kinetic energy (T_{ave}) is used, given by

$$T = T_{ave} = E_d \cdot \frac{\tau \ln(\tau) - \beta^2(\tau - 1) \pm \pi \alpha \beta \cdot (1 - \sqrt{\tau})^2}{\tau - 1 - \beta^2 \ln(\tau) \pm \pi \alpha \beta \cdot [2\sqrt{\tau} - \ln(\tau) - 2]}, \quad (5)$$

A more complete explanation of this procedure can be found additionally in [19]. The details of the MCCM (Monte Carlo assisted classical method) code system, created on the above mentioned bases and used for whole calculations in this work are also explained there.

The radiation damage calculations resulting from the action of gamma rays on BC60M were performed in a cylindrical shape sample (diameter 100 μm and thickness 10 μm), which is irradiated with monochromatic photons of a given energy. The photons impact perpendicularly and homogeneously distributed over the top surface of the cylinder. The atom displacement profile determination is performed in a voxel (10 μm x 10 μm x 10 μm) located exactly in the cylinder center. The mass density of the sample was set $\rho = 1.65$ g cm⁻³ [20].

The energy flux distributions ($\Phi(E_i, z)$) at a given depth z of secondary electrons and positrons resulting from the interaction of photons with the BC60M were calculated within the selected voxel using the MCNPX (Monte Carlo n - Particles Transport Code) software [21]. The flux values are normalized to source particle number.

These results were processed by the MCCM program to determine the number of atom displacements (N_{dpa}) for each particle type according to the classical method [19]:

$$N_{dpa} = \sum_i N_{dpa}^{e^-,e^+}(E_i) \Phi(E_i, z) \Delta E_i, \quad (6)$$

where $N_{dpa}^{e^-,e^+}(E_i)$ is the number of atoms displaced per electron or positron with kinetic energy E_i calculated following Oen-Holmes expression [22]:

$$N_{dpa}^{e^-,e^+}(E) = N_a \int_{E_c}^E \frac{\sigma_{dpa}(E')}{(-dE'/dx)} dE', \quad (7)$$

where E_c is the cutoff kinetic energy of electrons (or positrons) in order to displace an atom from its crystalline site, N_a is the number of atoms per volume unit in the sample, $(-dE/dx)$ is the electron stopping power, and $\sigma_{dpa}(E)$ is given by equation (1).

All Monte Carlo simulation results are reported with a relative statistical error lower than 1%, which was ensured using a large number (10^7) of histories (simulated incident photons and its secondary particles).

Results and Discussion

The behaviors of the displacements per carbon atom cross-sections with the secondary electrons and positrons kinetic energies for $E_d = 15$ eV and $E_d = 29.1$ eV are presented in figures 1 and 2 respectively. In the first figure it is clearly observed that for the lowest E_d the displacement processes in the C60 are energetically suitable for particle energy higher than 76 keV. This fact indicates that the interaction processes, which should occur with energy transfers well below 15 eV, are not harmful to the C60 molecules. For the highest E_d the generation of stable point defects by displacement processes starts at particle energy of 141 keV for both electrons and positrons.

The curves describing the displacement cross-section behaviors for both particles monotonically increase throughout all the studied energy range, except for the case of $E_d = 15$ eV, which shows a slight drop in $\sigma_{dpa}(E)$ values just before the displacement cascades process begins. This behavior is associated with the existing strong competition between the electron scattering angle dependence of the energy transferred to the target atom and the $\sigma_{PKA}(E)$ dependence with the particle energy.

It is observed that the electrons cross section values are in average $\sim 4.4\%$ higher than the positrons ones. At 100 MeV particles energy, the difference between both distributions is only 2.6% favoring electron contribution.

