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Positron Annihilation in Alkali-Metal-Saturation-Doped Fullerides

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The position annihilation in solids of alkali-metal fullerides with saturation composition; K_6C_{60}, Rb_6C_{60} and Cs_6C_{60} was found to consist of three processes with lifetimes of 0.21–0.24 ns, 0.60–0.75 ns and 3.2–3.7 ns at 300 K. The shortest and the intermediate lifetimes were almost independent of temperature, but the corresponding relative intensities were found to change with temperature in the range 290–480 K, which suggests that the distribution of positrons changes with temperature. The shortest lifetime is attributed to the annihilation of free positrons in the region where the wavefunctions of a positron and an electron overlap significantly, *i.e.*, inside and around C_{60} molecules in M_6C_{60} (M = K, Rb, Cs). The intermediate one is attributed to the annihilation of positrons at surfaces, and the longest one to that of *ortho*-positroniums.

Keywords: Positron annihilation, positron lifetime, alkali-metal fulleride, M_6C_{60} ($M = K, Rb, Cs$).

1. INTRODUCTION

When energetic positrons are injected into a condensed matter, they lose their kinetic energy by inelastic collisions with the matter within a few picoseconds. Positrons are positively-charged elementary particles, so that thermalized positrons in the bulk are strongly repelled from atomic cores, and then are preferentially distributed in the regions where interstices, open-volume defects, or negatively-charged ions are present. Their annihilation with electrons provides information on the electronic states of the regions where it occurs through their lifetime, angular-correlation of annihilation radiation and Doppler broadening.

Truncated icosahedral C_{60} molecules form a face-centered-cubic lattice with the lattice constant of 14.2 Å. The distance between the nearest carbon atoms belonging to neighboring C_{60} molecules is 3.1 Å, which demonstrates the existence of a large open volume around interstitial sites between the C_{60} molecules.[1] In a previous paper we studied the annihilation of positrons in highly purified C_{60} and C_{70} solids. Their positron-lifetime spectrum consists of only a single component of 0.43 ns and there is

no indication of positronium (Ps) generation.[2] The positron wavefunction has been theoretically predicted to be distributed throughout the interstitial regions between C_{60} molecules, the maximum density being at the octahedral sites. The corresponding positron lifetime has been calculated to be 0.370 ns. If the interstitial sites are occupied with other atoms, the positron density is expected to shift toward the centers of C_{60} molecules and the positron lifetime to decrease.[3]

Alkali-metal fullerides are formed by the doping of alkali-metal atoms into octahedral and/or tetrahedral interstitial sites between C_{60} molecules. A body-centered cubic structure has been reported for K_6C_{60}.[4] Positron distributions and lifetimes have been theoretically studied for $K_xC_{60}(x = 0, 3, 4, 6)$, $Rb_xC_{60}(x = 3, 6)$ and Cs_6C_{60}.[3,5,6] Positrons are almost confined inside C_{60} molecules of M_6C_{60}(M = K, Rb, Cs).[3,7]

Here we report three kinds of positron annihilation processes for alkali-metal-saturation-doped M_6C_{60} from the analysis of their lifetime spectra.

2. EXPERIMENTAL

Alkali-metal fullerides were prepared by the reaction of alkali-metal vapor with C_{60} powder (MER Corp. USA, 99.99%), which had been sublimed once *in vacuo* for removal of aliphatic hydrocarbon impurities. A weighed amoung of C_{60} powder (typically 200 to 300 mg) was loaded at one end of a 15 mm diameter Pyrex-glass tube equipped with a breakable glass seal and an excess amount of alkali metal was introduced to the other end of the tube by distillation *in vacuo*.The C_{60} powder and the alkali metal, being vacuum-sealed in the tube, were heated for 3 days at 430 and 400 K respectively, with the aid of a temperature-gradient electric furnace and then for a week at 520 and 470 K respectively, to form an alkali-metal fulleride. C_{60} turned silver black upon the reaction with potassium, and bluish black with rubidium and caesium. Finally the alkali-metal fulleride was annealed at 670 K for a week, which produced saturation-doped[8,9] M_6C_{60}.

