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Positron distributions and lifetimes in M_xC_{60} (M: alkali or alkaline-earth)

S. ISHIBASHI, N. TERADA, M. TOKUMOTO, N. KINOSHITA and H. IHARA

Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan

Abstract

Positron distributions and lifetimes in both bulk and trapped states have been calculated on M_xC_{60} ($M = K, Rb, Cs, Ba, x = 3, 4, 6$) using the superposed-atom model and the numerical relaxation technique. The effect of rotation of C_{60} molecules on positron states is also investigated.

Introduction

The C_{60} molecules form a crystal whose structure is regarded as a face-centered cubic (fcc) configuration of the molecules [1]. Each of them are orientationally disordered at room temperature, while they become ordered below 249 K [2]. The crystal structure changes to a simple cubic whose symmetry is $Pa\bar{3}$ [3,4].

The binary system M_xC_{60} (M: alkali or alkaline-earth) has various phases depending on x and temperature. For $M = K$ and Rb , three stoichiometric phases have been reported at room temperature: face-centered cubic (fcc) M_3C_{60} (space group $Fm\bar{3}m$) body-centered tetragonal (bct) M_4C_{60} ($I4/mmm$) and body-centered cubic (bcc) M_6C_{60} ($Im\bar{3}$) [5,6]. The M_3C_{60} ($M = K$ or Rb) phase is widely known as a novel superconductor [8,9,10]. These phases are also observed for $M = Cs$ except for $x = 3$ [5,6]. Recently, a novel phase with $x = 1$ has been found for $M = K, Rb$ or Cs [7]. The M_1C_{60} phase has the rhombohedral structure at 300 K while it transforms into the rock-salt one above 400 ~ 450 K. For $M = K$, an additional phase with fcc structure is also recognized in the intermediate temperature range [7].

Alkaline-earth metals also form compounds with C_{60} . The Ca_xC_{60} system has an fcc structure for $x < 5$ and transforms into a simple cubic structure at $x = 5$. This Ca_5C_{60} phase becomes superconducting below 8.4 K [21]. In contrast with this, the Ba_3C_{60} phase has a A15 structure (space group $Pm\bar{3}n$) [22] while Ba_6C_{60} , which is also a superconductor, shows a bcc structure, similar to the structure of M_6C_{60} ($M = K, Rb, Cs$) [23].

Positrons, which have positive charge, tend to be distributed at interstitial sites in condensed matters. The M_xC_{60} system has a structure in which alkali or alkali-earth metal is intercalated into interstitial sites of the C_{60} sublattice. The positron distribution and lifetime should be affected significantly by such an intercalation and the positron lifetime spectroscopy is expected to be utilized as an effective characterization tool of C_{60} -related compounds.

Both experimental and theoretical results support the above suggestion. Experimentally obtained positron lifetimes in pure C_{60} are around 400 ps [12,13,14,15,16]. The positron lifetime reduces to 265 ps for K_3C_{60} or to 269 ps for K_6C_{60} [16].

As for theoretical work, we have already reported calculated positron distributions and lifetimes in pure C_{60} as well as in four types of supposed crystals, in which K atoms occupy (1) octahedral sites, (2) tetrahedral sites, (3) both sites or (4) centers of the C_{60} molecules, respectively. We showed that the positron distribution and lifetime are drastically varied by the existence of K atoms at octahedral sites [11]. Calculations have been also performed on experimentally confirmed phases K_xC_{60} ($x = 3, 4, 6$) [17,18]. The obtained lifetimes are in good agreement with the experimental values. These calculations are based on the superposed neutral atom model developed by Puska and Nieminen [19]. They also calculated positron states in C_{60} and related materials and reported very similar results to ours [20]. Lou *et al.* utilized orthogonalized linear combination of atomic orbital (OLCAO) band calculations to obtain the Coulombic potential and the electron charge distribution and calculated positron distributions and lifetimes in K_xC_{60} ($x = 0, 1, 2, 3, 6$). Their obtained distribution of positrons for K_3C_{60} is quite different from ours. Positrons are almost confined inside C_{60} molecules in their result while positron density maxima exist at the outside of molecules in ours. The OLCAO method takes charge transfer into account. In this regard, this method should be more accurate. Our calculations reproduce the experimental lifetimes better, however. In order to reveal which is correct, a measurement of core annihilation radiations is desirable. In case that positrons are confined inside C_{60} , the overlap between positrons and core electrons of K atoms are negligibly small. If positrons are still distributed in interstitial region, the overlap is expected to be significant.

