



PERGAMON

CARBON



Positron annihilation in C_{60} fullerites and fullerene-like nanovoids

Mikhail M. Nishchenko^{a,*}, S.P. Likhatorovich^a, D.V. Schur^b, A.G. Dubovoy^b,
T.A. Rashevskaya^c

^a*Institute for Metal Physics, National Academy of Sciences of Ukraine (NASU), Vernadsky Blvd. 36, Kiev 03142, Ukraine*

^b*Institute for Materials Science Problems, NASU, Krzhizhanovsky str. 3, Kiev 03142, Ukraine*

^c*Ukrainian State University of Food Technologies, Vladimirskaya str. 69, Kiev 01033, Ukraine*

Received 13 August 2002; accepted 31 January 2003

Abstract

C_{60} fullerites, fatty-acid triglycerides containing nanovoids, and triglycerides with dissolved fullerenes were studied by means of positron annihilation spectroscopy. Two types of nanovoids with mean radii of 0.48 and 0.34 nm were found in the fatty-acid triglycerides. The nanovoids of the latter type change size in the course of structural relaxation and ordering at room temperature. The nanovoid radius is stabilized at the value of 0.355 nm, equal to the radius of C_{60} fullerenes, when the latter are dissolved in triglycerides. Tetrahedral interstitials in the f.c.c. lattice are shown to be the most probable positron-annihilation sites in C_{60} fullerites. The shell of the C_{60} molecule is a potential barrier for positron penetration to the interior of the fullerene. Vice versa, the nanovoid in triglycerides is a potential well for positively charged particles: positrons, protons and cations.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: A. Fullerene, Graphite; B. Arc discharge; D. Defects, Porosity

1. Introduction

Positron annihilation studies of crystalline fullerenes (fullerites) and polymers containing nanovoids [1–4] have shown both similarities and essential differences between these nanostructures. They have close dimensions and their shells contain covalently bound carbon atoms. However, conditions for positron annihilation differ substantially.

Positron annihilation spectroscopy is known to be an effective tool for the study of open-volume defects in amorphous metals, polymers, molecular solids, and fullerites. It enables one to determine the average size of the nanovoids, their size distribution [5] and anisotropy of their shape. For example, two types of voids with average sizes of 0.15 and 0.3 nm were found in some polycarbonates [6].

Positron annihilation studies of the fatty-acid triglycerides containing molecules with different lengths of hydrocarbon chains have shown that amorphization by

rapid cooling results in a more homogeneous state with the nanovoids having mean radius of 0.36 nm [4]. This value corresponds to the outer radius of C_{60} fullerene.

Theoretical studies of the positron density distribution in C_{60} fullerites have shown that the positron does not penetrate into the interior of C_{60} molecule. Annihilation characteristics result from positron annihilation in the sites between C_{60} molecules [2]. The reduction of the mean positron lifetime under hydrostatic pressure is evidence that the positron is localized in decreasing intermolecular spaces of a f.c.c. fullerite, because C_{60} molecules are practically incompressible. Calculations of the positron density distribution in C_{60} fullerites have shown that the positron is 'smeared' over octahedral interstitials, whereas its density inside a C_{60} molecule is negligible [7].

In the case of the fatty-acid triglycerides the positron penetrates the nanovoids and forms a bound electron-positron state (hydrogen-like positronium atom). As a result of annihilation of this localized positronium, a narrow component appears in the spectra of the angular correlation of annihilation photons (ACAP) [4]. Essentially different conditions for positron annihilation in fullerites

*Corresponding author. Fax: +38-044-444-2561.

E-mail address: pozit@imp.kiev.ua (M.M. Nishchenko).

and organic materials containing nanovoids indicate that the electric field distributions in these materials are different. While the nanovoids in the fatty-acid triglycerides are potential wells for positively charged particles, C_{60} molecules form a barrier for the penetration of positive particles into the interior. This is evidently due to the different structure of the fullerene shell and the inner surface of the nanovoids in triglycerides. Insertion of fullerenes into the fatty-acid triglycerides containing nanovoids may be supposed to result in formation of 'hybrid' nanostructures with new properties.

