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Positronium formation and annihilation in liquid crystalline smectic-*E* phase revisited

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The results of the positron lifetime measurements of the quenched smectic-*E* (Sm-*E*) phase of 4-butyl-4′-isothiocyano-1,1′-biphenyl (4TCB) are revisited. The sites of positronium formation and annihilation, according to the model with nanosegregated layered structure of the Sm-*E* phase and molten state of alkyl chains of molecules, are identified in the sublayer containing alkyl chains of molecules. The possibility of vitrification of the Sm-*E* phase for 4TCB consisting in freezing of the alkyl chain motions is considered as a cause of the thermally activated creation of sites where *o*-Ps is formed and annihilates in the quenched Sm-*E* phase. The description of the temperature dependence of *ortho*-positronium intensity is performed using the glass transition model which assumes that the molecules occupy two thermodynamic states: solidlike or liquidlike regarding mobility of their alkyl chains. The equilibrium temperature between solidlike and liquidlike domains of the model obtained from positron lifetime measurements coincides with the exothermic effect in the temperature dependence of the heat capacity.

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I. INTRODUCTION

The smectic liquid crystal phases formed by calamitic (rodlike) molecules have layered structures, with a well-defined interlayer spacing. In smectics molecules exhibit some correlations in their positions in addition to the orientational ordering. In most of the smectic phases the molecules are mobile in two directions within the layer and can reorient about long and short axes. The smectic-*E* phase (Sm-*E*), however, differs from the typical smectic phases. It has no fluidity and has the long range positional periodicity in three dimensions. It is characterized by the orthorhombic arrangement of molecules, orthogonal within smectic layers. Therefore, it is classed as soft crystal—crystal *E* (Cry-*E*) [1]. The molecules within the layer form a herringbone array. According to the traditional model of the Sm-*E* phase the layers are separated without interdigitation of molecules and the layer spacing along the *c* direction of the orthorhombic lattice is nearly equal to the length of the molecule [2]. The Sm-*E* phase of 4-*n*-alkyl-4′-isothiocyanato-1,1′-biphenyls (*n*TCB) has been extensively investigated and a new model of Sm-*E* lamellar structure with two types of sublayers consisting of aromatic cores and alkyl chains has been recently proposed [3,4]. Furthermore, the previous thermodynamic, structural, and spectroscopic studies indicated that alkyl chains of molecules are already molten in the Sm-*E* phase to the same extent as in the isotropic liquid [5,6]. The molten state of alkyl chains in the Sm-*E* phase of 4-butyl-4′-isothiocyano-1,1′-biphenyl (4TCB) has been confirmed also by positron annihilation lifetime spectroscopy (PALS) [7]. It seems that the new model of molecular arrangement proposed in Ref. [4] allows us to explain better the obtained PALS results and, on the other hand, the PALS results may help to differentiate between two proposed variants of the model.

PALS is a method widely applied to study local structure in molecular substances such as polymers, molecular crystals, low molecular weight glass formers, and liquid crystals. A positron in low electron density regions like local free volume holes of a molecular solid can form a bound state with an electron called positronium (Ps) [8]. Ps is formed in two spin states: *para*-Ps (*p*-Ps) and *ortho*-Ps (*o*-Ps) reflecting the different positron and electron spin alignment, i.e., antiparallel and parallel, respectively. In vacuum, *p*-Ps decays into two quanta with the lifetime of 125 ps and *o*-Ps decays into three quanta with the lifetime of 142 ns. The relative abundance of these two states is 1:3. In matter, as a result of *o*-Ps interactions with the electrons of surrounding molecules, its lifetime is determined mainly by the annihilation of the positron with one of these external electrons. This process called *pick-off* annihilation causes a reduction of *o*-Ps lifetime to several nanoseconds. Due to this the lifetime of *o*-Ps is very sensitive to the local free volume size. As a result of other processes affecting Ps formation and annihilation, e.g., spin conversion or chemical quenching, the observed relative intensity of the *p*-Ps and *o*-Ps components may vary from the 1:3 ratio. In liquids, Ps is strongly repelled by the molecules and creates for itself a bubble which hosts it [9]. In a bubble state the inwards pressure due to the surface tension and the external pressure are counterbalanced by the outwards pressure resulting from the Ps molecule repulsion and the zero point energy of Ps.

