Positron annihilation in C_{60} and C_{70} fullerenes and other carbon phases

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A positron-annihilation study was applied to C_{60} and C_{70} fullerenes and other carbon phases such as nanotubes and graphite. Positrons in C_{60} and C_{70} fullerenes and nanotubes display a single-component time-annihilation spectrum. The results of the lifetimes were 389 ± 2 psec for the C_{60} fullerene, 384 ± 2 psec for the C_{70} fullerene, and 387 ± 1 psec for the nanotube. In addition to the lifetime spectra, we measured the Doppler-broadened line shape of the 511-keV annihilation γ ray, which reflects the density distribution in momentum space of the annihilation electrons sampled by the positron. The annihilation γ-ray line shapes show a remarkable difference between the C_{60} and C_{70} fullerenes and graphite on one hand and nanotube phases on the other hand. The full width at half maximum of the distribution of the annihilation electron momentum decomposed from the obtained spectra are $2.36\times10^{-3}m_0c$ for C_{60}, $2.38\times10^{-3}m_0c$ for C_{70}, and $2.51\times10^{-3}m_0c$ for nanotube and graphite phases. [S0163-1829(99)14447-3]

As is well known, both C_{60} and C_{70} fullerenes have a closed net structure, comprising pentagonal and hexagonal carbon faces.[1] After discovery of the fullerene, many studies on the physical properties and on applications have been performed using various methods. In addition, measurements of the positron lifetime and/or the Doppler broadening of the annihilation γ ray have traditionally been used for material analysis. In this paper, we apply this technique to C_{60} and C_{70} fullerenes and other carbon phases.

The positron-annihilation characteristics depend on the positron and electron density distribution in the material and/or the amount of overlap between the positron and electron wave functions. The effect of the electron-positron correlation leads to an enhancement of the annihilation due to the pileup of electrons around the positron. The positron is fully thermalized at the time of annihilation; in order to conserve momentum, the longitudinal-momentum component of the electron (p_L) along the direction of the annihilated γ-ray emission is related to the Doppler broadening (ΔE) of the annihilation γ-ray energy by

$$p_L = 2\Delta E/c, \tag{1}$$

where c is the speed of light. Therefore, the annihilation γ-ray spectrum corresponds to the density in momentum space of the electrons sampled by the positron.

According to a calculation of the positron density distribution in C_{60}, a positron cannot be localized inside the cavity of the C_{60} molecule.[2–4] The origin of the annihilation characteristics is the result of positron annihilation at the interstitial sites between the C_{60} molecules, which thus yields unique information about these sites. At room temperature, where the directions of the C_{60} molecules are disordered, the positron lifetime between 327 and 408 psec has been calculated to be dependent on the theoretical treatment.[3–5] On the other hand, experimental values between 360 and 430 psec were reported,[2,6,7] and all authors reported a single lifetime component for the positron in the C_{60} fullerene. The observed lifetime is consistent with the theoretical lifetime, but it is difficult to compare the calculation and to estimate the positron density distribution in the C_{60} fullerene from the lifetime. This is because, in spite of a large difference in the positron density distribution due to the theoretical treatment of electron-positron correlation, this does not significantly affect the lifetime. As for the C_{70} fullerene, up to now, the positron lifetime in a mixture of C_{60} and C_{70} fullerenes[8–10] and in C_{70} fullerene[11] has been reported.

In this paper, in addition to the positron lifetime, we compared the Doppler-broadened spectra of the positron-annihilation γ ray in the C_{60} and C_{70} fullerenes and other carbon phases, such as nanotubes,[12] graphite, and diamond. We suggest here that the Doppler-broadened spectra can provide useful information about annihilation characteristics in the carbon phases. On the other hand, Ishibashi[4] has reported that a difference in the positron density distribution due to the theoretical treatment of the electron-positron correlation potential will appear in the annihilation γ-ray spectrum.

In this experiment, a high-quality C_{60} and C_{70} specimen made by a sublimation technique was used; according to a report by Bečvař *et al.*,[7] there is no difference in the lifetime spectra between using a sublimation specimen and a commercial C_{60} specimen without any treatment before the measurement. The sublimation crystals were made from a powder sample with a purity of better than 99.9% for C_{60} and 99% for C_{70} using the sublimation technique already reported by Meng *et al.*[13] The nanotube specimen was baked in a vacuum before the measurement in order to remove any residual solvents and various absorbed gases.

The positron source, ^{22}NaCl, was directly dropped onto specimens packed in a glass tube. All measurements presented here were performed at room temperature and under a vacuum of better than 5×10^{-6} torr. A conventional fast-fast coincidence system with a time resolution of 270 psec (full

TABLE I. Results of positron lifetimes in C_{60}, C_{70}, and nanotubes, and FWHM's of the momentum distribution of electron annihilation with positron decomposed from the Doppler-broadened γ-ray spectrum and Eq. (1).