In the present paper, following our previous work, we present calculated positron distributions and lifetimes in both bulk and trapped states on M_xC_{60} (M : alkali or alkaline-earth). We restrict ourselves to dealing with compounds whose structures have been definitely presented including atomic positions, namely, K_3C_{60} , K_4C_{60} , K_6C_{60} , Rb_3C_{60} , Rb_6C_{60} , Cs_6C_{60} [6], Ba_3C_{60} [22] and Ba_6C_{60} [21]. Furthermore, we have investigated effects of the molecular rotation on positron states. The results are also shown.

Calculations

Calculations were performed based on the superposed neutral atom model developed by Puska and Nieminen [19] assuming metallic screening ($\epsilon_\infty = \infty$). This assumption is quite reasonable for metallic phases and is expected to be valid for semiconducting phases such as K_6C_{60} since they are narrow gap semiconductors with rather large values of ϵ_∞ . Pure C_{60} , which has a band gap of ~ 1.5 eV, is an exception. Details of the method are described in our previous paper [11].

We made calculations for bulk states of positrons with two values of mesh spacings, $a_0/40$ and $a_0/20$, where a_0 represents the lattice constant of each material. For trapped states, a single value of $a_0/20$ is used. The wavefunction of the trapped positron is set to be zero, as a boundary condition, on the surface of a cube with dimensions of $4a_0 \times 4a_0 \times 4a_0$. The vacancy exists at the center of this cube. For tetragonal lattices, one of the lattice constants a_0 should be replaced by c_0 .

For simplicity, we assumed $Fm\bar{3}$ symmetry instead of $Fm\bar{3}m$ for K_3C_{60} and Rb_3C_{60} and $Immm$ instead of $I4/mmm$ for K_4C_{60} . In these cases, the double bonds of C_{60} molecules are ordered to be parallel.

Table 1: Calculated positron lifetimes and energies in M_xC_{60} systems. τ_{bulk}^I , E_{bulk}^I and τ_{bulk}^{II} , E_{bulk}^{II} are values for bulk states obtained with mesh spacings of $a_0/40$ and $a_0/20$, respectively. $\tau_{vacancy}$ and $E_{vacancy}$ are those for trapped states at M-site vacancies.

	τ_{bulk}^I (ps)	E_{bulk}^I (eV)	τ_{bulk}^{II} (ps)	E_{bulk}^{II} (eV)	$\tau_{vacancy}$ (ps)	$E_{vacancy}$ (eV)
K_3C_{60}	264	-3.25	263	-3.35	$360^O, 284^T$	$-4.41^O, -3.65^T$
K_4C_{60}	285	-3.21	284	-3.26	324	-3.81
K_6C_{60}	281	-2.79	281	-2.84	293	-2.97
Rb_3C_{60}	275	-3.33	274	-3.41	$375^O, 299^T$	$-4.54^O, -3.81^T$
Rb_6C_{60}	281	-2.75	281	-2.81	305	-3.01
Cs_6C_{60}	283	-2.72	283	-2.78	320	-3.02
Ba_3C_{60}	274	-3.02	273	-3.08	303	-3.67
Ba_6C_{60}	279	-2.57	280	-2.63	280	-2.62

O: octahedral site, T: tetrahedral site

We regard $C2s^22p^2$ and outermost s of alkali or alkaline-earth metals as the valence electrons and the rest as the core electrons.

Results and Discussions

Calculated positron lifetimes and energies for both bulk and trapped states are listed in Table 1. The positron binding energy to the vacancy is obtained by subtracting $E_{vacancy}$ from E_{bulk}^{II} . Since energy eigenvalues of positrons vary slightly with dimensions of the mesh spacings, it is reasonable to compare values calculated on the same mesh spacings. Several systematic variations are found among the listed lifetimes (and energies correspondingly). We describe them in the following.

Positron lifetimes in the bulk and trapped states are longer for Rb_3C_{60} than those for K_3C_{60} , respectively. It is easily understood if we consider the difference of the lattice parameters and the positron distributions therein. Positrons in the bulk state are predominantly distributed in the interstitial region between the octahedral and the tetrahedral sites for these compounds (see [11,17,18]). If lattice dimensions are expanded, free volume of the interstitial region is enlarged also. The situation is similar for the trapped states, in which positrons are localized at the octahedral or tetrahedral vacant sites. The positron lifetimes in Rb_3C_{60} are, therefore, longer than those in K_3C_{60} . Another prominent feature concerning these $x = 3$ compounds is a difference between lifetimes of positrons trapped at the octahedral site and the tetrahedral one. Since this difference is quite large, it is promising to examine the site selectivity of the K or Rb vacancy by the positron lifetime spectroscopy.

The positron distribution in the bulk of K_4C_{60} is, as we reported before [17,18], quasi-one-dimensional along the $[001]$ direction. The corresponding lifetime is the longest among those in the compounds listed in table 1 reflecting the loosest packing of the lattice.