The X-ray powder diffraction patterns for the prepared alkali-metal fulleride samples encapsulated in quartz tubes were the same with those reported in the literature,[10] and the Raman spectra of the samples also identified the compounds.[11] An ^{22}NaCl positron source of 0.64 MBq sealed between two Mylar films of 5 μm thick was buried in a powder sample of alkali-metal fulleride which was poured from the reaction tube *in vacuo* through a breakable glass seal. Positron lifetime spectra were obtained by means of a conventional fast-fast coincidence system equipped with a BaF_2 scintillator, the time resolution of which was determined to be 0.260 ns. The spectra, which had been corrected for positron source annihilation, were analyzed with the aid of a computer program PATFIT88.[12] Positron-electron annihilation spectra were obtained from Doppler-broadening of 511 keV radiation observed with the aid of a germanium spectrometer, the energy resolution of which was 1.01 keV (FWHM).

3. RESULTS AND DISCUSSION

The positron lifetime spectra for M_6C_{60} (M = K, Rb, Cs) are all reasonably analyzed by three exponential fits with $\chi^2 < 1.1$, as listed in Table 1. Lifetimes of a few nanoseconds

TABLE 1

Positron lifetime-components and the corresponding intensities for alkali-metal saturation-doped fullerides at 300 K

	τ_1 (ns)	I_1 (%)	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)
K_6C_{60}	0.23	32	0.60	54	3.7	14
Rb_6C_{60}	0.21	32	0.75	44	3.5	24
Cs_6C_{60}	0.24	38	0.66	51	3.2	11

have been generally accepted as resulting from annihilation of *ortho*-positronium (*o*-Ps) in a condensed matter and being proof of Ps generation.[13] Hence, the longest lifetime component (τ_3) observed is attributed to *o*-Ps, probably trapped in open-volume defects in a lattice. The component increases with an order of K, Rb and Cs. *Para*-positronium (*p*-Ps) is generally present in a sample where *o*-Ps is generated, of which density corresponds to one-third of *o*-Ps density. The observed value of the shortest lifetime component τ_1 is regarded as the weighted average of the lifetime due to free positron annihilation in the bulk (τ_b) and the lifetime of *p*-Ps ($\tau_p = 0.125$ ns). Thus the bulk lifetimes due to the free annihilation are estimated at 0.27, 0.28, and 0.27 for K_6C_{60}, Rb_6C_{60} and Cs_6C_{60} respectively, from the relation, $1/\tau_1 = f_p/\tau_p + f_b/\tau_b$, where $f_p = I_3/3I_1$ and $f_b = I_1'/I_1$. The intrinsic intensity for the free annihilation I_1' is estimated as the subtraction of $I_3/3$ attributable to *p*-Ps from the observed intensity I_1. These lifetime components of free positron annihilation are found to be close to the theoretically calculated values of 0.281, 0.281, and 0.283 ns for K_6C_{60}, Rb_6C_{60} and Cs_6C_{60} respectively,[7] though they could not be determined so finely as to be characterized by their sorts of alkali metals. Thus the annihilation of free positrons occurs in the region where the wavefunctions of a positron[6] and an electron[14] overlap significantly, *i.e.*, inside and around C_{60} molecules in M_6C_{60}. Lou *et al.*[5] reported the corresponding component of 0.269 ns and the second component of 0.406 ns (intensity of 51.1%) for K_6C_{60}. They prepared the potassium fulleride by heating the mixture of a stoichiometric ratio of potassium metal and C_{60} powder at 225°C *in vacuo*, followed by annealing for many cycles at 250°C.

The intermediate lifetime component τ_2 lies in the range 0.60–0.75 ns, and is less dependent on temperature, *e.g.*, 0.60 ns at 300 K and 0.56 ns at 480 K for K_6C_{60}, though the corresponding intensity I_2 changes markedly. The lifetimes of positrons in the trapping states at alkali-metal site vacancies have been calculated to be 0.293–0.320 ns,[7] but they are much shorter than the intermediate lifetime components observed in the present work. The intensity I_2 is very high, in the range 44–54%, which indicates that the component correlates with the inherent structure and property of the fullerides. This component is ascribed to the annihilation of positrons at outer surfaces and/or large defects (*i.e.*, inner surfaces), because it is close to the lifetime values reported for positrons in the surface state. The lifetimes of positrons in the surface state have been reported to be 0.400 ns for a hydrogenated carbon film,[15] longer than 0.520 ns for a 6-vacancy cluster in Si,[16] and 0.580 ns for a clean well-annealed single crystal of Al.[17] The lifetime components τ_1 and τ_2 are almost independent of temperature, as shown in Figure 1, which demonstrates that the distribution of electrons annihilating with positrons