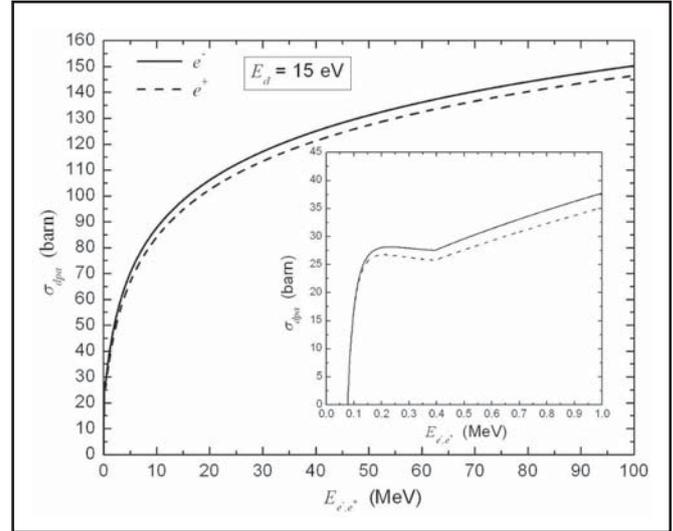


Figure 1. Displacement cross-section behaviors with the electron and positron kinetic energy for C60 fullerene and $E_d = 15$ eV.

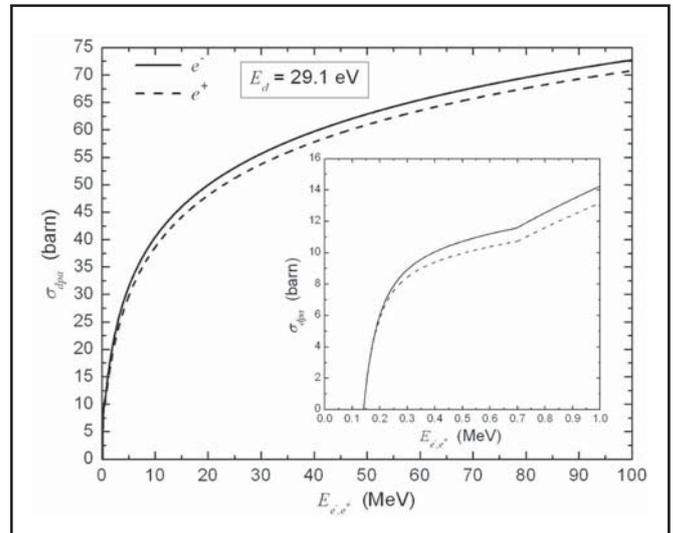


Figure 2. Displacement cross-section behaviors with the electron and positron kinetic energy for C60 fullerene and $E_d = 29.1$ eV.

As the particle energy increases, the probability of creating secondary displacements grows, so the cascade contribution to damage also increases. The beginning of the displacement cascades process is perfectly observed in figures 1 and 2 in the points where an abrupt curve slope change takes place. This occurs at 390 keV for the bulk material where $E_d = 15$ eV, and at 696 keV for $E_d = 29.1$ eV have been considered. These particles energy values can be considered the thresholds for electron and positron for having the possibility to transfer to the target atoms enough energy to be able by themselves to displace other atoms from their structural positions.

In the analysis of these processes it is worthwhile, mentioning that, although carbon nanostructures are our main concerns the present study in the dimensionality of which is not favorable to stimulate the occurrence of cascade processes, in this paper we are dealing with a massive material having 10 μm thickness. For example, this may be a thick layer deposited on a gi-

ven substrate, or a buckypaper, or other application. At 10 μm a thick layer can be linearly placed an average of 10 000 fullerene C60 molecules, considering the diameter of each molecule equal to 1.01 nm and an ideally zero porosity. Consequently there is a high probability that primary displaced atoms with high enough kinetic energies displace other atoms from their stable crystallographic positions. Even in C60 monolayers these processes are still viable due to the spherical characteristics of fullerene molecule, but with a low probability.

The $\sigma_{\text{dpa}}(E)$ values calculated with the first and smaller E_d are twice higher than those calculated with the second higher one. This correlation is a consequence of the existing dependence of the displacement cross-section with the threshold displacement energy (eq. (2)). The lower the displacement energy, the higher is the probability that an atom could be moved out of their equilibrium position when it is impacted by an energetic particle.

The presented figures show that both electrons and positrons have very similar probabilities for producing atom displacements (slightly higher for electrons) in the studied material.

