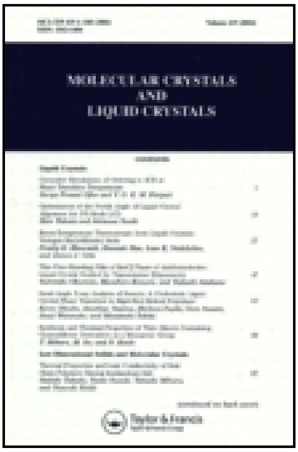

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Electron-Positron Interaction in Aromatic Crystals

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ELECTRON-POSITRON INTERACTION IN AROMATIC CRYSTALS

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Abstract Electron-positron annihilation spectra obtained from Doppler broadening of 511 keV radiation for hexamethylbenzene (HMB), hexachlorobenzene (HCB) and 2,3-dichloro-9,10-anthraquinone (DCAQ) crystals reveal anisotropic electron momentum distribution, the momentum along the molecular planes being lower than the momentum along the other direction. Positronium is formed in HMB, HCB, and the complexes of durene with trinitrobenzene (TNB), *p*-chloranil and *p*-bromanil, but not in DCAQ, anthracene, 9,10-anthraquinone, *p*-chloranil, nor in the complexes of anthracene with TNB and pyromellitic dianhydride in the solid state.

INTRODUCTION

Positrons injected into aromatic crystals decay in various ways, accompanied with the emission of 511 keV radiation; the free annihilation of positron-electron pairs in the bulk and the generation of positronium (Ps). The free annihilation provides information on the electron momentum distribution in the crystals. We have studied the electron-positron momentum distribution and the lifetime of positrons in graphite and its intercalation compounds.[1-4] Here we extend our study of electron-positron interaction to aromatic crystals. Positron annihilation in aromatic crystals has been studied with polycrystalline materials with a few exceptions. Even with monocrystalline materials, planar aromatic molecules take mutually inclined orientations in most of aromatic crystals, so that their anisotropic properties are smeared out and only information on average values of the physical quantities is obtained. Here we selected the aromatic crystals in which planar aromatic molecules lie preferentially in a plane; single crystals of hexamethylbenzene (HMB), hexachlorobenzene (HCB) and 2,3-dichloro-9,10-anthraquinone (DCAQ).

The formation of positronium through positron-electron interaction has been studied by the measurement of positron lifetime. Solid benzene, for example, shows a 1.5 ns lifetime component (38% yield), but solid anthracene, polycrystalline as well as monocrystalline,[5] does not show such a long-lived component, which indicates that Ps is formed in the former, but not in the latter. We have studied the formation of Ps in single-component crystals mentioned above as well as two-component crystals formed through charge-transfer interaction.

EXPERIMENTAL

Aromatic impurities such as anthracene and fluorene in *p*-terphenyl, and naphthalene and phenanthrene in pyrene with concentrations more than 10^{-4} mole fraction have been reported to provide long-lived components in positron annihilation spectra,[6] and hence, in this study, HMB, HCB, DCAQ, durene, anthracene and 9,10-anthraquinone were highly purified by zone-refining. A $CDCl_3$ solution of the zone-refined HMB does not show any ^{1}H-NMR peak attributable to a proton bound directly to a benzene ring, which indicates the purity higher than 99.99998%, as far as aromatic impurities are concerned. Single crystals of HMB, HCB, DCAQ and anthracene, 20 mm in diameter, were melt-grown in a Bridgman furnace.

A single crystal sample, *ca.* 14 x 8 mm^2 in area along a well-pronounced cleavage plane and *ca.* 6 mm in thickness, was cleaved into two halves through its center, and a ^{22}NaCl positron source of *ca.* 7.4 x 10^5 Bq encapsulated with two 7.5 μm Kapton films was sandwiched between the two halves. Positron annihilation spectra from the crystal mounted on a goniometer were obtained from Doppler broadening of 511 keV radiation observed with the aid of a pure germanium spectrometer, the energy resolution of which was determined to be 1.01 keV (FWHM) using a monochromatic 512 keV radiation emitted by ^{106}Ru. Positron lifetime spectra were obtained by means of a fast-fast coincidence system equipped with a BaF_2 scintillator, the time resolution of which was determined to be 211 ps by use of the program RESOLUTION.[7]

