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LETTER TO THE EDITOR

Positron states in C_{60} and potassium-doped C_{60} crystals

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Abstract. Positron lifetimes and distributions in C_{60} and potassium-doped C_{60} crystals are calculated using the superposed-atom model and the numerical relaxation technique. In the calculation on pure C_{60} , the high-frequency dielectric constant is treated as a parameter and has been determined to be ~ 3.5 by fitting the lifetime to the experimental value. Positrons are distributed predominantly at the octahedral interstices in pure C_{60} . The lifetime and the distribution of positrons are significantly affected by potassium doping when the dopant atoms occupy the octahedral sites, whereas they are not altered much by doping at the tetrahedral sites or at the centre of the C_{60} cluster. It is revealed that the positron is a very sensitive probe of dopant atoms occupying the octahedral sites. Possible applications are discussed.

The successful synthesis of bulk quantities of C_{60} [1] and the discovery of superconductivity in potassium-doped C_{60} [2] have caused a great enhancement of interests in carbon clusters. The truncated icosahedral structure of the C_{60} molecule was originally suggested by Kroto *et al* [3]. In the crystal form, the C_{60} molecules are orientationally disordered at room temperature and the crystal structure is regarded as a face-centred cubic (FCC) configuration of the C_{60} clusters [4,5]. Below 249 K, the molecules becomes orientationally ordered [5] and the crystal structure changes to simple cubic, whose symmetry is $Pa\bar{3}$ [6].

There are one octahedral and two tetrahedral interstices per C_{60} molecule in the FCC lattice. The superconducting K_3C_{60} has an intercalated FCC structure in which potassium atoms occupy both of these interstitial sites [7, 8]. Three two-fold axes of the C_{60} molecule are along the crystal axes and the molecules are disordered between the two possible orientations [8]. In this case, the space group is $Fm\bar{3}m$. Theoretical calculations by Saito and Oshiyama [9] indicate that potassium atoms prefer the tetrahedral sites to octahedral sites.

The positron is a sensitive probe of the open volume in condensed matter and has been utilized for crystalline defect spectroscopies [10]. In the C_{60} crystal, there are three kinds of open spaces; octahedral and tetrahedral interstices and the inner space of the C_{60} molecule. It is interesting to investigate a positron state in such a material. Experimentally, Azuma *et al* [11] reported a single positron lifetime of 393 ps at room temperature.

In this letter, we present theoretically calculated results of positron lifetimes and distributions in C_{60} and potassium-doped C_{60} crystals and discuss the applicability of positron annihilation as a characterization tool for these materials.

Calculations were performed using the superposed-atom model developed by Puska and Nieminen [12]. The positron potential $V(r)$ is denoted as

$$V(r) = V_C(r) + V_{\text{corr}}(n_-(r)) \quad (1)$$

where V_C is the Coulombic part from the nuclei and electrons, while V_{corr} is a correlation potential due to positron-electron correlation effects. The practical form of V_{corr} as a function of $n_-(r)$ was given by Boroński and Nieminen [13]. $n_-(r)$ and $V_C(r)$ were obtained by the superposition of neutral-atom electron densities and potentials [14]. The positron Schrödinger equation can be solved by the numerical relaxation technique proposed by Kimball and Shortley [15]. The differential equation is replaced by a set of linear algebraic equations on a set of three-dimensional mesh points.

The positron lifetime is obtained as an inverse of the annihilation rate which is represented as follows:

$$\lambda = \int dr n_+(r) [\lambda_v(n_v(r)) + \lambda_c(n_c(r))] \quad (2)$$

where n_+ , n_v and n_c represent the density of positron, valence and core electrons, respectively. $\lambda_v(n_v)$ is the partial annihilation rate of positrons with valence electrons and is given in atomic units by:

$$\lambda_v(n_v) = \pi r_0^2 c n_v \Gamma_v = 16 \pi n_v \Gamma_v = (12/r_s^3) \Gamma_v \quad (3)$$

where r_0 is the classical electron radius and c is the speed of light. r_s is the density parameter defined by

$$r_s = (3/4\pi n_v)^{1/3}. \quad (4)$$

Γ_v is the enhancement factor for valence electrons. For metals, in which valence electrons can be treated as nearly free electron, we can use the Brandt-Reinheimer expression [16] (metal model):

$$\Gamma_v = 1 + \frac{r_s^3 + 10}{6}. \quad (5)$$

The partial annihilation rate becomes:

$$\lambda_v(n_v) = \frac{12}{r_s^3} \left(1 + \frac{r_s^3 + 10}{6} \right) = 2 + 134 n_v. \quad (6)$$