	Lifetime (psec)	FWHM of electron momentum
C_{60}	389 ± 2	$2.36\times10^{-3}m_0c$
C_{70}	384 ± 2	$2.38\times10^{-3}m_0c$
Nanotube	387 ± 1	$2.51\pm10^{-3}m_0c$

width at half maximum, FWHM) was used for the lifetime measurements. The spectra were decomposed by the PATFIT package by a two-component analysis. In the C_{60}, C_{70}, and nanotube specimens, the positron lifetimes were represented well by one component ($\sim$390 psec), which means that all of the positrons in these specimens have a rather similar history between annihilation. The values of the observed positron lifetime are listed in Table I. The lifetimes in C_{60} and C_{70} obtained in this experiment are consistent with those in the previous experiments reported in Refs. 6–11. We also report here that a similar positron lifetime exists for nanotubes as in both the C_{60} and C_{70} fullerenes. It is interesting that positrons in nanotubes have a single lifetime component, in spite of our nanotube specimen consisting of multilayer coaxial graphitic tubes. In Fig. 1, we show the lifetime spectrum in a nanotube and a graphite specimen. In graphite, as shown in Fig. 1, one can easily identify two lifetime components of 220 ± 10 psec, due to positron annihilation in the bulk, and 430 ± 10 psec, due to positron annihilation on the surfaces or the open spaces of graphite.[14] In nanotubes, our result shows that the positron does not annihilate between the coaxial layer of graphitic tubes, but annihilates on the surface of the tube.

The Doppler-broadening measurements discussed here were performed using a Ge detector with a resolution of 1.06

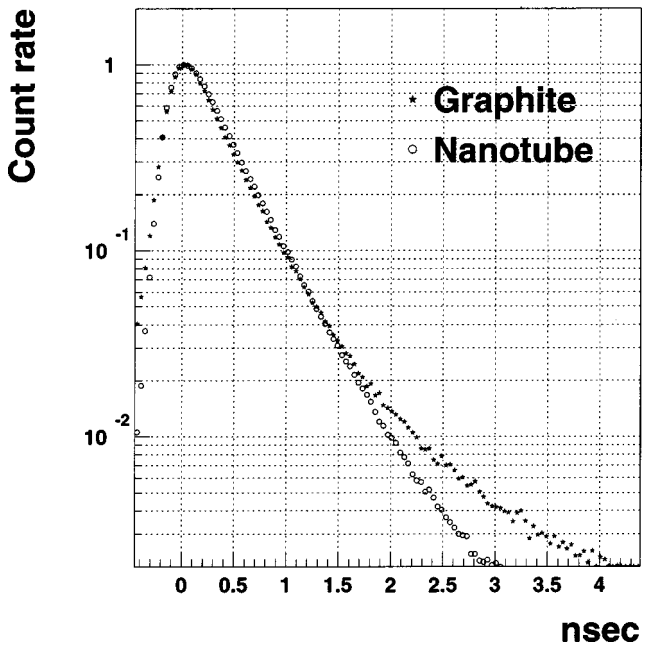

FIG. 1. Positron lifetime spectra in nanotubes (○) and graphite (★). A positron in nanotubes has a single lifetime component, although it has two lifetime components in graphite.

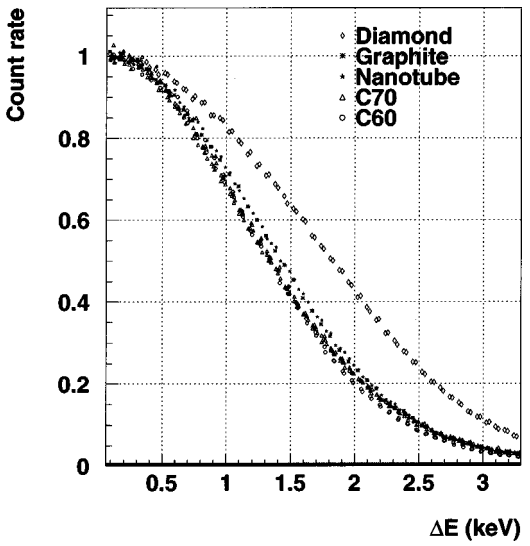

FIG. 2. Positron-annihilation γ-ray spectra in C_{60} (○), C_{70} (△), nanotubes (★), graphite (∗), and diamond (◇). The spectra were normalized by the peak height, and the energy (ΔE) is the difference from the 511-keV γ ray. Differences of the electron momentum distribution between these specimens are clearly observed.