The purpose of the paper is twofold: first, to locate the local free volumes probed by *ortho*-positronium (*o*-Ps) in the Sm-*E* phase of 4TCB in the frame of the new model and second, to revisit the problem of thermally activated creation of sites where *o*-Ps is formed and annihilates in the quenched Sm-*E* phase of 4TCB in terms of the two-state model of glass transition [10]. Detailed understanding of molecular arrangement in the Sm-*E* phase is important because mesogens showing this phase are candidates for organic semiconductors [11,12]. However, taking into account the universality of the alkyl chain molten state in any liquid-crystalline mesophases, description of the 4TCB glass softening can shed light on the processes taking place in supercooled liquid crystals of other phases, e.g., Sm-*A*, and their influence on the results of PALS measurements.

II. EXPERIMENTAL RESULTS

The PALS experimental data for the quenched Sm-*E* phase of 4TCB are taken from Ref. [7] where the experimental procedure is also described. On heating of the quenched sample

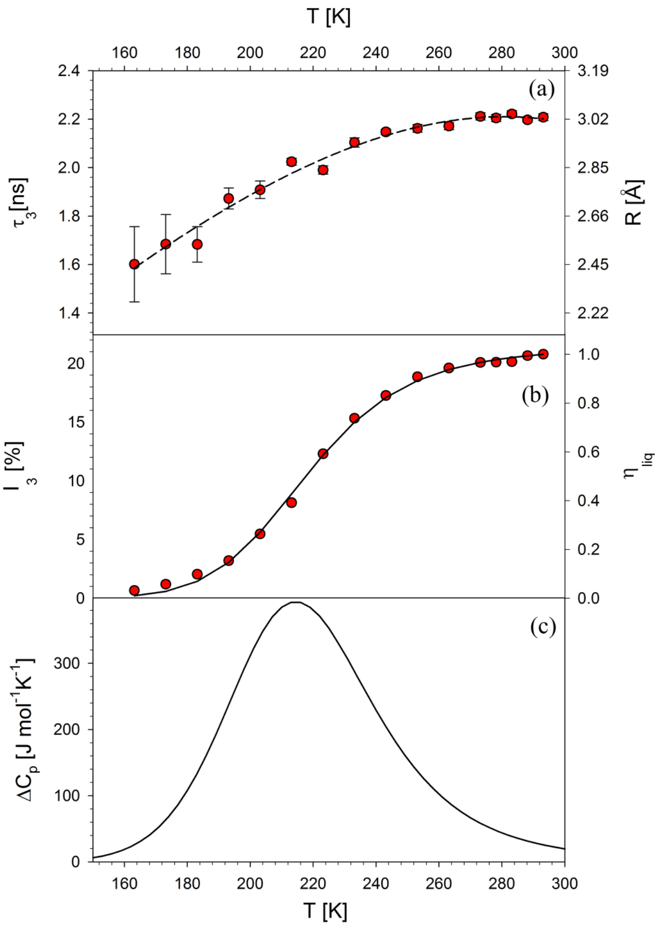

FIG. 1. Temperature dependence of τ_3 for the Sm-*E* phase of 4TCB (a). The dashed line is meant as a guide for the eye. Temperature dependence of I_3 for the Sm-*E* phase of 4TCB (b). The right vertical axis shows the values of the fraction of liquidlike molecules n_{liq}, which is proportional to I_3. The solid line is the fit of the relation given by Eq. (2) to the experimental points. Temperature dependence of configurational heat capacity ΔC_p within the bond-lattice model given by Eq. (3) for parameters obtained from the fit of Eq. (2) (c).

only one positron lifetime component coming from positron annihilation in a free state was resolved for temperatures lower than 163 K. For higher temperatures the spectra can be deconvoluted into three components. The shortest component τ_1 corresponds to *p*-Ps decay, the intermediate one, τ_2, to the annihilation of free positrons and the longest one, τ_3, to *o*-Ps decay due to the pick-off annihilation. Dependencies of the longest lifetime component τ_3 and its intensity I_3 on temperature for the quenched Sm-*E* phase of 4TCB are shown in Fig. 1. After appearing at 163 K, τ_3 increases, reaching the value of 2.21 ns at 293 K. Assuming that pick-off is the main process of *o*-Ps annihilation, i.e., $\tau_3 = \tau_{po}$, this value corresponds to the radius of the spherical free volume $R = 0.30$ nm according to the following equation:

$$\tau_{po} = \tfrac{1}{2}\{1 - R_0/(R_0 + \Delta R) + (1/2\pi)\sin[2\pi R_0/(R_0 + \Delta R)]\}^{-1}, \qquad (1)$$

where τ_{po} is the pick-off lifetime, R_0 is the radius of a spherical free volume hole, and $\Delta R = 0.166$ nm is an empirical parameter [13,14]. The intensity I_3 increases sigmoidally with temperature from 0% to 21%. Additionally, the PALS spectrum was measured for a 4-*n*-hexyl-4′-isothiocyanato-1,1′-biphenyl (6TCB) sample at room temperature. For 6TCB, $\tau_3 = 2.4$ ns which corresponds to $R = 0.32$ nm with intensity of 14% at 295 K.