$\lambda_c(n_c)$ is a partial annihilation rate with core electrons and is represented as follows using a constant enhancement factor $\Gamma_c = 1.5$:

$$\lambda_c(n_c) = \pi r_0^2 c n_v \Gamma_c = 24 \pi n_v = 18/r_s^3. \quad (7)$$

In semiconductors, the positive charge of the positron is less effectively screened compared with the case for metals because of the existence of a bandgap. Equation (6) is modified using a high-frequency dielectric constant, ϵ_∞ , as a parameter [17] (semiconductor model):

$$\lambda_v(n_v) = \frac{12}{r_s^3} \Gamma_v^{\text{semi}} = \frac{12}{r_s^3} \left(1 + \frac{(1 - 1/\epsilon_\infty) r_s^3 + 10}{6} \right) = 2 \left(1 - \frac{1}{\epsilon_\infty} \right) + 134 n_v \quad (8)$$

where Γ_v^{semi} is an enhancement factor in the semiconductor model. Accompanied with this modification, the correlation term V_{corr} should be changed according to a scaling argument [18]:

$$V_{\text{corr}}^{\text{semi}} = V_{\text{corr}} \left(\frac{\Gamma_v^{\text{semi}} - 1}{\Gamma_v - 1} \right)^{1/3} = V_{\text{corr}} \left(\frac{(1 - 1/\epsilon_\infty)r_s^3 + 10}{r_s^3 + 10} \right)^{1/3}. \quad (9)$$

Calculations have been performed in an irreducible $1/24$ volume of the unit cell using a mesh spacing of $a_0/40$, where a_0 is the lattice constant of the C_{60} crystal. We regard $C 2s^2 2p^2$ as the valence electrons and $C 1s^2$ as the core electrons.

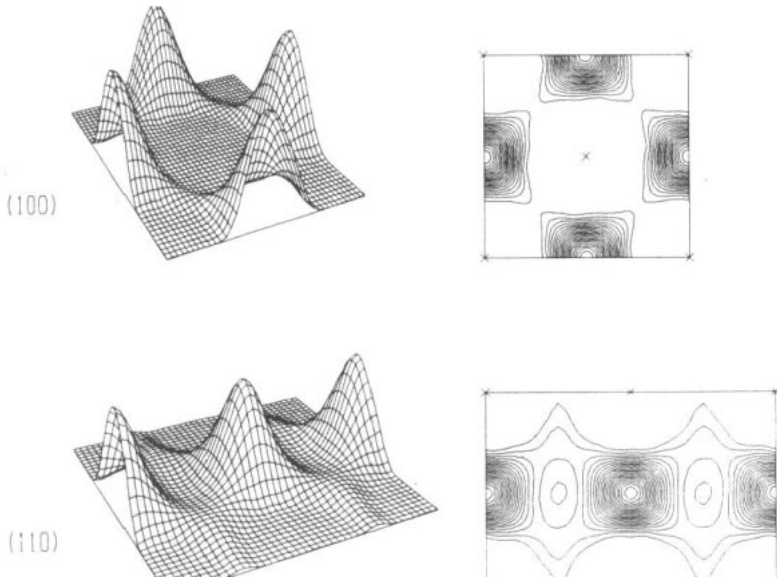


Figure 1. Positron density distribution in the C_{60} crystal on the (100) and (110) planes. The contour spacing is $1/20$ of the maximum value. Crosses represent centres of the C_{60} molecules.

Figure 1 represents the positron distribution in the C_{60} crystal calculated using the metal model and the experimental structural data at 5 K ($a_0 = 14.041 \text{ \AA}$) [6]. It is shown that positrons are predominantly distributed at octahedral interstices. The corresponding positron lifetime is 323 ps, which is considerably shorter than the experimental value of 393 ps [11] even if thermal expansion of the lattice is taken into account. In order to calculate the lifetime at room temperature, we assumed a structure in which atomic coordinates are uniformly expanded so that the lattice constant matches the experimental value at room temperature (14.198 \AA [4]). The resultant lifetime is 327 ps. This discrepancy between the experimental and calculated lifetimes is due to the application of the inadequate metal model; the pure C_{60} crystal is a semiconductor.