RESULTS AND DISCUSSION

Positron annihilation spectra of HMB, HCB and DCAQ crystals are found to be bell-shaped, and their full-widths at half-maximum (FWHM) are dependent on the direction of observation. The spectrum of an HMB crystal is sharpened in a magnetic field of 2 kOe. This change of spectrum is ascribed to the enhancement of a *para*-Ps component by a magnetic mixing of the *p*-Ps singlet ground state with the m=0 substate of the *ortho*-Ps triplet state. The planes of HMB molecules lie nearly in a well-pronounced cleavage plane, the ab plane, with only a 1° tilt out of the plane.[8] The planes of HCB make an angle 23.3° with the ac plane in the monoclinic crystals.[9] The orientation dependence of FWHMs is a quite similar between HMB and HCB, the FWHMs observed in the direction perpendicular to the ab plane of HMB and to the ac plane of HCB being wider than those in the direction parallel to these planes. Their ratios are found to be 1.02 and 1.01 for HMB and HCB, respectively. The spectrum of a highy oriented pyrolytic graphite (HOPG) crystal observed in the direction perpendicular to the graphite hexagonal plane is bimodal and wider than the spectrum observed along the plane.[4] This result demonstrates that the electron momentum in the direction normal to the molecular planes is higher than that in the planes.

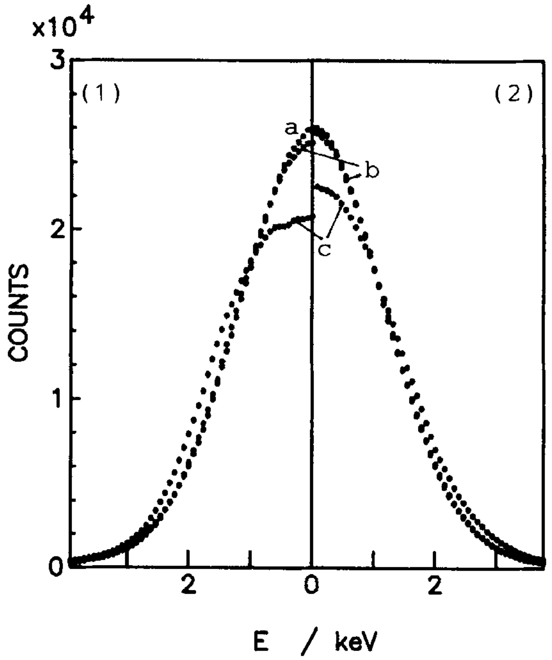

FIGURE 1 Doppler-broadened annihilation spectra of (a) HCB, (b) HMB, and (c) HOPG in the directions nearly (1) perpendicular, and (2) parallel to molecular planes.

The orientation dependence of spectrum for a DCAQ crystal is a little complicated. The molecules can be regarded as planar in the orthorhombic crystals, and the z molecular axis is taken along the twofold axis and the y, z-plane as the plane of the molecule. The x, y and z molecular axes are nearly parallel to the c, b and a crystallographic axes, respectively.[10] The FWHMs observed along the b and c axes are found to be nearly the same, while the FWHM along the a axis is the narrowest, though all these FWHMs are wider than the FWHMs for HMB and HCB. These results can not be explained clearly yet, but the electron momentum along the molecular in-plane long-axis seems to be lower compared with the electron momenta along the other axes.

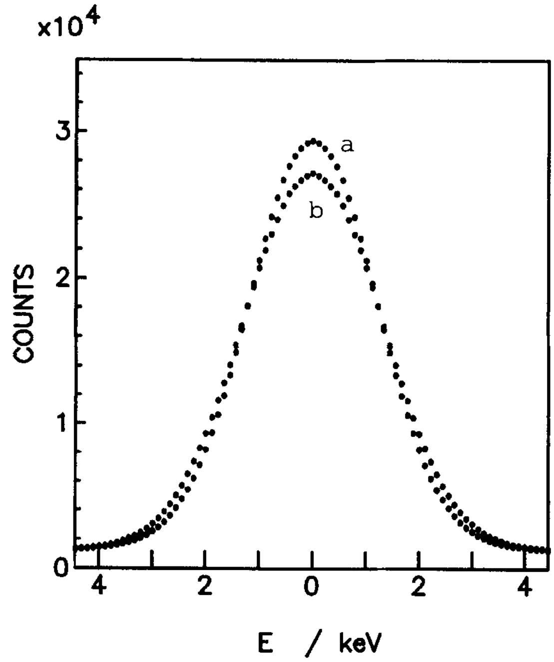

FIGURE 2 Doppler-broadened annihilation spectra of a DCAQ crystal observed in the directions (a) γ//a, and (b) γ//b.