III. ARRANGEMENT OF MOLECULES IN SMECTIC-*E* LAYERS AND THE SITES OF POSITRONIUM FORMATION

Within the commonly accepted structural model of the Sm-*E* phase, molecules form perfect and separated layers. Two such layers are shown schematically in Fig. 2(a). The spacing Δl between the molecules in the adjacent layers along the axis perpendicular to the layers, i.e., $\Delta l = c–L$, is 1.6 Å for 4TCB and 2.0 Å for 6TCB, where c is the lattice constant and L is the molecule length [15]. These values are markedly smaller than the average diameter of Ps bubbles, which is equal to 6 Å for 4TCB and 6.4 Å for 6TCB. As it was discussed in Ref. [8] the molten state of the alkyl chains of molecules allows the Ps atom to create a bubble in a similar way as in isotropic liquids. However, the presence of molecular dipoles and high electron density on the sulfur atoms of the NCS groups can quench the *o*-Ps unless the disorder in the head-to-tail arrangement creates a shell of a few butyl chains surrounding the *o*-Ps bubble. The new model of molecular arrangement in the Sm-*E* phase proposed by Saito *et al.* supports the idea of such a surrounding for the *o*-Ps bubble through nanosegregation of alkyl chains and other parts of molecules (biphenyl core and NCS group) [4]. There are two variants of the model. The first one assumes that alkyl chains and other parts of molecules are nanosegregated due to so-called chemical amphiphilicity [Fig. 2(b)], while according to the second one they are nanosegregated due to difference in dynamics [Fig. 2(c)]. In both cases the structure is characterized by sublayers of higher and lower electron density. In the first case Fig. 2(b) the width of the layer with higher electron density l_1 is equal to the length of the high-density part of the molecule (NCS+biphenyl) ≈ 12 Å. In the second case the width of this layer is higher due to the shift of molecules ensuring the chemical interaction (the so-called π-π interaction) between the phenyl rings of the adjacent molecules. According to Saito *et al.* the nonmolten part of the alkyl chain in the Sm-*E* phase has a length of ca. 3 Å. The width of the sublayer with a higher electron density l_2 is ca. 15–15.4 Å as a sum of the length (ca. 12 Å) of the high electron density parts (NCS+biphenyl) of a molecule and the length of the NCS group (ca. 3.4 Å). The length of the aromatic core is ca. 8.6 Å. The width of the lower electron density sublayer can be compared with the Ps bubble diameter (2R) because in this area the Ps bubble can be formed. The values describing both variants of the model are gathered in Table I. It can be seen that the average diameter of the free volume holes is larger than the width of the lower electron density sublayer for the second variant of the model. Then, it seems that for the Sm-*E* phase of 4TCB the PALS results indicate the molecular arrangement proposed in the first variant of the model. The situation is similar for 6TCB, for which the Ps bubble is larger than for 4TCB. However, the Ps bubble diameter for 6TCB is smaller than the sublayer width in this variant.

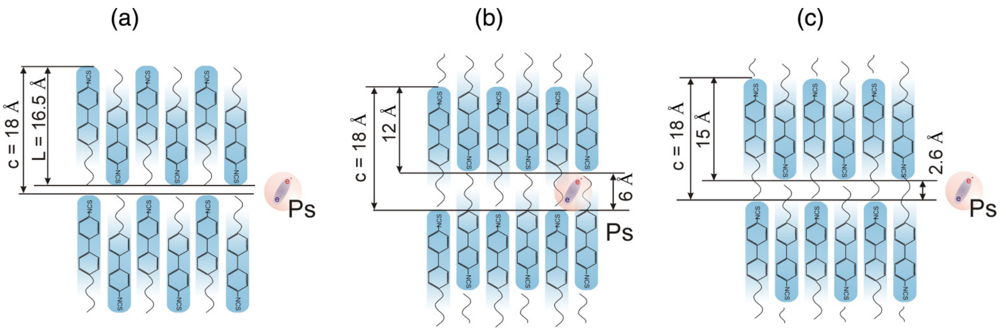

FIG. 2. Arrangement of molecules in the Sm-E phase: traditional model (a). New model proposed in Ref. [4] with two variants: with nanosegregation due to so-called chemical amphiphilicity (b), and with nanosegregation due to difference in dynamics (c). The estimated dimensions of the sublayer and the size of the Ps bubble are given for 4TCB.