We then performed calculations using the semiconductor model. In figure 2, obtained lifetime values are shown as a function of $(1 - 1/\epsilon_\infty)$. Results obtained in the same way as above at room temperature are also included. The positron

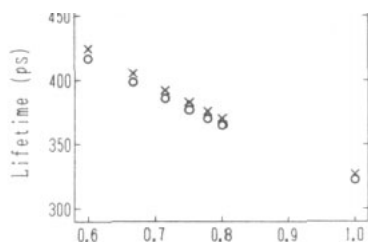


Figure 2. Calculated positron lifetime values as a function of $(1 - 1/\epsilon_\infty)$. Open circles are results for the structural data at 5 K [6] and crosses represent values for room temperature.

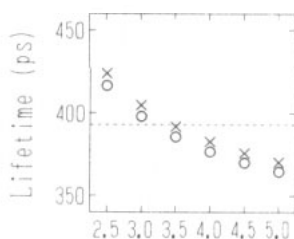


Figure 3. Calculated positron lifetime values as a function of ϵ_∞ . Open circles and crosses have the same meaning as in figure 2. The break line represents the experimental value of 393 ps [11].

lifetime increases with decreasing $(1 - 1/\epsilon_\infty)$. Figure 3 represents the variation of lifetime with ϵ_∞ . By comparing the calculated results for room temperature with the experimental results [11], the value of ϵ_∞ can be estimated to be ~ 3.5 . The positron distribution is not altered much by varying ϵ_∞ , as shown in figure 4 for $\epsilon_\infty = 3.5$.

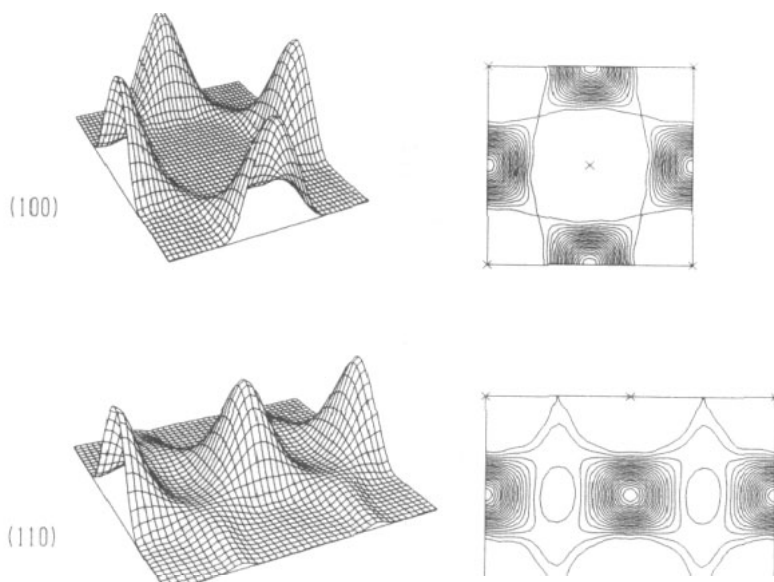


Figure 4. Positron density distribution in the C_{60} crystal on the (100) and (110) planes for $\epsilon_\infty = 3.5$. The contour spacing is $1/20$ of the maximum value. Crosses represent centres of the C_{60} molecules.