Lifetime spectra of HMB and HCB crystals are resolved into four exponentially decaying components using the program POSITRONFIT.[7] Lifetimes longer than 600 ps have been generally accepted as resulting from annihilation of *o*-Ps and hence being a proof of Ps formation.[11] The lifetime components for an HMB single crystal at 294 K are determined as follows, the shortest-lived component τ_1 due to *p*-Ps being fixed at 125 ps[12] and the intensity ratio[13] of *p*-Ps to *o*-Ps at 1/3: τ_1=125 ps (intensity=11.0±0.1%), τ_2=344±1 (56.1±0.4), τ_3=953±8 (31.8±0.2) and τ_4=(2.7±0.2) x 10^3 (1.1±0.2), which give χ^2 < 1.1 consistently. The component (τ_3) of *ca.* 10^3 ps is attributed to pick-off annihilation of *o*-Ps and the longest one (τ_4) to annihilation of *o*-Ps in defects. A lifetime spectrum of DCAQ, monocrystalline as well as polycrystalline, can, however, be analyzed only with a single component of 310±1 ps. This result indicates the occurrence of free annihilation only and no formation of Ps. The same results were obtained for anthracene (301 ps), 9,10-anthraquinone (321 ps), 2-chloro-9,10-anthraquinone (312 ps), *p*-chloranil (284 ps) and graphite (215 ps) crystals.

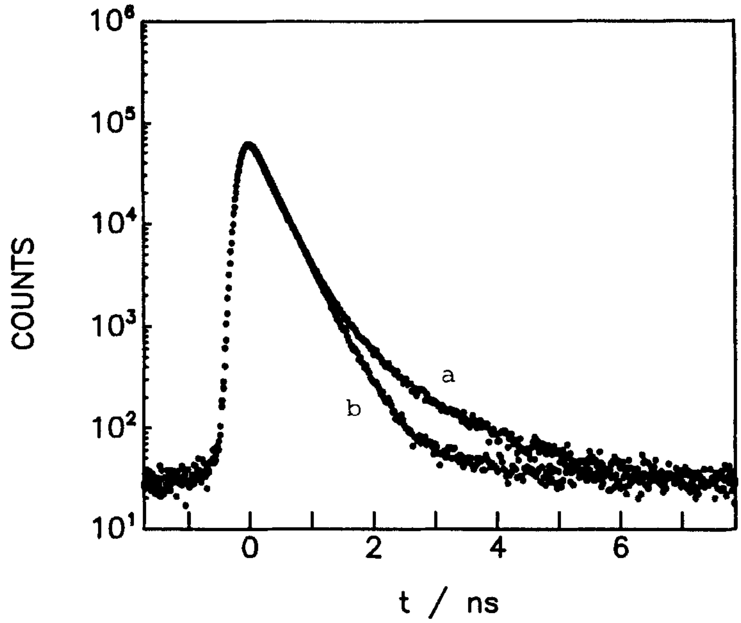

FIGURE 3 Lifetime spectra of (a) durene-*p*-bromanil and (b) anthracene-PMDA crystals.

We have examined positron annihilation in charge-transfer complexes in the solid state. Positronium is found to be formed in the complexes of durene with trinitrobenzene (TNB) (τ_{Ps}=3.1 ns), *p*-chloranil (1.1 ns) and *p*-bromanil (0.96 ns), but not in the complexes of anthracene with TNB and pyromellitic dianhydride (PMDA), nor in the complexes of HMB with TNB, PMDA and *p*-chloranil. The formation of Ps seems to be explained in terms of a balance between the energy release from binding of a Ps atom and the sum of electron and positron affinities.[11]

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