2. Experimental

The samples were prepared from the high-melting fraction of the fatty-acid triglycerides, which are characterized by saturated bonds, and C_{60} fullerenes crystallized from solution in toluene.

ACAP spectra were measured on a long-slit spectrometer with an angular resolution $\sigma_r = 0.55$ mrad (standard deviation of the Gaussian resolution function). ACAP spectra of the fatty-acid triglycerides were fitted to the sum of three Gaussians:

$$N(\theta) = \sum I_i \exp(-\theta^2/2\sigma_i^2)$$

where θ is the correlation angle; I_i and σ_i are the intensities and standard deviations of broad (BG), medium (MG), and narrow (NG) Gaussians. In the case of the fatty-acid triglycerides the method enables one to detect the presence of nanovoids, to measure their size and its variation caused by structural relaxation, ordering, and insertion of molecular admixtures.

It was shown in Ref. [4] that the positrons annihilating with the outer-shell electrons of oxygen atoms contribute mainly to the MG component of ACAP. NG is due to the self-annihilation of positronium (Ps). One of the mechanisms of its formation may be electron tunneling through the barrier at the inner surface of the nanovoid under the action of the electric field of the positron charge, and subsequent formation of a bound electron-positron state. The Ps radius is almost exactly equal to that of the hydrogen atom, $r_{Ps} = 0.053$ nm. The nanovoid radius was calculated according to the formula [6]:

$$R = 1.66/\sigma - 0.166 \text{ [nm]}$$

where σ is the full width at half-maximum of the NG. The relative area of NG is equal to the Ps annihilation probability inside the nanovoids.

ACAP spectra for crystallized C_{60} fullerenes were approximated by the sum of only two Gaussians due to the absence of NG. The electron localization radius, r_m , in interstitials was calculated using MG parameters according to Ref. [8]:

$$r_m = (3/2)^{1/2} (\hbar/mc\sigma)$$

where m is the electron rest mass, c is the velocity of light, σ is the MG standard deviation. BG is related to positrons annihilating with carbon electrons or it is due to the presence of cavities (free volume, vacancies) of atomic scale, which have lower electron density, and disturb ideal packing in a fullerene molecule. The electron localization radius in these regions was also calculated using the aforementioned formula.

The high-melting triglyceride fraction was prepared by means of fractional crystallization of milkfat solution in acetone at 20 °C. The low-melting fraction solidified at -18 °C.

X-ray diffraction analysis was carried out at room temperature using Fe $K\alpha$ radiation ($\lambda = 0.19373$ nm). The cell constant of the fullerite cubic lattice was determined to be 1.42 nm.

3. Positron annihilation in fatty-acid triglycerides

Fig. 1 shows the general distribution of the mean radii of the nanovoids, which can change in the course of structural relaxation and ordering of the fatty-acid triglycerides. Dashed areas in Fig. 1 denote the ranges of the radii of nanovoids, in which Ps is not formed. At nanovoid radii smaller than that of Ps (0.053 nm) the latter cannot be placed in such a small cavity, whereas at $r > 0.76$ nm the Ps annihilation probability at room temperature tends to zero (Fig. 2).

Energetically, the most favourable state of the hydrocarbon chains in a triglyceride molecule is in the form of an asymmetric tuning fork. The directions of the chains change so that the chain directed to one side is followed by an oppositely directed one. Disturbed packing of molecules

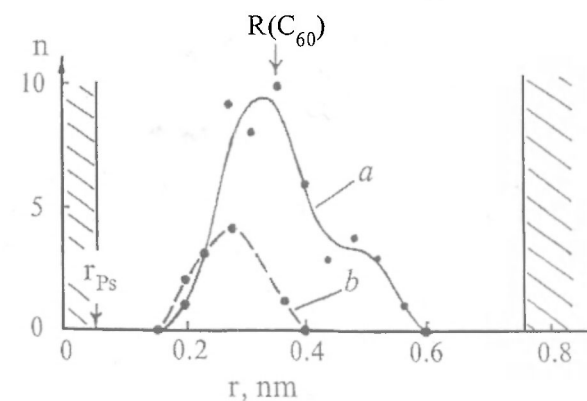


Fig. 1. Size distribution of the nanovoids in the fatty-acid triglycerides: general distribution (a) and for the mixture of the high- and low-melting fractions after partial extraction of the latter fraction (b).