The total displacements number ($\text{Total}N_{\text{dpa}}$) behaviors with the incident photon energies, which take place in the selected target sample voxel for both E_d values, are presented in figure 3. Here, the reported $\text{Total}N_{\text{dpa}}$ values refer to the total number of stable defects generated by gamma rays in 1 μm thick parallel layers located continuously within the evaluated voxel and perpendicular to the incident photons direction. $\text{Total}N_{\text{dpa}}$ values are also normalized by the primary incident photons number.

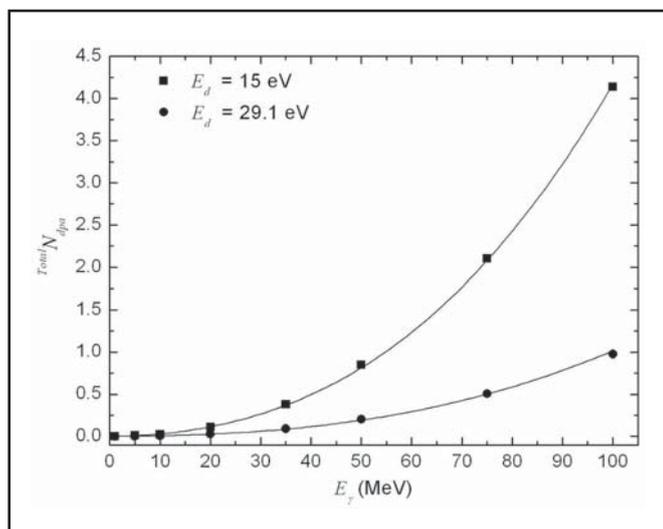


Figure 3. Behavior of $\text{Total}N_{\text{dpa}}$ with the photon energy for two E_d values. The lines are visual guides.

Figure 3 shows that $\text{Total}N_{\text{dpa}}$ for both threshold displacement energies monotonically increase with the gamma energy. The calculated ratios of both curves are practically constant in the whole energy interval (~ 4.35), favorable for the case with the lowest average displacement threshold energy, as its atoms are more weakly bounded to the structure.

Frequently, in gamma radiation damage studies in materials exposed to photons with energies higher than 1.02 MeV, the positron contribution to the generated damage is completely ignored, considering that these particles after its creation will be immediately annihilated by combining with electrons [12].

However, as discussed above, according to the electron and positron $\sigma_{\text{dpa}}(E)$ behaviors, the probabilities of generating displacements are very close for both particles. Furthermore, it is known that the tracks of positrons in a material are similar to those of electrons, and the stopping powers and range are also roughly the same, for the same initial energies. Using the code system GAMOS [23] we additionally calculated the positrons range, R , for different kinetic particle energies inside the studied material. For positron energy of 1 keV, R reaches value of 0.02 μm , for 100 keV, R is 100 μm , and for 1, 10 and 100 MeV, $R = 3.3 \text{ mm}$, 168 mm and 336 mm, respectively.

As can be seen the positron range increases significant with its energy, especially at high energy values, where R can reach the order of tenths of meters. With these lengthy paths followed by positrons in the material, the probability to interact with atoms producing displacements is very high. Taking into account the exposed facts, the dismissal of the positron contribution to the radiation damage apparently is not a good assumption.

To evaluate the positrons contribution to the $\text{Total}N_{\text{dpa}}$ values the figures 4 (a-d) are presented. They show the in-depth distribution of the two components (electron and positron) of atom displacements number calculated within the studied sample for four selected photon energy values. Here the positron component refers only to the atom displacements contribution which is only caused by the interaction of positrons with target atoms. Photons resulting from the positron annihilation, as the primary photons, are not able to produce dpa, except through the secondary electrons and positrons generated through their interactions with matter.

For $E_\gamma = 1 \text{ MeV}$, figure 4 (a), the photon energy is still not enough to energetically allow the occurrence of the "pairs formation" interaction phenomenon, so there will be neither positron generation nor its transport in the target. Due to this, the single electron contributions are observed in figure 4 (a). Its linear and increasing path with depth behaviours has the higher slope for the smallest E_d case. Such increasing behavior with depth is also observed in other cases given below.

