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# High sensitivity of the positron-density distribution to the K doping in $C_{60}$

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Distinct positron lifetimes in $C_{60}$ and in $K_3C_{60}$ superconductors are observed: a single lifetime (375 ps) in pure $C_{60}$ and two lifetimes (265 and 425 ps) in $K_3C_{60}$. The positron densities, computed by using the self-consistent orthogonalized linear combination of the atomic-orbital band structure in $K_xC_{60}$ ($x=0$, 1, 2, 3, and 6) are presented. The strong dependence of the positron-density distribution on the amount of K doping, varying from interstitial sites outside the ball to the cavity inside the ball, demonstrates the use of the positron to probe local charge densities in $C_{60}$-based superconductors.

Recent discoveries that bulk quantities of the $C_{60}$ molecules can be crystallized[1] and intercalated by metallic ions to give superconductivity[2,3] have prompted various investigations of the physical properties of both $C_{60}$ and doped fullerenes. Positron annihilation spectroscopy (PAS) is a special probe for the characterization of electronic and defect structures of solids.[4] Recently, we[5] and other groups[6] have discovered that there exists a single positron lifetime in $C_{60}$ solids. PAS has been successfully used to probe the local charge densities of oxide superconductors.[7] It is therefore of much interest to study positron annihilation in $C_{60}$-based superconducting materials. In this paper, we report the experimental measurement of positron lifetimes and the determination of positron-density distributions (PDD) from band-structure calculations in $K_3C_{60}$ superconductors. Contrary to the single lifetime observed in $C_{60}$,[5,6] we observe two distinct positron lifetimes in $K_3C_{60}$. In order to understand the positron results, we have performed a complete calculation of PDD by means of the first-principles orthogonalized linear combination of atomic orbital (OLCAO) method[8] in the local-density approximation (LDA). From both experimental and theoretical results, we report evidence that the PDD is highly sensitive to the amount of alkali-metal ion doped into $C_{60}$ systems.

The $C_{60}$ samples were purchased from MER Corp. (Tucson, AZ) with a chemical purity of 99.9 at.% $C_{60}$. No contamination of $C_{70}$ was detected in column chromatography for solutions with samples dissolved in 5% toluene in hexane passing through alumina. The superconducting $K_3C_{60}$ and nonsuperconducting $K_6C_{60}$ samples were synthesized by a direct chemical reaction by mixing a stoichiometric ratio of high-purity K metals (Alfa Chem. 99.93%) and $C_{60}$ powders under high vacuum at 225 °C. The synthesized $K_3C_{60}$ materials were annealed for many cycles at 250 °C until a maximum Meissner signal (50% diamagnetic shielding compared to Nb) is obtained. The dc magnetic susceptibility $\chi(T)$ curve shows an onset at $T_c=19.0$ K. The shape of the $\chi(T)$ curve is very similar to those reported in the literature for K-fullerite superconductors.[2,3] Raman and x-ray spectra all show consistently a $K_3C_{60}$ superconducting phase. The powder samples with a grain size of $\sim 1$ $\mu$m were pressed under a pressure of 500 bars into disks with a size of 4 mm diam and a thickness of 1 mm under an atmosphere of dry high-purity He.

The positron source (15-$\mu$Ci $^{22}$Na supported in 1.0-mg/cm$^2$ Al foils) was sandwiched between samples and then sealed in an Al can under a He atmosphere. The positron lifetime spectra were obtained by the conventional fast-fast coincidence method. The lifetime spectrometer has a resolution function of two Gaussians (95% of 260 ps and 5% of 350 ps full width at half maximum) as resolved from the RESOLUTION program.[9] All lifetime spectra were least-squares fitted using the POSITRONFIT program[9] where a source correction has been made. The results of lifetime spectra analysis for $C_{60}$, $K_3C_{60}$, and $K_6C_{60}$ samples are listed in Table I.

As shown in Table I, in pure $C_{60}$ there exists only one lifetime component (375 ps with an intensity of 99%) while in $K_3C_{60}$ there exist two positron lifetimes. No positronium formation is found in any sample, as determined from the spectra of angular correlation of positron annihilation radiation. The result of a single positron lifetime in pure $C_{60}$ is consistent with those recently reported by oth-

TABLE I. Experimental positron lifetimes in $C_{60}$, $K_3C_{60}$, and $K_6C_{60}$.