The positron lifetimes in the bulk state for K_6C_{60} , Rb_6C_{60} and Cs_6C_{60} are almost the same, in contrast with the case of $x = 3$. In these $x = 6$ compounds, positrons are mostly confined inside the C_{60} molecules (see [17,18]). With the ionic radius of the intercalated metal increasing, the size of the C_{60} molecules is invariant whereas the lattice constant increases. This is the reason for the constant lifetime. As for the trapped state, the situation is different. Since the positron

Figure 1: Positron density distribution in the Ba_3C_{60} crystal on the (001) and (011) planes. The contour spacing is $1/20$ of the maximum value. Crosses and closed circles represent centers of the C_{60} molecules and Ba atoms, respectively.

trapping center exists in the interstitial region, the positron lifetime there increases with the ionic radius increasing as it does for both bulk and trapped states in the M_3C_{60} ($\text{M} = \text{K}, \text{Rb}$) system.

The bulk positron lifetimes in Ba_3C_{60} and Ba_6C_{60} are very close to those for M_6C_{60} ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$). This is also because positrons are almost confined inside the C_{60} cages as shown in figures 1 and 2 for these two Ba-intercalated compounds. Although Ba_6C_{60} has the same structure as those of M_6C_{60} ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$), there is a remarkable difference in the positron-vacancy interaction. The positron binding energy to the metal vacancy is estimated to be nearly zero only for Ba_6C_{60} . Corresponding positron distribution has its density maxima not at the vacant Ba site but at the centers of neighboring C_{60} molecules. These results imply unstableness of the trapped state of positrons at the Ba vacancy, which is calculated under compulsion that the positron wavefunction should be zero on the boundary. This would be due to the significantly smaller lattice constant of Ba_6C_{60} [23] compared with the other $x = 6$ compounds. It is supposed that the free volume of the Ba vacancy is not large enough to localize positrons.

In the introduction, we mentioned conflicting results of calculations of the positron distribution and lifetime in K_3C_{60} . The question is whether positrons are mainly in the interstitial region [11,20] or inside the C_{60} molecules [16]. To measure the positron lifetime in Rb_3C_{60} is one way to answer it, since the present calculations imply that the positron lifetime is expected to increase with the lattice parameter increasing for the former case while to keep nearly constant for the latter. The bulk positron lifetimes in K_3C_{60} and Rb_3C_{60} should be compared with each other.

The effect of the molecular rotation is investigated on pure C_{60} . We assumed the truncated icosahedron C_{60} molecule whose bond length is $1.45 \text{ \AA}$ for single bonds and $1.39 \text{ \AA}$ for double

Figure 2: Positron density distribution in the Ba_6C_{60} crystal on the (001) and (011) planes. The contour spacing and symbols as for figure 1.

bonds [6]. As a starting structure, we adopted that of $\text{Fm}\bar{3}$ symmetry with parallel double bonds. The molecule at the origin was rotated anticlockwise about the $[111]$ direction in 10° steps from 0° to 120° . The other three molecules in the unit cell were rotated also keeping $\text{Pa}\bar{3}$ symmetry. We assumed metallic screening ($\epsilon_\infty = \infty$) in the calculations. Though such an assumption is not correct for semiconducting pure C_{60} , it is enough to estimate relative changes. Obtained positron lifetimes and energies are shown in figure 3 as functions of the rotation angle θ . The variations of the lifetime and the energy are relatively small and within 3 ps and 0.02 eV, respectively. The molecular orientation is not so significant for these values. Correspondingly, the positron distribution is almost unchanging with θ . Positrons are predominantly distributed at the octahedral sites for every θ , as we showed before for the low-temperature ordered structure of the pure C_{60} crystal [11]. Our assumptions that C_{60} molecules are ordered to have parallel double bonds, which are used in the calculations for several M_xC_{60} compounds, are reasonable.

Summary

We have calculated positron distributions and lifetimes in both bulk and trapped states on the M_xC_{60} ($\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{Ba}, x = 3, 4, 6$) system. It has revealed that the positron lifetime increases with the lattice constants increasing when positrons are mainly distributed in the interstitial region. In contrast with this, the positron lifetime is nearly constant in case that positrons are almost confined inside the C_{60} molecules. No positron trapping is expected for Ba_6C_{60} due to the small volume of the interstitial region. The orientation of C_{60} molecules does not significantly affect positron states.

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Figure 3: Positron lifetimes and energies in pure C_{60} as functions of the rotation angle θ . The crystal structure at $\theta = 0^\circ$ corresponds to the $Fm\bar{3}$ configuration. The rotation has been made keeping $Pa\bar{3}$ symmetry. Metallic screening is assumed ($\epsilon_\infty = \infty$).

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