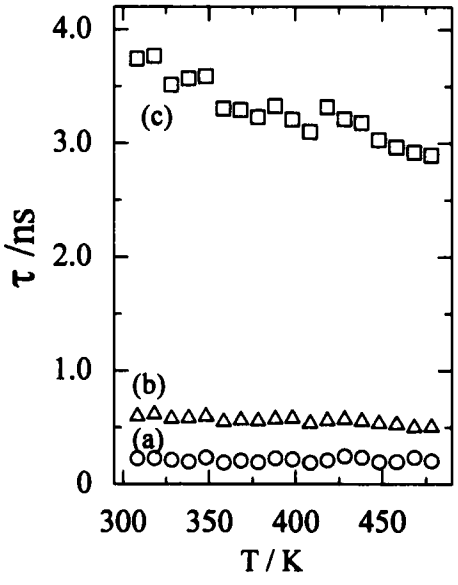

FIGURE 1 Temperature dependence of positron lifetime components for K_6C_{60}: (a) τ_1, (b) τ_2 and (c) τ_3.

does not change with temperature in the range 300–400 K. The intensity I_2 was found to increase while the intensity I_1 to decrease with a change in temperature, as shown in Figure 2. This change in intensity is explained in terms of the shift of positron distribution from the centers of C_{60} molecules toward the region of surfaces.

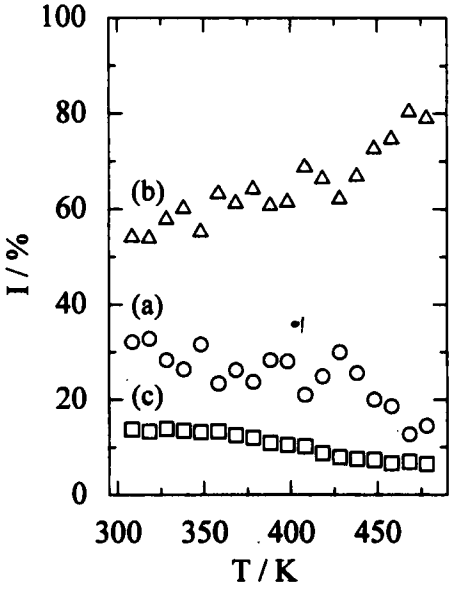

FIGURE 2 Temperature dependence of relative intensities of positron-annihilation for K_6C_{60}: (a) I_1, (b) I_2 and (c) I_3.

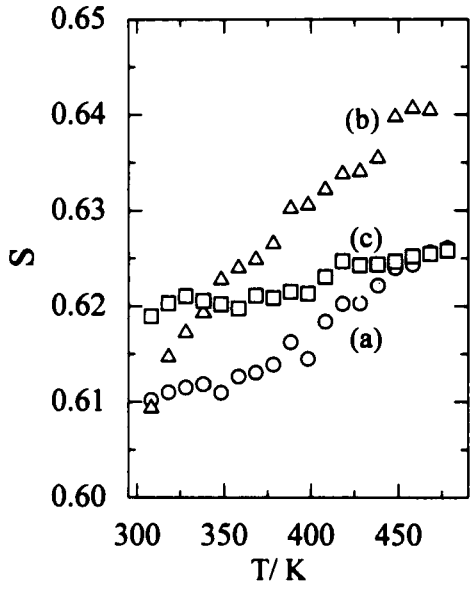

FIGURE 3 Temperature dependence of S parameters for (a) K_6C_{60}, (b) Rb_6C_{60} and (c) Cs_6C_{60}.