| | One-component fit | | Two-component fit | | | |
|---|---|---|---|---|---|---|
| Samples | $\tau$ (ps) | Variance of fit | $\tau_1$ (ps) | $\tau_2$ (ps) | $I_2$ (%) | Variance of fit |
| $C_{60}$[a] | 354 | 1.72 | 170 | 356 | 98.0 | 1.05 |
| (97%) | ±1 | | ±25 | ±1 | ±0.1 | |
| $C_{60}$[b] | 374 | 1.34 | 200 | 375 | 99.0 | 1.00 |
| (99.9%) | ±1 | | ±40 | ±2 | ±0.1 | |
| $K_3C_{60}$[c] | 343 | 5.76 | 265 | 425 | 48.0 | 0.99 |
| | ±1 | | ±12 | ±12 | ±0.7 | |
| $K_6C_{60}$ | 340 | 12.3 | 269 | 406 | 51.5 | 0.99 |
| | ±1 | | ±5 | ±4 | ±1.1 | |

[a]For this $C_{60}$ (97%, the rest are $C_{70}$), the results are from Ref. 5.
[b]Results from this work.
[c]This is a superconducting material with $T_c=19.0$ K.

 

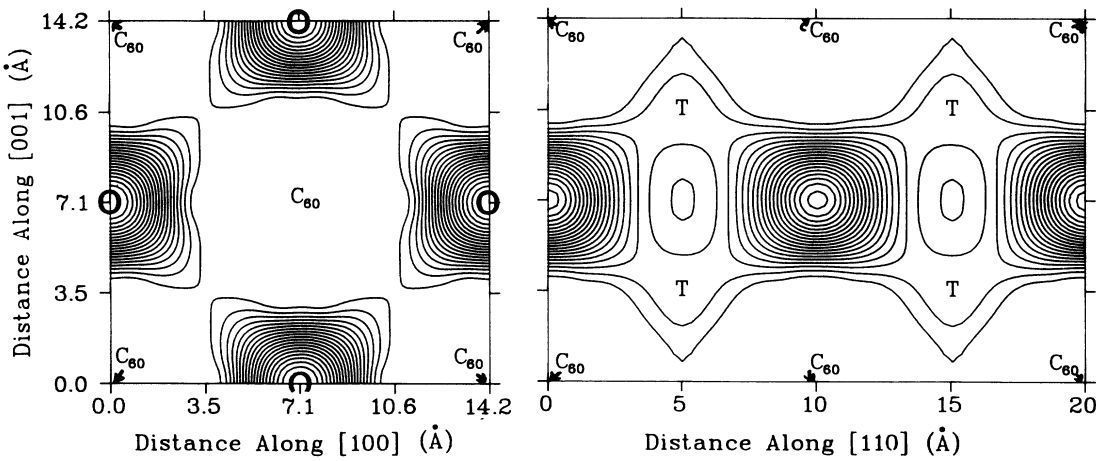


FIG. 1. The contour plots of the positron-density distribution in $C_{60}$ fcc lattices for planes (100) and (110) using OLCAO method. The maximum positron densities are seen at the center of contours which are also the octahedral sites and the minima are seen at the center of the $C_{60}$ structure. *O* and *T* notations in the figures refer to the octahedral and tetrahedral sites, respectively.

ers[6] including ours.[5] The distinct difference in positron lifetimes between $C_{60}$ and $K_3C_{60}$, which has the same fcc structure, indicates that the PDD has been dramatically changed as the K is doped in $C_{60}$.

In order to understand these PAS results, we have performed a series of PDD calculations by solving the single-particle Schrödinger equation for a positron in five systems: $K_xC_{60}$ ($x=0$, 1, 2, 3, and 6). The positron potential is constructed from band calculations of these systems using the OLCAO method[8] as

$$V_+ = V_C(\mathbf{r}) + V_{\text{corr}}(n(\mathbf{r})) , \quad (1)$$

where $V_C$ is the Coulomb part of the crystal potential in the one-electron Hamiltonian obtained from the OLCAO band calculations. The electron-positron correlation potential $V_{\text{corr}}(n(\mathbf{r}))$ is obtained from the LDA scheme.[10,11] The positron wave function was solved numerically in real space under periodic boundary conditions using the numerical relaxation method. The details of the computational procedures can be found in our previous paper.[11] The lattice parameters were taken from the published experimental values.[12]

The calculated PDD's for fcc $C_{60}$ using the OLCAO method are shown in Fig. 1, for the (100) and (110) planes. The maxima of the PDD are found to be located at the octahedral (interstitial) sites of the fcc lattice. The PDD at the center of $C_{60}$ molecules is found to be minimal. The volume fraction of PDD distributed at the tetrahedral sites is found to be very small, about 2%. The present more accurate calculation shows that the PDD is distributed more in the octahedral sites than those obtained using the atomistic approximation.[5] As expected, the difference of PDD's between these two methods for pure $C_{60}$ is very small because electrons are tightly bound to C atoms in fcc $C_{60}$.

