Positron study of the structure of nonadecane-tricosane mixed solid

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Abstract. Positron annihilation lifetime and intensity were measured as a function of temperature for a binary mixture of two normal alkanes. The rotator phase is preceded by the range of about 7 K, in which one observes instability of spectrum parameters. In that range the mixed solid, being initially introduced into rotator phase, transforms to a rigid one in the time scale of several hours.

Key words: positron annihilation • *n*-alkanes • binary mixture

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Introduction

Normal alkanes, C_nH_{2n+2} (for shortness: Cn) belong to the most important components of organic matter. In majority of practical applications they appear as mixtures of various carbon chain length. Therefore, it seems interesting to investigate the differences in structure and properties of pure and mixed alkanes.

All solid phases of long-chain *n*-alkanes exhibit a lamellar structure. In a broad range of alkane homologous series liquid state is preceded by rotator phases. In the rotator phase the translational symmetry of the crystal is preserved, but the molecules have a rotational degree of freedom about their long axis. Decreased ordering of the structure is accompanied by a large concentration of non-planar conformers deteriorating further the symmetry of the crystal. In a mixed alkane crystal the range of rotator phase is broadened [5]. This paper is devoted to the positron study of the structure of an alkane mixture, in particular of the range and stability of rotator phase in a selected mixture of *n*-nonadecane C19 and 4% of *n*-tricosane C23.

Experimental

The samples were from Sigma-Aldrich, 99% nominal purity. The concentration of impurities in C19 was tested by gas chromatographic and mass spectrometric methods. The content of neighbouring C18 and C20 was found equal to 0.07% each.

The polycrystalline samples in the form of two pellets with a positron source between them were placed in a chamber viewed by scintillation counters connected to a standard fast-slow lifetime spectrometer. The activity

of ^{22}Na positron source (0.5 MBq) allowed to collect the statistics of 8×10^5 coincidences during 1 h. The spectra were assumed as consisting of three exponentials convoluted with the instrumental resolution curve. The lifetimes and relative intensities of respective components were determined using the LT program [3]. The longest-lived component (mean lifetime τ_3, intensity I_3) was ascribed to the decay of *ortho*-positronium (*o*-Ps) and only this component will be discussed below. At low temperatures the intensity of *o*-Ps component can be modified by Ps formation on trapped excess electrons [2]. However, this effect does not appear in the rotator phase and can be assumed negligible in the range of several K below the rigid-rotator transition point.

Results and discussion

In our earlier measurements [6] we have shown that the *o*-Ps lifetime in the low temperature ("rigid") phase of mixed *n*-alkanes is longer than that in the neat ones, due to locally increased width of interlamellar gap that accommodates the positronium atom. In the case presented in this paper the *o*-Ps lifetime near the transition point to rotator phase is 2.1 ns, while in the neat *n*-nonadecane it is 1.5 ns only.

The lamella interior is packed too tightly to accommodate Ps atom, unless distorted non-planar molecules appear in substantial concentration; this takes place in the rotator phase abundant in kink-shaped conformers [4]. An empty channel along the kinked molecule represents an increased free space to locate the Ps atom.
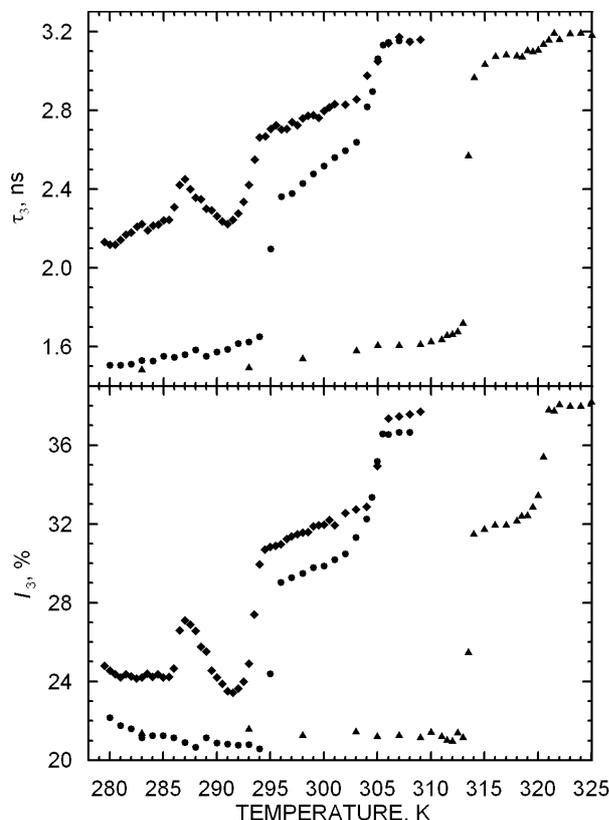
As a result, the *o*-Ps lifetime in the rotator phase is evidently longer than in the rigid one. It always exceeds 2 ns tending, for longer chains, to the value of 3.15 ns, which is typical also for liquid phase near the melting point [1].