keV (FWHM), determined by the ^{85}Kr 514-keV standard γ ray. Several measurements were performed for each specimen, and we obtained good reproducibility of the results. In Fig. 2, Doppler-broadened γ-ray spectra for positron annihilation in C_{60} (○), C_{70} (△), nanotube (★), graphite (∗), and diamond (◇) are shown. Because each spectrum was collected with sufficient statistics, the statistical errors are almost the same as those for the marker sizes. Each spectrum was normalized by the height of the annihilation γ-ray peak; also, the energy (ΔE) is the difference from the 511-keV γ ray. There is no distinct structure in these spectra, which are represented well by a one-component Gaussian distribution. If we fitted the spectra with one Gaussian function, the FWHM of each spectrum could characterize the momentum distribution of the annihilation electron. The obtained FWHM for C_{60}, C_{70}, and nanotubes are also listed in Table I. The spectra in Fig. 2 clearly show differences in the annihilation γ-ray distribution for each specimen.

In Fig. 2, diamond, which is a good insulator, has the largest FWHM of the annihilation γ-ray distribution among these carbon phases. According to a positron-distribution-probability calculation,[3,15] in diamond, a positron is delocalized and annihilates in the interstitial space between the bond of the carbon ion. The FWHM of the longitudinal-momentum distribution of the electron (p_L) along the annihilated γ-ray emission, obtained from Fig. 2 and Eq. (1) and unfolded by the detector resolution, is $3.22\times10^{-3}m_0c$.

The graphite spectrum obtained in this experiment shows good agreement with that obtained by Colombino, Fiscella, and Trossi[16] and S. Berko, Kelley, and Plaskett.[17] In graphite the relative positron density at the carbon bonds is much smaller than that at the bonds in the diamond structure. The positron annihilates with both π and σ electrons on the graphite planes.[3] Contributions of the π electrons on positron annihilation have been estimated at 45.5–48 %.[16,17] As mentioned concerning the lifetime measurement in nanotubes, positrons annihilate predominantly on the surfaces of the

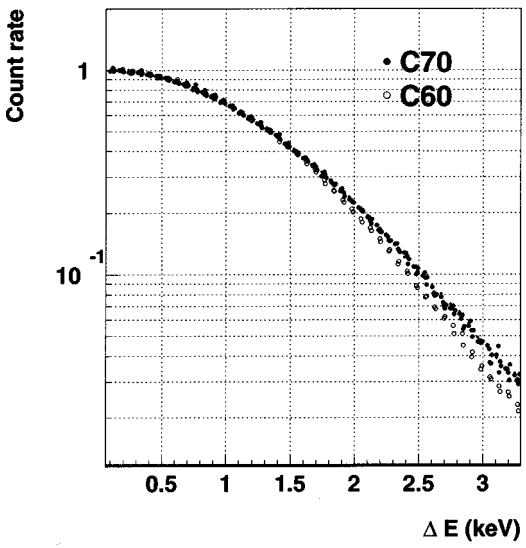

FIG. 3. Logarithmic plot of the annihilation γ-ray spectra in C_{60} (○) and C_{70} (●). The difference between C_{60} and C_{70} in the spectra can be clearly observed.

tubes. However, no difference in the positron-annihilation spectrum between nanotubes and graphite was observed, in spite of the graphite spectrum being composed of the positron-annihilation γ rays on the surfaces and bulk of the graphite. The result of the FWHM of the momentum distribution of electrons sampled by the positrons for the graphite and nanotube phases is $2.51\times10^{-3}m_0c$.

The positron density at the center of a C_{60} molecule is negligible, which is concentrated at interstitial sites between the C_{60} molecules. The differences in the annihilation γ-ray distribution between the fullerene and graphite phases can be clearly observed in Fig. 2. The value of the obtained FWHM of the momentum distribution of electrons in C_{60} is $2.36\times10^{-3}m_0c$ and $2.38\times10^{-3}m_0c$ in C_{70}.

The difference between C_{60} and C_{70} in the annihilation γ-ray distribution is observed in the tail of the annihilation γ-ray spectrum. To clarify this difference, we plot the annihilation γ-ray spectra with a logarithmic plot in Fig. 3. The fast component of the annihilation γ-ray spectrum for C_{70} is similar to that for C_{60}, though it deviates from the C_{60} spectrum at the positron annihilation with an electron having a higher momentum. Here the spectrum is close to that for the graphite and nanotube phases.

In summary, we have reported on the lifetime and Doppler-broadened γ-ray spectra of positron annihilation in C_{60}, C_{70}, and nanotubes. We have observed the single lifetime ($\sim$390 psec) of positrons in C_{60}, C_{70}, and nanotubes in spite of the graphite having two lifetime components. From the Doppler-broadened spectra we observed an interesting difference in the annihilation γ-ray distribution among these specimens, which reflects a difference in the momentum distribution of the electron annihilated with the positron. In particular, the difference between the C_{60} and C_{70} fullerenes proves interesting in future studies.

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