Next we report the calculated PDD results in fcc $K_3C_{60}$ where K occupies both the octahedral and the tetrahedral sites. The PDD's along the (100) and (110) planes using the OLCAO method are shown in Fig. 2. We found that

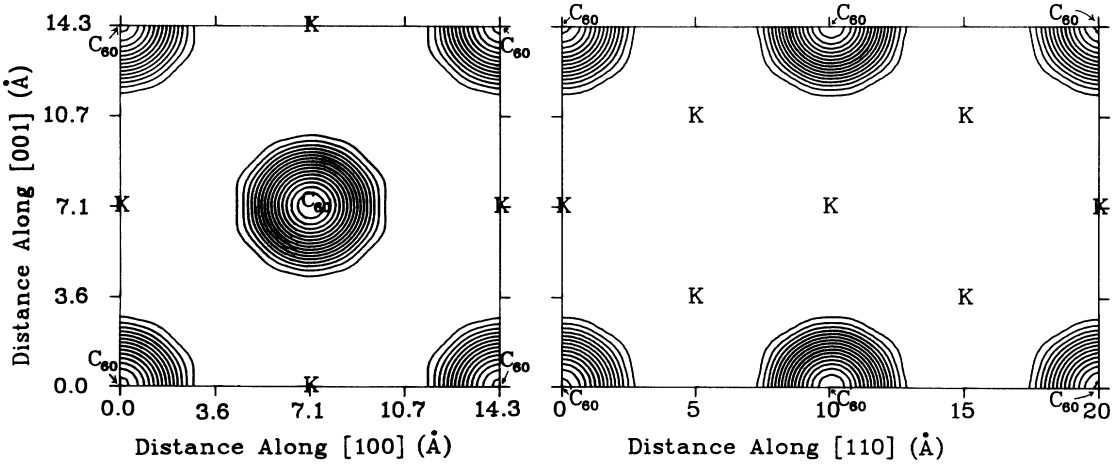


FIG. 2. The contour plots of the positron-density distribution in $K_3C_{60}$ fcc lattices for the (100) and (110) planes. The maximum positron densities are seen at the center of $C_{60}$ and the minima are seen at the doped K, both octahedral (*O*) and tetrahedral (*T*) sites.

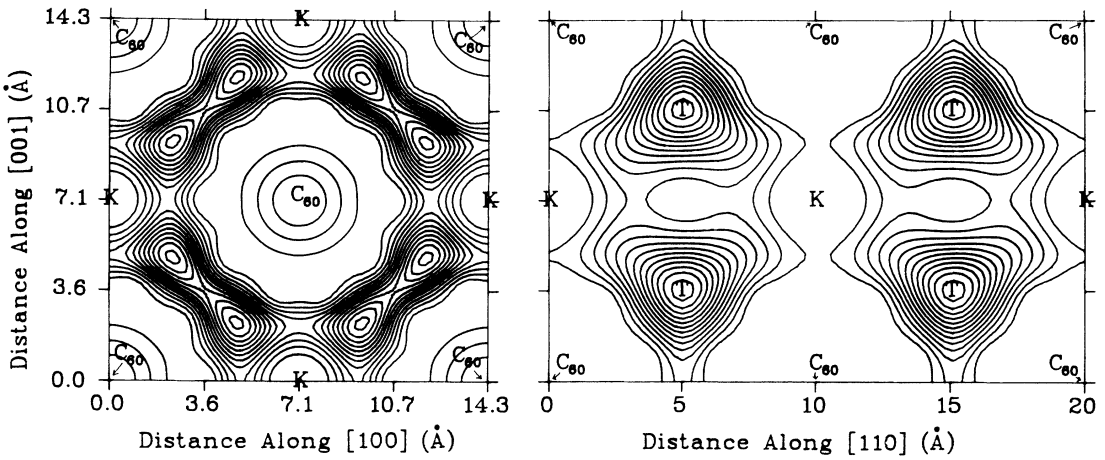


FIG. 3. The contour plots of the positron-density distribution in $KC_{60}$ fcc lattices for the (100) and (110) planes using OLCAO method. The maximum positron densities are seen at the tetrahedral sites ($T$) and the minima are seen at the doped K (octahedral sites).