Since Ps is formed and annihilates in the sublayer containing alkyl chains, comparison of the results with the PALS data for liquid n-alkanes would be purposeful. For liquid n-alkanes the positron lifetime near the melting point is equal to $\tau_3 = (3.10\text{–}3.15)$ ns and does not depend on the number of carbon atoms in the chain for n from 6 to 50 [16]. The lifetime corresponds to the Ps bubble radius 3.75 Å. The independence of the o-Ps lifetime from the chain length is explained by the fact that, like in polymers, Ps interacts only with short segments of molecules regardless of the chain length. For the Sm-E phase of 6TCB the radius of the Ps bubble, i.e., 3.2 Å, at a temperature close to the molecular crystal M1 to Sm-E transition (294 K), is lower than for liquid n-alkanes including n-heptan. It seems that in the partially ordered system such as the Sm-E phase conformational changes of alkyl chains are more restricted than in liquid n-alkanes. This can be related to higher local surface tension or to the influence of the nonmolten parts of the alkyl chains of 6TCB molecules in the Sm-E phase. However, influence of the latter is not observed for 4TCB.

IV. THE TWO-STATE MODEL OF GLASS TRANSITION IN THE QUENCHED SMECTIC-*E* PHASE OF 4TCB

Liquid crystalline mesophases, even those characterized by a high degree of order as the Sm-E phase, can undergo vitrification process [17,18]. The possibility of vitrification of the Sm-E phase for 4TCB was reported previously [19]. The glass transition was considered as consisting of freezing in the head-to-tail disorder. However, in the light of the new model of the Sm-E phase the glass state can consist of freezing of the alkyl chain motions. The model of molecular arrangement in the Sm-E phase proposed by Saito *et al.* may also help to explain the thermally activated creation of sites, where o-Ps is formed in the quenched Sm-E phase of 4TCB [4]. The successful approach to description of crystallization of a metastable Sm-E phase of 4TCB on heating in Ref. [7]—with the assumption that o-Ps is formed and annihilates in the fraction of the sample which is in the liquid state—can be also applied in the case of the temperature dependence of the o-Ps intensity for the quenched Sm-E phase of 4TCB.

TABLE I. The diameter of the Ps bubble ($2R$) and the width of the sublayer containing alkyl chains of molecules for two variants of the model proposed in Ref. [4]: c is the lattice constant perpendicular to the smectic layer; the width of the layer with higher electron density l_1 in the first variant of the Sm-E phase model is equal to the length of the high-density part of the molecule (NCS+biphenyl); l_2 in the second variant of the Sm-E phase model is equal to the length of the high-density part of the molecule (NCS + biphenyl) and NCS due to shift of molecules.

	$2R$	c–l_1 [Fig. 2(b)]	c–l_2 [Fig. 2(c)]
4TCB	6 Å	18–12 Å = 6 Å	18–15.4 Å = 2.6 Å
6TCB	6.4 Å	21–12 Å = 9 Å	21–15.4 Å = 5.6 Å

We assume that at a certain temperature alkyl chains of molecules within a sublayer can be in two distinct structural states; i.e., they may form two types of domains: liquidlike in the viscoelastic state, and solidlike in the rigid state. In liquidlike domains, mobility of alkyl chains is high enough that Ps can form a bubble and then annihilates in the pick-off process. In solidlike domains, thermal motions of alkyl chains of molecules are relatively slow as a result of their cooperative nature and Ps is not formed. If, similarly to crystallization, the o-Ps intensity is proportional to the sample fraction in the liquidlike state, a two-state model of glass transition can be used for description of the obtained temperature dependency of o-Ps intensity [10,20–22]. The model assumes the free energy difference between the states $\Delta G = G_{\mathrm{liq}}\text{–}G_{\mathrm{sol}}$. When the two states are in equilibrium $\Delta G = \Delta h\text{–}T_e\Delta s = 0$ and $T_e = \Delta h/\Delta s$ is the temperature at which the supercooled liquid and the glass have the same free energy. It can be considered as the melting point of the solidlike domains. The fraction $n_{\mathrm{liq}}(T)$ of the molecules in liquidlike state as a function of temperature T is as follows [23]:

$$n_{\mathrm{liq}}(T) = \frac{1}{1 + \exp\left[\frac{H}{T}\left(1 - \frac{T}{T_e}\right)\right]}, \tag{2}$$

where, basing on the bond-lattice model of glass transition, $H = h_b z_{\mathrm{eff}}/k_B$, h_b is the energy difference per closed bond, z_{eff} is the effective coordination number of the first shell, and k_B is Boltzmann's constant [10]. For 4TCB, the curve fitted to the o-Ps intensity is shown in Fig. 1(b). The obtained parameters are the following: $H = (2980 \pm 133)$ K and $T_e = (219 \pm 1)$ K. The value RH should describe the enthalpy per 1 mole of excitations, i.e., per 1 mole of created o-Ps annihilation sites, and it is equal to $24.8 \pm 1.1\ \mathrm{kJ\,mol^{-1}}$; the entropy is equal to $113 \pm 1\ \mathrm{J\,mol^{-1}\,K^{-1}}$.

The fitted parameters can be used to obtain for example the corresponding temperature dependence of configurational heat capacity $\Delta C_p(T)$ within the bond-lattice model [24]:

$$\Delta C_p(T) = \frac{RH^2}{T^2} n_{\mathrm{liq}}(T)[1 - n_{\mathrm{liq}}(T)] \quad (\mathrm{J\,mol^{-1}\,K^{-1}}). \qquad (3)$$

The dependency presented in Fig. 2(c) shows that $\Delta C_p(T)$ does not exhibit any singularity and it can be described as an asymmetrical humplike rise. In Ref. [19] the temperature dependence of heat capacity in the quenched Sm-*E* phase of 4TCB was also specified as a hump between 150 and 250 K. However, the values of the obtained excess of enthalpy and entropy are much smaller, i.e., $3\,\mathrm{kJ\,mol^{-1}}$ and $15\,\mathrm{J\,mol^{-1}\,K^{-1}}$. The discrepancy between these values and the values obtained from the *o*-Ps intensity dependence may be explained by the fact that creation of one site of *o*-Ps annihilation requires more than one molecule with the alkyl chain in a liquidlike state. Assuming simple arithmetic, one can see that on average eight neighboring molecules with molten alkyl chains are required to fulfill the results.

This model was applied to description of the temperature dependence of the annihilation parameters of Ps in 1,1-bis(paramethoxy-meta-methyl-phenyl)-cyclohexane (BMMPC) [23]. However, in the case of BMMPC, *o*-Ps is formed in both kinds of domains, i.e. solidlike and liquidlike, where it annihilates with different lifetimes. The fitting procedure applied to the *o*-Ps lifetime temperature dependence is more complicated. The equilibrium temperature T_e, for BMMPC obtained from the *o*-Ps lifetime temperature dependence, was significantly lower than the values obtained from experimental data analyzed also in terms of the two-state model, obtained using other methods, i.e., dielectric relaxation spectroscopy, viscosity measurements, and the position of a wide exothermic peak in differential thermal analysis [23]. The discrepancy was explained as a result of the release of unknown molecular motions along with the phase transition.

It seems that in the case of 4TCB, due to the fact that *o*-Ps is not formed in the quenched Sm-*E* phase below a certain temperature, the description of the experimental data using the two-state model is simpler and more reliable. Moreover, the obtained equilibrium temperature T_e coincides with the exothermic effect in the temperature dependence of the heat capacity [19].

V. CONCLUSIONS

The *o*-Ps lifetime for the Sm-*E* phase of 4TCB and 6TCB confirms the model of arrangement of molecules with nanosegregation of alkyl chains and other parts of molecules proposed by Saito *et al.* [5]. Thermally activated creation of sites where *o*-Ps is formed in the quenched Sm-*E* phase of 4TCB can be explained in terms of the two-state model of glass transition, assuming that the glass transition consists in freezing of the alkyl chains' motions. Assumption that *o*-Ps intensity is proportional to the fraction of molecules with mobile alkyl chains allowed us to obtain the equilibrium temperature, $T_e = (219 \pm 1)\,\mathrm{K}$, which coincides with the exothermic effect detected in the temperature dependence of heat capacity [19].

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