This interpretation was supported by the observation of a Doppler-broadening spectrum. A line-shape parameter of the spectrum S was determined as the ratio of the positron annihilation intensity obtained by the integration over the central part of the spectrum (± 0.9 keV) to that over the entire spectrum (± 4.0 keV). S parameters for M_6C_{60} were also found to increase with an increase in temperature, as shown in Figure 3, which demonstrates that electron-positron pairs with lower momentum contribute much more to the annihilation at higher temperatures, compared with those with higher momentum. In general, electrons with low momentum are those loosely bound with atomic cores, such as conduction electrons in metals, so that electrons spreading over the region of surfaces are expected to possess lower momenta than those confined to C_{60} molecules in alkali-metal fullerides. Thus the annihilation of positrons with electrons with lower momentum occurs in the region of surfaces where the density of positrons increases with temperature, showing the increasing intensity I_2 with an increase in temperature. High-temperature alkali-metal doping has been reported to induce severe C_{60} crystal fragmentation, and typical grain size of the fulleride powder is *ca.* 1 μm.[18] From the plots of $\ln(I_2/I_1)$ against reciprocal temperature, the energy difference between the energy for the positrons distributed preferentially inside and around C_{60} molecules and that distributed in the region of surfaces was estimated at *ca.* 0.07, *ca.* 0.05 and *ca.* 0.03 eV for K_6C_{60}, Rb_6C_{60} and Cs_6C_{60}, respectively.

The charge-transfer complex formation and the subsequent crystal fragmentation seem to be responsible for the generation of the surface state in which positrons are highly populated, compared with that for pristine C_{60} crystallites.

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References

1. W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature* **347**, 354 (1990).
2. M. Sano and H. Murakami, *Synth. Metals* **64**, 315 (1994).
3. M. J. Puska and R. M. Nieminen, *J. Phys. Condens. Matter* **4**, L149 (1992).
4. O. Zhou, J. E. Fischer, N. Coustel, S. Kycia, Q. Zhu, A. R. McGhie, W. J. Romanow, J. P. McCauley, Jr, A. B. Smith III and D. E. Cox, *Nature* **351**, 462 (1991).
5. Y. Lou, X. Lu, G. H. Dai, W. Y. Ching, Y.-N. Xu, M.-Z. Huang, P. K. Tseng and Y. C. Jean, *Phys. Rev.* **B46**, 2644 (1992).
6. S. Ishibashi, N. Terada, M. Tokumoto, N. Kinoshita and H. Ihara, *Synth. Metals* **55**, 3074 (1993).
7. S. Ishibashi, N. Terada, M. Tokumoto, N. Kinoshita and H. Ihara, *J. Phys. IV, Colloque C4, Suppl. J. Phys.* **II3**, 153 (1993).
8. J. P. McCauley, Jr., Q. Zhu, N. Coustel, O. Zhou, G. Vaughan, S. H. J. Idziak, J. E. Fischer, S. W. Tozer, D. M. Groski, N. Bykovetz, C. L. Lin, A. R. McGhie, B. H. Allen, W. J. Romanow, A. M. Denenstein and A. B. Smith III, *J. Am. Chem. Soc.* **113**, 8537 (1991).
9. Q. Zhu, O. Zhou, N. Coustel, G. B. M. Vaughan, J. P. McCauley, Jr., W. J. Romanow, J. E. Fischer and A. B. Smith III, *Science* **254**, 545 (1991).
10. R. M. Fleming, M. J. Rosseinsky, A. P. Ramirez, D. W. Murphy, J. C. Tully, R. C. Haddon, T. Siegrist, R. Tycko, S. H. Glarum, P. Marsh, G. Dabbagh, S. M. Zahurak, A. V. Makhija and C. Hampton, *Nature* **352**, 701 (1991).
11. S. J. Duclos, R. C. Haddon, S. Glarum, A. F. Hebard and K. B. Lyons, *Science* **254**, 1625 (1991).
12. P. Kirkegaard, N. J. Pedersen and M. Eldrup, *Risø M-2740* (1988).
13. P. Hautojävi and A. Vehanen, *Positron in Solids*, Ed. P. Hautojävi, (Springer Verlag, Berlin), pp. 1–23 (1979).
14. W. Andreoni, P. Giannozzi and M. Parrinello, *Phys. Rev.* **B51**, 2087 (1995).
15. G. Kögel, D. Schödlbauer, W. Triftshäusoer and J. Winter, *Phys. Rev. Lett.* **60**, 1550 (1988).
16. S. Dannefaer, *Phys. Stat. Solidi (a)* **102**, 481 (1987).
17. K. G. Lynn, W. E. Frieze and P. J. Schultz, *Phys. Rev. Lett.* **52**, 1137 (1984).
18. J. A. Schlueter, U. Welp, H. H. Wang, U. Geiser, J. M. Williams, M. J. Bauer, J. M. Cho, J. L. Smart and S. A. Taha, *Physica* **C216**, 305 (1993).