PDD's are distributed only inside the $C_{60}$ cavity of $K_3C_{60}$. The maxima of PDD's are located at the center of the $C_{60}$ cavity. Comparing the PDD's in $C_{60}$, and in $K_3C_{60}$, we found a distinct difference: In pure $C_{60}$ the positron is outside the molecule while in $K_3C_{60}$ the positron is inside the $C_{60}$ cage. This distinct difference of PDD's between two systems can be understood from a view that K is positively charged in $K_3C_{60}$ after occupying the low electron-density regions outside the molecule. The resulting repulsive potential due to the doping of the K ions makes the cavity of the $C_{60}$ molecules a more favorable site for PDD.

In order to understand the sensitivity of PDD's in K-doped $C_{60}$ structures more thoroughly, we have calculated the PDD's in $KC_{60}$ and $K_2C_{60}$ systems where K occupies the octahedral and the tetrahedral sites, respectively.[8] The results are shown in Figs. 3 and 4 for $KC_{60}$ and $K_2C_{60}$, respectively. In the case of $KC_{60}$, where all the octahedral sites have been occupied by K, the PDD's are found to be distributed near the tetrahedral sites and only a small fraction (about 3%) are distributed inside the molecule. On the other hand, in the case of $K_2C_{60}$, where K occupies all the tetrahedral sites, the PDD's are all distributed near the octahedral sites. Comparing the PDD's of $C_{60}$ (Fig. 1) and $K_2C_{60}$ (Fig. 4), one finds that the small fraction of PDD (about 2%) near the tetrahedral site in $C_{60}$ is shifted to the octahedral sites and no PDD is found inside the $C_{60}$ molecules of $K_2C_{60}$.

Having obtained the PDD's, we proceed to calculate the positron lifetimes in $K_xC_{60}$ systems and compare them with the experimental values. The lifetime is the inverse of the annihilation rate $\lambda_{tot}$, which is a sum of the annihilation rate $\lambda_{val}$ from the valence electrons and $\lambda_c$ from the core electrons. $\lambda_{val}$ is calculated by taking into account the enhancement due the local electron density around the positron using[10,11]

$$\lambda_{val}=\int |\Phi_+(\mathbf{r})|^2[2+134n_v(\mathbf{r})]d\mathbf{r}\,, \tag{2}$$

where $n_v(\mathbf{r})$ is the valence-electron density obtained from the OLCAO calculations.[9] The annihilation rate from the

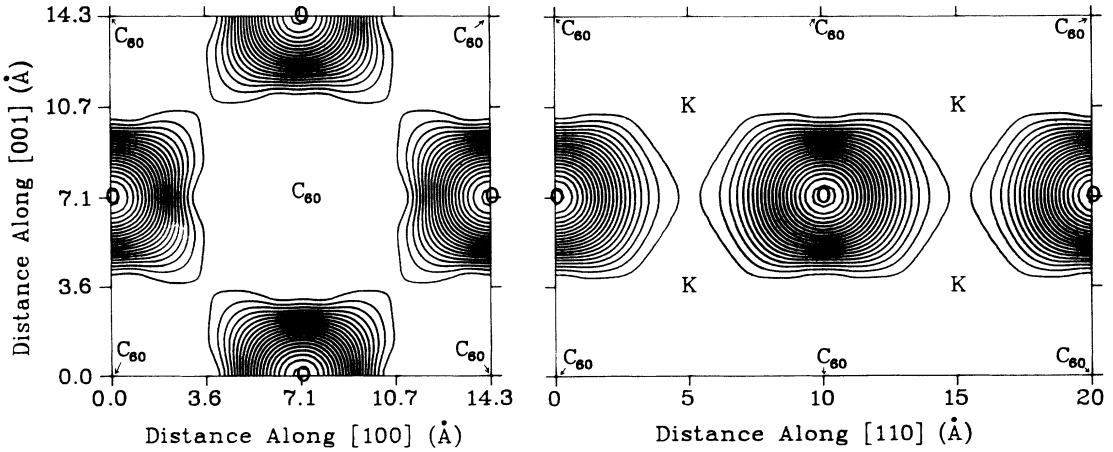


FIG. 4. The contour plots of the positron-density distribution in $K_2C_{60}$ fcc lattices for the (100) and (110) planes. The maximum positron densities are seen at the center of contours which are also the octahedral sites ($O$) and the minima are seen at the center of the $C_{60}$ and at the doped K (tetrahedral sites).

core electron is obtained by calculating the overlap of the positron and core electron density in the independent-particle approximation:[10]

$$\lambda_c = 16\pi \int |\Phi_+(\mathbf{r})|^2 n_c(\mathbf{r}) d\mathbf{r} . \quad (3)$$