We have also calculated positron lifetimes and distributions in potassium-doped C_{60} , putting potassium atoms into the pure C_{60} lattice [6] which was used in the above calculations. Calculations have been done on four structural models— KC_{60} (K at the octahedral interstices), K_2C_{60} (K at the tetrahedral interstices), K_3C_{60} (K at both the interstices) and $K@C_{60}$ (K at the centre of the C_{60} molecule)—using both the metal

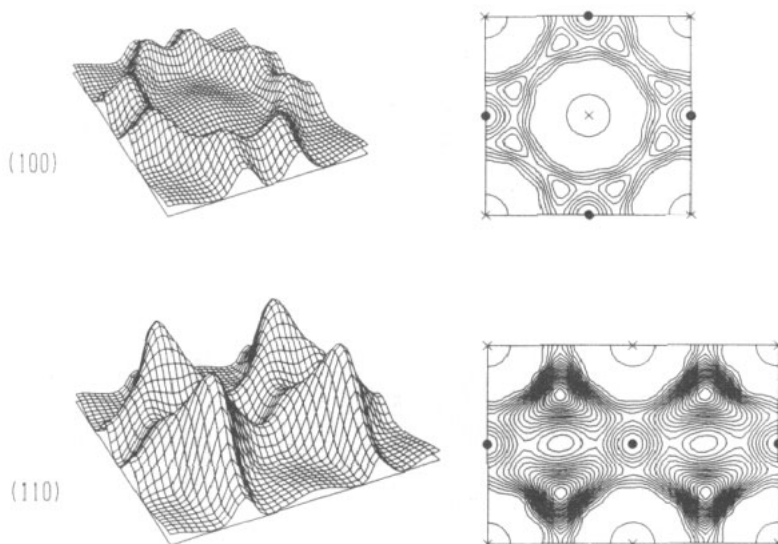


Figure 5. Positron density distribution in the KC_{60} (K at the octahedral interstices) crystal on the (100) and (110) planes. The contour spacing is $1/20$ of the maximum value. Closed circles are potassium atoms and crosses represent centres of the C_{60} molecules.

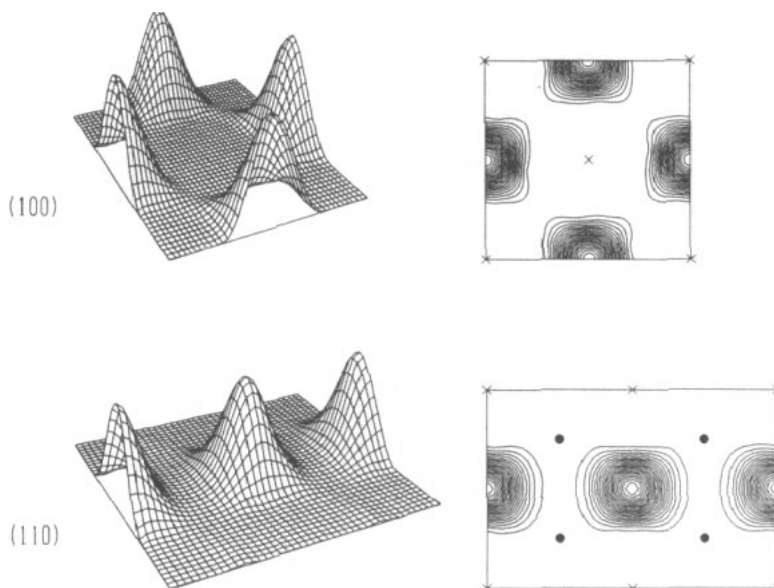


Figure 6. Positron density distribution in the K_2C_{60} (K at tetrahedral interstices) crystal on the (100) and (110) planes. (Contour spacing and symbols as for figure 5.)

and semiconductor ($\epsilon_{\infty} = 3.5$) models. Figures 5–8 show the positron distributions in each material on the (100) and (110) planes, which are obtained using the metal