For photons energy above 1.02 MeV positrons appear as a result of the pairs formation. Figure 4 (b) shows that, at photon energy 10 MeV, the positron contribution to the total displacements is very small, not exceeding 11% of the total, corresponding the other 89% to the electrons contribution; independently of the E_d . In Figures 4 (c) and 4 (d) for gamma energy 50 and 100 MeV respectively, presented behaviors evidence that with increasing photon energy, the positrons contribution to the total displacements continues growing,

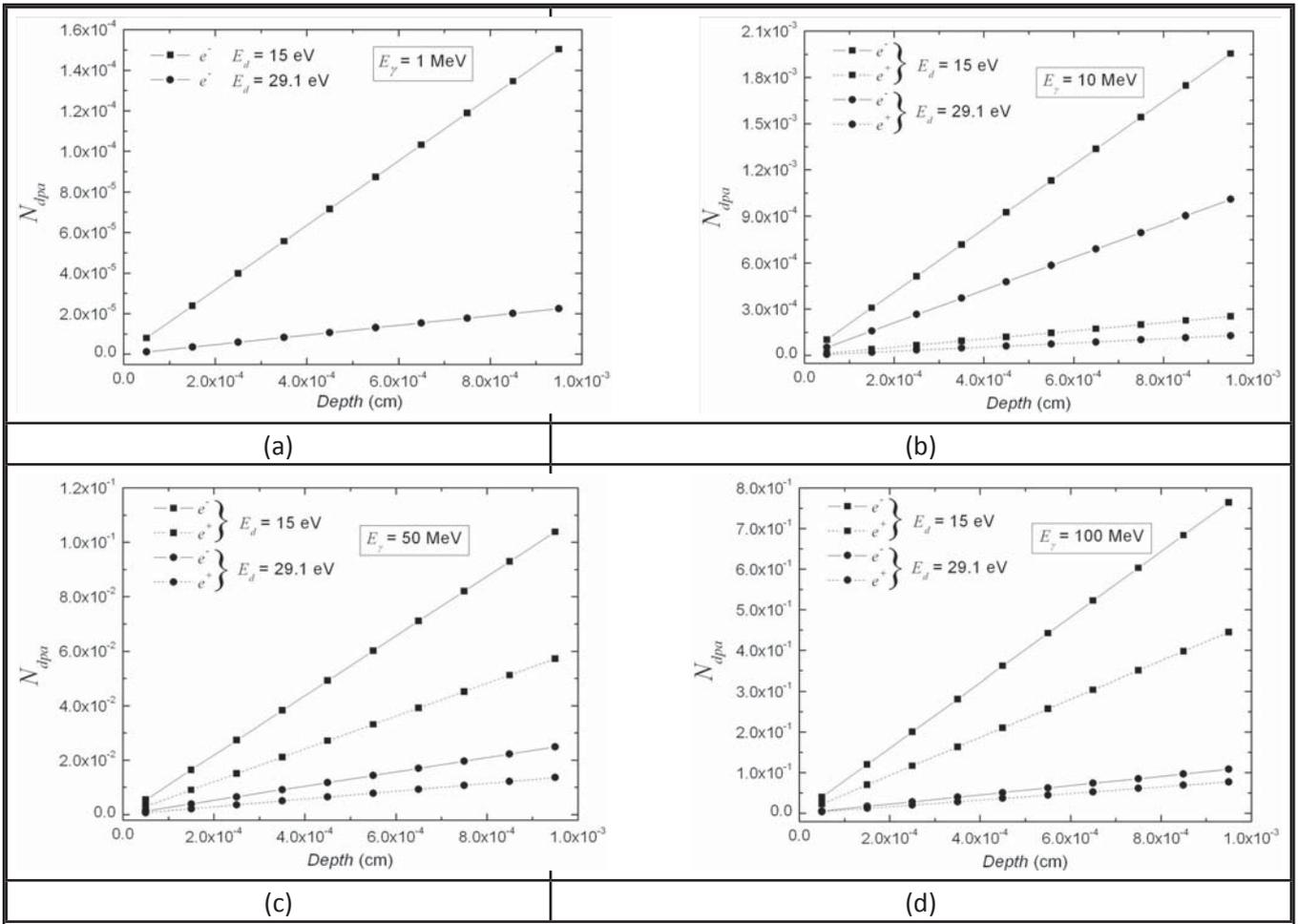


Figure 4. Electron and positron contributions to N_{dpa} in-depth profiles for photon energies 1, 10, 50 and 100 MeV ((a) – (d) respectively) and two E_d values. The lines are visual guides.

reaching significant values with respect to the electrons contribution.

Table presents the calculated values for the total number of dpa, its electron and positron contributions, and the ratio between both contributions, complementing the results showed in figures 3 and 4 (a-d). In table it can be observed that with increasing photon energy the contribution of positrons to the total number of dpa also increases significantly. If for $E_\gamma = 10$ MeV the positrons contribution to the total displacements is only 11%, at 50 MeV it reach 36%, while at $E_\gamma = 100$ MeV the positron contribution is 42%, i.e. the

weight of the positron contribution to N_{dpa}^{Total} is very significant and close to the electrons one at the highest studied energies.

Another conclusion from table, is that the ratio between the two particles contribution to the total number of dpa is almost independent of the target carbon atom displacement threshold energy.

These results confirm the positron contribution importance to the total number of atom displacements in processes which involve the interaction of gamma quanta up to 100 MeV energy with nanostructured bulk samples composed of C60 fullerenes.

Values of total number of dpa and its electron and positron contributions in the studied BC60M sample for four incident photon energies and two different displacement threshold energies