In order to check the accuracy of the calculated lifetimes in $K_3C_{60}$, we first calculate the positron lifetime in diamond where the electron density and potentials[8] and the experimental lifetime[13] are available. The calculated positron lifetime of 83 ps which is in reasonable agreement with the experiment value of $97.5 \pm 1.5$ ps.[13] The results of calculated positron lifetimes for $K_xC_{60}$ systems using the OLCAO method are listed in Table II. The calculated lifetimes show a large variation as a function of K doping. This variation is directly correlated with the PDD in the $K_xC_{60}$. In $C_{60}$ and $K_2C_{60}$, where the positron is near the octahedral sites, the calculated lifetimes are found to be nearly the same, i.e., 325 and 326 ps, respectively. In $KC_{60}$ where the positron is near the tetrahedral site, the lifetime is 268 ps, which is significantly lower than that in the octahedral sites (325 ps). On the other hand, in $K_3C_{60}$ where the positron is distributed inside the $C_{60}$ molecule, the lifetime is 232 ps. Furthermore, we found consistently a short lifetime (250 ps) in $K_6C_{60}$ where the PDD is also found to be inside the molecule. Comparing the calculated lifetime with the experimental positron lifetime in $C_{60}$, and in diamond, we found that the calculated lifetimes are consistently shorter than the experimental values. This discrepancy is attributed to the approximations used in evaluating the lifetimes according to Eqs. (2) and (3) described above. The calculation of an exact positron lifetime is a very difficult quantum-mechanical problem due to the difficulties in evaluating the accurate positron-electron correlation. At this stage, we employ the calculated lifetimes to interpret qualitatively the two experimentally observed lifetimes in $K_3C_{60}$ (Table I). A short lifetime (265 ps) is assigned to the positron lifetime in bulk $K_3C_{60}$. It is close to but slightly larger than the calculated lifetime (232 ps) and the discrepancy is consistent with the differences between the theory and the experiments. A long lifetime (425 ps) is assigned to the positron annihilation on the surface and in the spaces in between the grains of $K_3C_{60}$ solids. This lifetime is close to the observed surface lifetimes ($425 \pm 25$ ps) in graphite powders.[14] The positron-surface binding energy in graphite was measured to be $3.0 \pm 0.2$ eV.[14] As shown in Table II, the positron binding energy in $K_3C_{60}$ is smaller than that in $C_{60}$ and is closer to that of the surface of graphite. Therefore the positron is expected to diffuse to the surface more easily in $K_3C_{60}$ than in $C_{60}$. Furthermore, the observed two lifetimes in $K_6C_{60}$ with a surface lifetime 406 ps (51.5%) and the low value of the binding energy also consistently support this assignment.

TABLE II. Calculated positron lifetimes in $K_xC_{60}$ systems. All results were calculated by using OLCAO band-structure method.

| Systems | $\lambda_v$ ($ns^{-1}$) | $\lambda_c$ ($ns^{-1}$) | $\lambda_{tot}$ ($ns^{-1}$) | $\tau_{calc}$ (ps) | $\tau_{expt}$ (ps) | $-E_+$[a] (eV) |
|---|---|---|---|---|---|---|
| $C_{60}$ | 3.056 | 0.0155 | 3.072 | 325 | 375[b] ± 2 | 4.6 |
| $KC_{60}$ | 3.686 | 0.0366 | 3.723 | 268 | · · · | 3.7 |
| $K_2C_{60}$ | 3.041 | 0.0220 | 3.063 | 326 | · · · | 4.1 |
| $K_3C_{60}$ | 4.259 | 0.0400 | 4.299 | 232 | 265[c] ± 12 | 4.0 |
| $K_6C_{60}$ | 3.961 | 0.0288 | 3.990 | 250 | 269[c] ± 5 | 3.6 |
| Diamond | 11.737 | 0.2613 | 11.998 | 83 | 97.5[d] ± 1.5 | |

[a] $E_+$ are the positron binding energies in the bulk.
[b] From this work (Table I).
[c] From this work (the short lifetime taken from Table I).
[d] From Ref. 13.

In summary, we have observed a distinct difference of the positron lifetimes in $C_{60}$ and in $K_3C_{60}$ solids. Theoretical calculations of PDD's using OLCAO method show that the positron may be distributed outside the molecule at the interstitial octahedral or tetrahedral sites or inside the molecule depending on the amount of K doping. Both experimental and calculated results show evidence of high sensitivity of the positron-density distribution to the doping of K in $C_{60}$ fullerenes. Applications of PAS to probe superconductivity in $C_{60}$-based materials appear to be very promising.

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