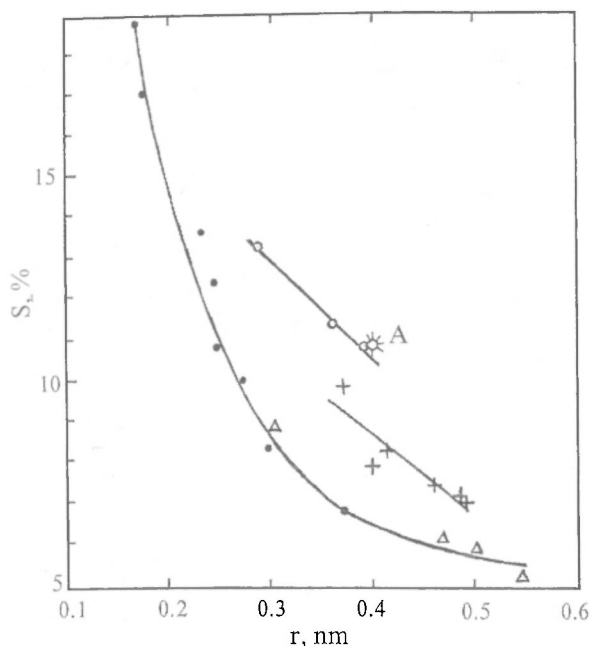


Fig. 2. Positronium annihilation probability (S) versus the nanovoid radius (r) for: the rapidly cooled high-melting triglyceride fraction (Δ); as-prepared high-melting, line a (+) and low-melting, line b (O) fractions; the mixture of high- and low-melting fractions, point A (*); the mixture of high- and low-melting fractions after partial extraction of the latter fraction (\bullet).

results in the appearance of cages near the polar (glycerol moiety) ends of molecules, which connect three hydrocarbon chains. Other type of cages are the voids formed between the shortest chains near unpolar molecular sections.

The asymmetric shape of the nanovoid size distribution is related to the presence of the two types of nanovoids. The larger nanovoids with radii in the range of 0.40–0.56 nm (0.48 nm on average) can be prescribed to the first type, while smaller ones (0.20–0.48 nm) with average radius of 0.34 nm to the second type. The latter nanovoids are surrounded with CH_2 and CH_3 molecular moieties and their radius in thermodynamically stable triglycerides is close to the outer radius of C_{60} fullerene.

After the extraction of the low-melting fraction from the mixture of two triglyceride fractions differing in melting point and the length of the hydrocarbon chains, the appearance of empty quasi-one-dimensional cavities should be expected. The width of such nanovoids can be reduced to the thickness of molecular hydrocarbon chains. This suggestion is validated by the experiment. The dependence of positron-annihilation probability (S) in the vicinity of nanovoids on the nanovoid radius, r , is shown in Fig. 2. For comparison, the same dependence is also shown for (a) the high and (b) the low melting point

