Ortho-Positronium in Alkanes 
under High Pressure

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Phase transitions in \( n \)-alkanes were observed by using the positron annihilation lifetime method. In the case of alkanes, application of pressure is equivalent to temperature lowering (1 K corresponds to \( \approx 4 \) MPa). When argon at high pressure penetrates the sample one observes a non-monotonous dependence of the melting point on pressure. This effect is observed also in even-numbered alkanes, in which there is no rotator phase.

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1. Introduction

Ortho-positronium (\( \alpha \)-Ps), formed in condensed matter at the end of the ionization track of an energetic positron (e.g. from \( \beta^+ \) decay), locates in free volumes, i.e. the voids or arbitrary low-electron density spaces in the bulk. Structural changes of the medium are usually accompanied by the changes in the free volume. Positronium can serve as a probe of these free volumes; its lifetime is determined by the size and shape of the void in which it is trapped. The larger the void is, the longer is the lifetime [1].

Solid odd-numbered alkanes, \( C_nH_{2n+2} \), of moderate chain length (9 < \( n < 25 \)) can appear in two phases: at low temperature as a rigid crystal, and in the range of about 10 K below the melting point, as the so-called rotator (waxy) phase. This phase is characterized by large concentration of non-planar conformers; in their vicinity empty spaces are enlarged, that leads to distinct increase in \( \alpha \)-Ps lifetime, from \( \approx 1.4 \) ns to (2–3) ns.

Owing to the high sensitivity of \( \alpha \)-Ps lifetime to the free volume changes, one can apply the positron annihilation technique to observe the influence of various factors on phase transitions. In the following we present some data about the changes of phase transition point induced by applying a high pressure to samples of \( n \)-alkanes.

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2. Experimental

The measurements were performed in two versions: (a) with the access of high pressure gas to the sample (intercalation) and (b) without that access. In case (a), a pair of polycrystalline samples in the form of pellets with positron source inside was pressed together (when in rotator phase) and placed directly into the high pressure chamber of Unipress U-11 compressor with argon as a working gas. In case (b), similar, but smaller, sandwich of samples and source was placed in a small tube, closed by two pistons. The air was evacuated from the tube interior via side opening and then one of pistons was moved down, below the opening. In this way, the whole volume between the pistons was filled by the samples, which have no contact with the gas outside. The whole device was placed in the chamber of the compressor; the pressure was applied via the pistons. Temperature could be regulated in a narrow range by a heating coil and Peltier cell.

Positron annihilation lifetime spectra were measured using a standard fast-slow delayed coincidence setup. Collection of one spectrum lasted at least 3 h, because achieving the sample saturation by gas needed comparable time. The spectra were processed by the LT program [2] assuming that the spectrum consists of 3 exponential components convoluted with the instrumental resolution curve. The longest-lived component was ascribed to the decay of ortho-positronium. The ortho-Ps lifetime $\tau_3$ is unambiguously determined by the size and shape of voids, but the intensity $I_3$ (relative probability of ortho-Ps formation) usually depends on sample history due to radiation induced radiochemical processes. Such effects dominate at low temperatures, however, in the rotator phase and its neighborhood the intensity is stable in time and its value is fully reproducible.

3. Results and discussion

It is known that the temperature of phase transition $T_{tr}$ in alkanes is approximately a linear function of pressure; $dT_{tr}/dp$ is positive [3]. The effect of temperature decrease is equivalent to the increase in pressure; 1 K corresponds roughly to 4 MPa. Figure 1 shows an example of the pressure dependence of $\tau_3$ for a sample of $n$-nonadecane at 301 K. At zero pressure the sample was in the rotator phase. Already at 32 MPa the transition to rigid phase was observed as a drastic lifetime decrease. Upon a further pressure increase, the reduction of lifetime was very slow, and the intensity in the range from 200 MPa up to 1300 MPa was practically constant. Rod-like all-trans molecules of alkane are tightly packed, parallel to each other, forming lamellae like in a smectic liquid crystal. This kind of packing is responsible for very low compressibility and also for an absence of phase transitions at highest pressures (and extremely low temperatures).

When the pressure is applied through the gas penetrating the samples, one can observe several interesting features:

— negative compressibility of free volumes [4]. With the rise of pressure a slight increase of ortho-Ps lifetime can be observed (at moderate pressures);
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Fig. 1. Ortho-positronium lifetime in \( n \)-nonadecane as a function of pressure. Inset shows the initial fragment in an extended scale. Temperature 301 K.

- shift of phase transition point from rotator to rigid phase toward higher pressures;
- the most interesting feature observed in the case of argon intercalation only, is nonmonotonous dependence of the melting point, \( T_m \), on pressure.

This effect, found by differential scanning calorimetry (DSC) thermal analysis in pentadecane by Josefiak et al. [5], can be clearly demonstrated using the positron annihilation method. Such a measurement was performed by us for the case of nonadecane [6]. Below we present similar measurements for the next odd-numbered alkane, \( n \)-heneicosane \( C_{21}H_{44} \). At normal pressure the transition rigid-rotator occurs at \( T_{tr} = 305.5 \) K, while melting is at \( T_m = 313 \) K. Figure 2 shows the dependence of o-Ps lifetime on pressure for three temperatures: 309, 310, and 311 K. At 309 and 310 K the lifetime shows small variations with pressure until the phase transition point is reached and the \( \tau_3 \) value is reduced. When approaching the melting point one observes a different picture: at 18 MPa the lifetime increases in a stepwise way to the value of about 3 ns, typical of liquid. Transition to low \( \tau_3 \) occurs at 50 MPa. It means that the sample, initially in the rotator phase, melts when exposed to argon at high pressure, and on continuing the pressure increase, solidifies directly in the rigid phase. There is no rotator phase at the pressures over 50 MPa. The triple point (rotator, rigid, liquid) is now at [48 MPa, 311 K], while without argon it appears at [215 MPa, 353 K]. The region of rotator phase is greatly limited.

The non-monotonous dependence of \( T_m \) on pressure seems to be a common property of odd-numbered alkanes, experimentally demonstrated in pentadecane [5], heptadecane and nonadecane [6]. However, it is difficult to demonstrate its appearance for carbon chains longer than \( n = 21 \) using the positron annihili-
The lifetime $\tau_3$ rises with chain length and the difference of $\tau_3$ between rotator and liquid disappears.

The slope of $T_m$ vs. $p$ curve, in the range where rotator phase exists, is negative. However, the value of $dT_{tr}/dp$ is always positive. It seemed to us interesting to perform the measurements for an even-numbered alkane, in which there is no rotator phase. We have chosen $n$-octadecane (melting point 301.3 K at normal pressure). The temperature was fixed at 300.0 K. The result is shown in Fig. 3. At the lowest pressures, the lifetime was characteristic of the rigid phase, but at
12.5 MPa it rose to almost 3.0 ns and then at 25 MPa returned to the value typical of rigid phase. Therefore, even in the alkane in which there is no rotator phase, at the temperature 1.3 K below melting point at normal pressure, a range of liquid phase exists. Let us note that the change of $o$-Ps lifetime at the transitions shown in Fig. 3 is exceptionally high.

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References