| E_γ [MeV] | 1 | | 10 | | 50 | | 100 | |
|----------------------------------|----------|----------|--------|----------|--------|--------|--------|--------|
| E_d [eV] | 15 | 29.1 | 15 | 29.1 | 15 | 29.1 | 15 | 29.1 |
| Total N_{dpa} | 7.933E-4 | 1.186E-4 | 0.0116 | 0.00598 | 0.8478 | 0.2022 | 4.0211 | 0.9762 |
| $N_{dpa}(e^-)$ | 7.933E-4 | 1.186E-4 | 0.0103 | 0.0053 | 0.5466 | 0.1307 | 2.3395 | 0.5691 |
| $N_{dpa}(e^+)$ | - | - | 0.0013 | 6.766E-4 | 0.3012 | 0.0715 | 1.6816 | 0.4071 |
| $N_{dpa}(e^-) / N_{dpa}^{Total}$ | 1 | 1 | 0.887 | 0.886 | 0.645 | 0.646 | 0.582 | 0.583 |
| $N_{dpa}(e^+) / N_{dpa}^{Total}$ | - | - | 0.112 | 0.114 | 0.355 | 0.354 | 0.418 | 0.417 |

Conclusions

The behaviors of displacements per carbon atom cross-sections for spherical fullerene C60 molecules with the kinetic energy of electrons and positrons were calculated for two different displacement threshold energies. The $\sigma_{\text{dpa}}(E)$ increasing behaviors show an average difference between the electrons and positrons curves only in 4.4% higher for electrons. The threshold energy values of the displacement processes beginning and the displacement cascades startup for the bulk C60 material were determined, observing that they were the same for both electron and positron, but different for each displacement energy value.

The $N_{\text{dpa}}^{\text{Total}}$ calculated for both E_d show a monotonically increasing behavior with the gamma energy, maintaining a practically constant ratio in the whole energy interval, favorable for the case with the lowest average displacement threshold energy.

The in-depth N_{dpa} distributions of the electron and positron contributions show that at low energy the positron contribution is very slight, but with increasing photon energy, it begins to grow in importance, becoming responsible for the 42% of all atoms displacements occurring in the material at photon energy 100 MeV. This confirms the importance of the positrons contribution to the total number of atom displacements in processes which involve the interaction of gamma radiation with bulk C60 fullerenes material.

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