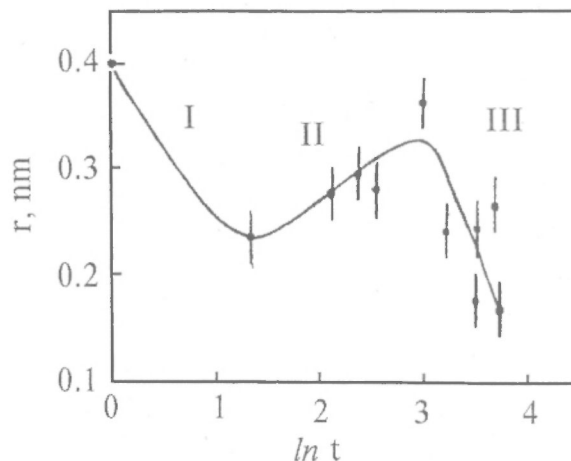


Fig. 3. Temporal dependence of the mean radius of the nanovoids in the mixture of high- and low-melting fractions after partial extraction of the latter fraction (t =days).

fractions of the milkfat triglycerides. Point A on a straight line b corresponds to an as-prepared mixture of the aforementioned fractions (55 and 45 wt%, respectively). It is seen that after partial extraction of low-melting fraction (3 wt%) the dependence $S = f(r)$ not only changes shape (as compared to those, approximated the straight lines, for the pure high- and low-melting fractions), but is significantly shifted towards the smaller radii of the nanovoids. Average nanovoid radius in this case tends to the intermolecular carbon radius, 0.175 nm, and the positronium annihilation probability, S , increases up to 18%.

The time dependence of the average nanovoid radius in the mixture of the two aforementioned fractions after partial extraction of the low-melting fraction is shown in Fig. 3. The dependence is not monotonous, indicating that the structure of the mixture with excess concentration of nanovoids is unstable. Three stages of structural change are observed. In the course of structural ordering the system of triglyceride molecules passes through the most chaotic state with the largest mean radius of the nanovoids (Fig. 3). The ordering results in the nanovoid radius approaching the intermolecular carbon radius, which lies, according to different authors, in the range of 0.17–0.18 nm. In the case of graphite its value is 0.17 nm.

4. Positron annihilation in crystalline C_{60} fullerenes

Calculated parameters of the broad (BG) and medium (MG) Gaussians of the ACAP spectra for graphite and C_{60} fullerenes are listed in Table 1. In order to determine the sites of the positron annihilation, it is necessary to determine the correlation between the electron localization

Table 1

Calculated parameters of the broad and medium Gaussians of the ACAP spectra for graphite and C₆₀ fullerites

Sample	Medium Gaussian (MG)		Broad Gaussian (BG)		ΔX (nm)
	r_m (nm)	S (%)	r_m (nm)	S (%)	
Graphite	0.112 (± 0.001)	82.5	0.0352 (± 0.005)	17.5	0.245 (± 0.005)
Fullerite C ₆₀	0.121 (± 0.001)	78.3	0.0410 (± 0.005)	21.7	0.292 (± 0.005)

radius (r_m) in the intermolecular spaces and the intermolecular distances, ΔX .

The positron annihilation sites will be those intermolecular spaces, which fall on the linear correlation line $r = f(\Delta X)$. The initial correlation curve $r = f(\Delta X)$ was plotted according to the dependence of the electron localization radius, r_m , in interionic spaces determined from ACAP data on the width of interionic spaces, ΔX , in Sm_{1+x}Ba_{2-x}Cu₃O_y with different x . The master curve, approximated by the least-squares linear fit, has the form:

$$R_m(e^-) = 0.029 + 0.30 \cdot \Delta X \text{ (nm)}$$

This straight line is shown in Fig. 4. Also shown are the data for graphite and C₆₀ fullerite. The distance between C₆₀ molecules (Van der Waal's spaces) across the tetrahedral voids, ΔX , in the crystal lattice was found using X-ray diffraction. In the case of graphite ΔX was found under the suggestion that broad (BG) Gaussian results from positrons annihilating covalent bond electrons, i.e.:

