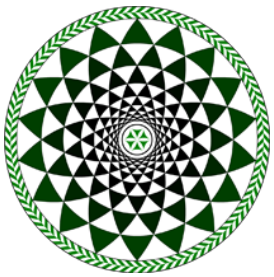

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Positron annihilation in smectic E phase of 4-alkyl-4– isothiocyanatobiphenyls (nTCB)

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Probing of intermolecular or intramolecular regions in molecular solids by positron annihilation lifetime spectroscopy (PALS) is well established. In such substances, the formation and decay of positronium (Ps) – the positron-electron bound state is expected to be influenced by the nature of intermolecular interactions and the internal structure. Structural changes, phase transformations and changes of local microscopic properties are reflected in the measured PALS spectra what is particularly pronounced in the case of liquid crystals. It can be demonstrated in the case of compounds from homologues series of nTCB. The results of PALS measurements for 4TCB and 6TCB are presented. For 4TCB, the measurements of positron lifetime as a function of temperature were performed between 93 K and 293 K in order to study supercooled smectic E (SmE) phase [1].
The obtained value of the ortho-positronium (o-Ps) lifetime equal to 2.21 ns at room temperature in the SmE phase of 4TCB can be explained by formation of Ps bubbles. The bubbles are created due to a liquid-like state of the butyl chains of 4TCB molecules in the SmE phase. However, setting out the new models of SmE by Saito et al. [2] allowed us to better understand the Ps formation in SmE phase. The new models of SmE lamellar structure with nano-segregation of alkyl chains and other parts of molecules are examined in terms of the local free volume in nTCB probed by Ps atom. The other question is the thermal activation of sites where Ps bubbles are formed in supercooled SmE phase of 4TBC. The issue is approached basing on the bond lattice model of glass transition [3]. This approach is also applied to the results of the PALS measurement for 6TCB performed as a function of external pressure.
The PALS spectra were also measured during isothermal crystallization of the 4TCB SmE phase. The analysis of the obtained results using the Avrami equation indicates the low dimensional crystal growth. The o-Ps lifetime in ordered molecular crystal was interpreted as originating from the annihilation of o-Ps confined in molecular vacancy-type of imperfections in the crystal lattice. The phase transition between ordered crystal and SmE phase is reflected in the abrupt increase of the o-Ps lifetime and intensity.

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