Temperature dependence of lifetime and intensity was measured in 1 K or 0.5 K steps. Before the measurements the sample was kept for 1 h at 298 K (close to the melting point), then the temperature was lowered to several degrees below the rigid phase and next it increased in 1 h steps. The result obtained at such step-by-step measurements with increasing temperature is shown in Fig. 1. The striking feature of temperature effects is non-monotonous dependence of both lifetime τ_3 and intensity I_3 on temperature. After rapid increase at 286 K, the lifetime and intensity begin to decrease and their higher values are restored near the transition point in neat nonadecane. It seemed to us worthwhile checking whether the spectrum parameters observed in the range 286–293 K are stable in time. For this reason, the samples, kept initially at 298 K, were cooled to 279 K and then at a possibly short time the temperature was increased to the selected value in the range 286–295 K. A series of spectra was recorded at that fixed temperature. This procedure was repeated for several temperatures. A straight line was fitted to the I_3 data in the range of rotator phase (294–303) K and extrapolated to lower temperatures. Directly after reaching the selected temperature the *o*-Ps lifetime and intensity had the values close to these expected for pure rotator phase, i.e. close

Fig. 1. *Ortho*-positronium lifetime and intensity as a function of increasing temperature (1 h per point). Dots – neat C19, triangles – neat C23, diamonds – binary mixture C19 + 4% C23.
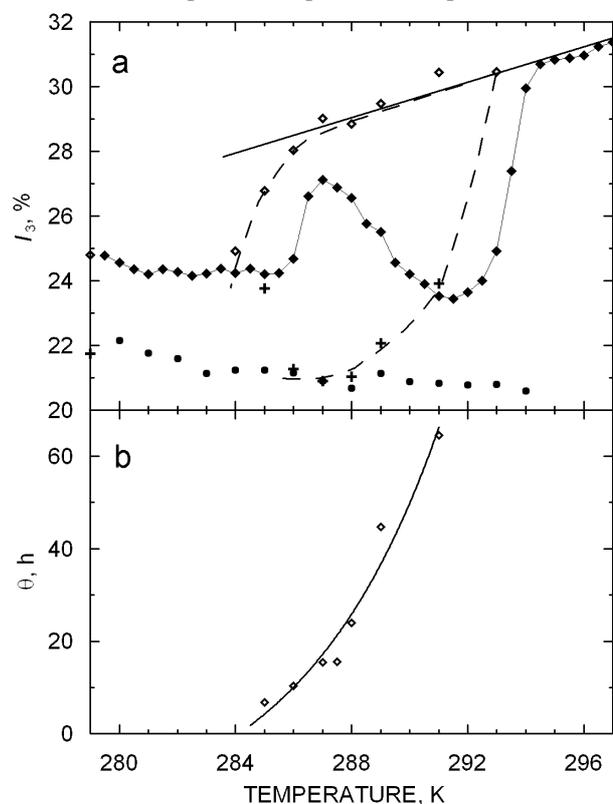
Fig. 2. a – *Ortho*-positronium intensity as a function of temperature. Empty diamonds – directly after lifting the temperature from 279 K; crosses – after reaching the final stable values; full diamonds – the curve from Fig. 1 (for comparison). Dashed lines show the limits of instability region; solid straight line is fitted to the experimental data in the range 294–303 K; b – time constant of the transition to the stable state.

to the extrapolated line. These values were not stable but they decreased with time. The decrease, at least in the initial part, was not strictly exponential, but at least approximately one can determine the time constant of that decrease. The initial and final values of intensity are shown in Fig. 2a, while in Fig. 2b the time constants of sample recovery are plotted. The time constant rises with temperature and at 292 K the values of spectrum parameters become stable.

In the region of instability the mixture components still crystallize together. In the transition time the sample is composed of domains, rigid and rotator separately, but the domains contain the molecules of both lengths. This is seen in the lifetime in rigid phase. During the transition and after reaching the final state, the lifetime remains long; it does not return to the values observed in neat samples. The intensity undergoes much larger changes; final I_3 value in the unstable region is small, like in the rigid phase of neat sample.

Conclusions

In the mixture of two alkanes, differing in length of chains by about 20%, one observes the range, where the phase composition is unstable. In that range directly after the increase of temperature (starting from rigid phase) the whole sample transforms to rotator phase, but then returns, at least partially, to low-temperature phase. The time constant of transition is of the order of many hours; thus in classic DSC measurements, at rapid

temperature scan, the instability can escape notice. In the case discussed here, the admixture of an other alkane of the same evenness is quite small (4%) but its influence on the structure is noticeable. It means that if the sample purity is, as in many practical cases, of the order of 99%, the impurity (crystallizing together) can substantially modify the sample properties.

It seems to be interesting to extend the investigations of alkane mixtures to a broad range of component concentrations and at various molecular lengths.

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