$$\Delta X = 0.34 - 2(0.0352 \cdot 1.35) = 0.245 \text{ nm}$$

The normalization factor (1.35) was taken from [9]. The

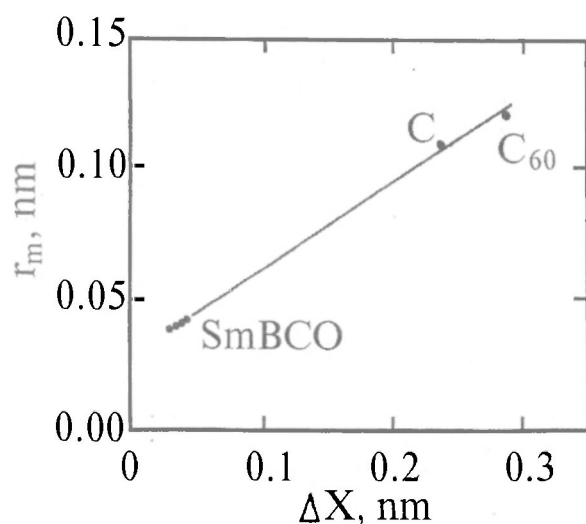


Fig. 4. Electron localization radius, r_m , in the intermolecular space versus the distance, ΔX , between electron shells of the molecules.

measured values of r_m and ΔX for graphite and C₆₀ are near the master straight line (Fig. 4). Therefore, the most probable annihilation sites in C₆₀ fullerites are tetrahedral interstitials, whereas in graphite positrons annihilate mainly in the space between adjacent atomic layers. The results obtained are evidence that positron annihilation in graphite and C₆₀ fullerites occurs in the region of Van der Waal's forces.

The correlation dependence $r = f(\Delta X)$ indicates generality of annihilation mechanisms in interionic and intermolecular spaces of metal oxides (with mixed ionic-covalent bonds) and graphite or C₆₀ fullerite (Van der Waal's bond}. This also allows one to determine the preferential places of localization of positively charged particles in fullerites.

5. Positron annihilation in the fatty-acid triglycerides, containing C₆₀ fullerenes

After crystallization of the triglyceride high-melting point fraction doped with C₆₀ fullerenes, ACAP spectra were measured at increasing temperature: two spectra at 17 °C, eight spectra at 40 °C and five spectra at 70 °C. The positron annihilation parameters are shown in Fig. 5. For comparison, the data for the pure high-melting fraction without fullerenes (dashed line) are also shown. Points corresponding to the high-melting point fraction with fullerenes at 17 °C are near the dashed line. After heating to 40 °C the curve $S = f(r)$ becomes more extended (radii in the range of 0.24–0.63 nm). Such relatively large intermolecular spaces are due to the influence of C₆₀ fullerenes on the crystalline structure of the fatty-acid triglycerides. The heating of the sample to 70 °C shifts the curve $S = f(r)$ towards larger nanovoid radii and higher Ps annihilation probabilities (13–14%). The smallest nanovoid radii are in the range of 0.35–0.36 nm. These values are characteristic of the outer radius of C₆₀ (0.355 nm) [1]. An increase of Ps annihilation probability by a factor of 1.5 and the growth of the minimum nanovoid radius from 0.24 to 0.36 nm is related to the processes of structural ordering in the vicinity of nanovoids. It should be expected that cylindrical nanovoids in the initial state of the fatty-acid triglycerides will transform to the spherical ones, which are energetically more favourable.

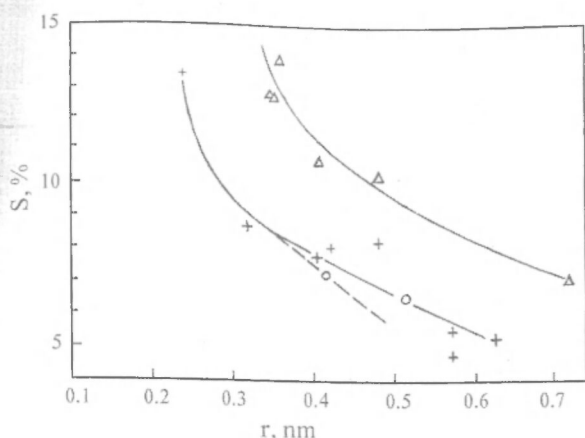


Fig. 5. Positronium annihilation probability (S) versus the nanovoid radius (r) in the fatty-acid triglycerides with dissolved C_{60} fullerenes: at 17 °C (O), 40 °C (+) and 70 °C (Δ). For comparison, dashed line represents pure high-melting fraction.