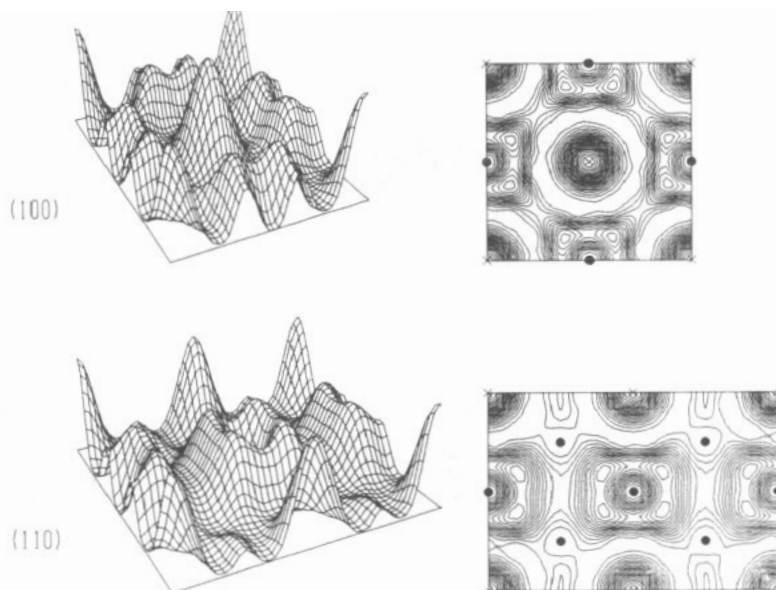


Figure 7. Positron density distribution in the K_3C_{60} (K at both interstices) crystal on the (100) and (110) planes. (Contour spacing and symbols as for figure 5.)

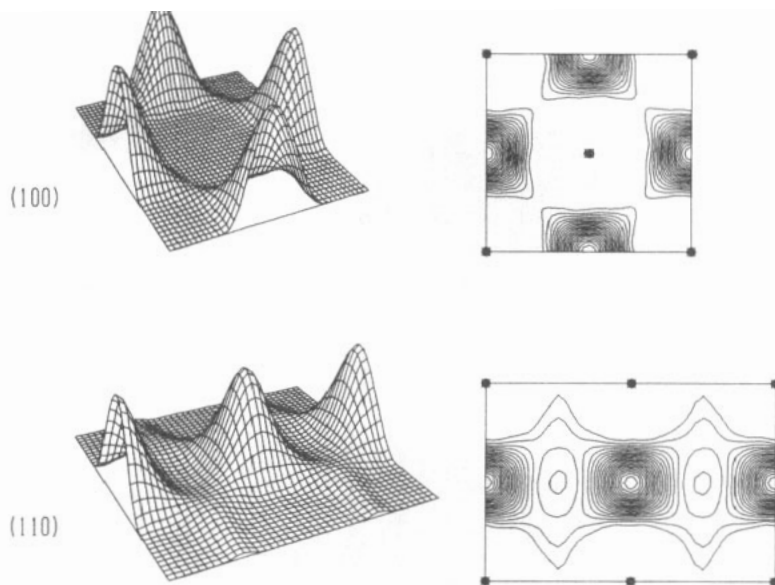


Figure 8. Positron density distribution in the $K@C_{60}$ (K at centres of C_{60} molecules) crystal on the (100) and (110) planes. (Contour spacing and symbols as for figure 5.)

model. Corresponding lifetime values are shown in figure 9 together with results for the semiconductor model.

It can be seen that both the lifetime and distribution of positrons are strongly affected by the presence of potassium atoms at the octahedral sites. In the KC_{60}

case, positrons show a maximum density at the tetrahedral sites, while in K_3C_{60} the maximum position is the centre of the C_{60} molecule. In contrast with these cases, the positron distributions are not altered much by the addition of potassium atoms on the tetrahedral sites or at the centre of the C_{60} molecule.

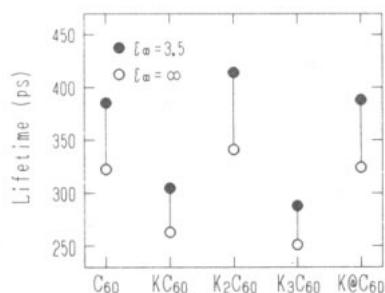


Figure 9. Calculated positron lifetime values in the potassium-doped C_{60} as well as pure C_{60} crystals. Open circles represent values obtained for the metal model and closed circles for the semiconductor model ($\epsilon_\infty = 3.5$).

The lifetime results can also be classified into two categories with the limiting values of 310–320 ps. Even considering that potassium doping causes an increase in ϵ_∞ , positron spectroscopy can distinguish whether or not potassium atoms occupy the octahedral sites.

It may appear somewhat strange that the positron lifetime in K_2C_{60} is slightly higher than that in pure C_{60} at the same value of ϵ_∞ . The reason is considered to be because the positron is more confined in K_2C_{60} around the octahedral sites (figure 6), where the electron density is relatively low due to repulsion from potassium atoms at the tetrahedral sites.