Penetration of positrons to the interior of nanovoids and the absence of such a phenomenon in fullerites can be accounted for by the presence of an electric field at the nanovoid boundary, which is directed inwards. This field may be generated by the dipole ($C^- - H_2$), which form a spherical capacitor whose inner plate consists of negatively charged carbon atoms, whereas the outer plate contains more electropositive hydrogen atoms. This electric field forms the potential well for positively charged particles. In this case, the nanovoids should be also penetrable by other positive atomic species, e.g. protons and cations. In case of fullerite such penetration was not found.

The proximity of the values of nanovoid radii in the thermodynamically most stable triglycerides (0.35–0.36 nm) to the outer radius of C_{60} fullerene (0.355 nm) indicates that nanovoids are fullerene-like structural elements of the fatty-acid triglycerides. Taking into account geometrical characteristics, fullerenes could be placed inside the nanovoids producing a material with a number of new properties. This is supported by the data shown in Fig. 5 for the fatty-acid triglycerides with dissolved fullerenes. On heating to 70 °C, C_{60} molecules probably penetrate the nanovoids and create long-range fields, which lead to an ordering of the nanovoid sublattice and stabilization of the nanovoid radius at 0.355 nm. Positrons do not penetrate inside fullerene residing in the triglyceride matrix, because in this case their radii would be smaller by a factor of two, but they penetrate to the nanovoid interior.

6. Conclusions

1. The size distribution of the nanovoids, changing in the course of structural relaxation and ordering of the fatty-acid triglycerides has been found. The asymmetry of the distribution function is related to the presence of two types of nanovoids: first, near the polar (glycerol moiety) part of the molecule, with a mean radius of 0.48 nm, and second, between the hydrocarbon chains, with a mean radius of 0.34 nm.
2. The positron annihilation probability (S) is found to decrease with increasing nanovoid radius (r) and tends to zero at $r \geq 0.76$ nm.
3. The mean nanovoid radius can be reduced to the intermolecular carbon radius of 0.17 nm.
4. The most probable sites of positron annihilation in C_{60} fullerites are the tetrahedral voids in the f.c.c. lattice.
5. The nanovoid in the fatty-acid triglycerides is shown to be a potential well for positively charged particles such as positrons, protons, and cations. In the case of f.c.c. C_{60} fullerite, positron penetration into the interior of C_{60} molecule is not found.
6. Fullerenes dissolved in fatty-acid triglycerides lead to an ordering of the nanovoid sublattice and stabilization of the value of the nanovoid radius at 0.355 nm (the radius of the C_{60} molecule).

References

- [1] Shafer HE, Forster M, Wurschum R. Phys Rev B 1992;45(20):12164–6.
- [2] Ito Y, Suzuki T. Phys Rev B 1999;60(23):15636–8.
- [3] Novikov YA, Suptel ZK. Acta Phys Polon A 1999;95(4):659–62.
- [4] Rashevskaya T, Guly I, Pryadko M, Nishchenko MM, Likhtorovich S. Int Agrophys 2000;14:221–5.
- [5] Kudryavtsev VY, Yablochkov SM, Likhtorovich SP. Func Mater 2000;7(3):525–8.
- [6] Jean YC, Rhee Y, Lou Y. Phys Rev B 1996;54(3):1785–90.
- [7] Jean YC, Lu X, Lou Y. Phys Rev B 1992;45(20):12126–9.
- [8] Ferrel RA. Rev Mod Phys 1956;28(3):308–59.
- [9] Nishchenko MM, Likhtorovich SP, Gerasimov AY. Met Phys Adv Technol 2000;18:721–31.