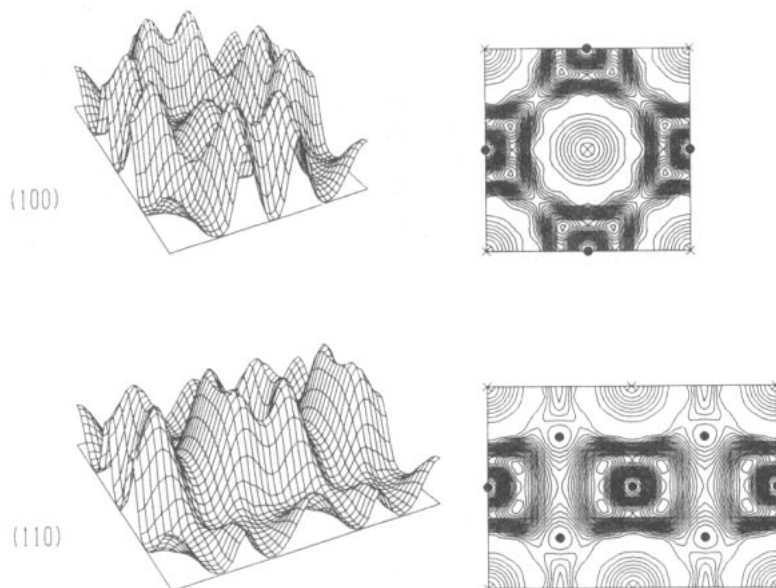


Figure 10. Positron density distribution in the K_3C_{60} (experimentally obtained structure [8] assuming a space group of $Fm\bar{3}$) crystal on the (100) and (110) planes. (Contour spacing and symbols as for figure 5.)

As for K_3C_{60} , the existence of this phase has been confirmed experimentally and its crystal structure determined [8] (no experimental confirmation exists for the other three forms of doped C_{60}). We also performed a calculation on this structure, assuming the space group to be $Fm\bar{3}$ for simplicity and using the metal model. The resultant positron distribution is shown in figure 10. Compared with the results shown in figure 7, the positron density maximum changed its position from the centre of the C_{60} molecule to the position between the octahedral and the tetrahedral sites. As for the lifetime, the resultant value of 264 ps is slightly longer than 251 ps corresponding to figure 7 (if we use the experimentally obtained lattice constant of 14.24 Å, then the result is 256 ps). This value is still quite a lot smaller than the lifetimes for C_{60} , K_2C_{60} and $K@C_{60}$ in which potassium atoms do not occupy the octahedral sites.

Thus, the positron is a very sensitive probe of potassium atoms at the octahedral sites. Considering that the positron lifetime is 397 ps in potassium metal, positron lifetime spectroscopy can be used as a characterization technique in the preparation of superconducting K_3C_{60} . The positron lifetime is expected to be lower than 300 ps when proper doping is accomplished; if not, a value greater than 320 ps should be observed.

There is a question whether or not a phase separation occurs in nominal composition K_xC_{60} ($0 < x < 3$) into pure C_{60} and K_3C_{60} . As mentioned above, phases such as KC_{60} , K_2C_{60} and $K@C_{60}$ have not been realized experimentally. The recent NMR results have suggested that only the C_{60} and K_3C_{60} phases are stable for $x \leq 3$ [20]. While the NMR spectroscopy observes the charge states of the C_{60} molecules, positron lifetime spectroscopy directly detects the potassium atoms at the octahedral sites. In this regard, they complement each other.

According to the theoretical prediction [9], potassium atoms first fill the tetrahedral interstices. If the phase separation does not occur, then the present results suggest that positron lifetimes decrease slowly to a value of 340–350 ps, reflecting an increase of ϵ_∞ with carrier doping up to $x \sim 2$ followed by a further decrease to ~ 260 ps. The x dependence of the lifetime should change at around $x = 2$. In contrast with this, for the case when phase separation occurs, the mean positron lifetime is expected to decrease continuously up to $x = 3$. The positron technique can present the answer to the above question.

In summary, positron states in C_{60} and potassium-doped C_{60} crystals have been calculated. It is revealed that positrons prefer the octahedral interstices in pure C_{60} and that this is a very sensitive probe of dopant atoms occupying this site. The positron technique is expected to be useful for characterizing these materials.

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