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POLYMERS

Detailing of Deformation Processes in Polymeric Crystals

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Abstract—Structural changes in polymer crystals (polyethylene, polyimide, and others) have been studied using the X-ray diffraction and Raman spectroscopy methods under different influences: tensile loading along the chain molecule axis and heating from 90 to 350 K. An increase in the molecule axial length under loading and a decrease in the molecule axial length upon heating have been identified and measured using X-ray diffraction. A decrease in the skeletal vibration frequency during loading and heating has been identified and measured using Raman spectroscopy, which indicates an increase in the molecule contour length in both cases. A technique for determining the change in the polyethylene molecule contour length in the crystal from the measured change in the skeletal vibration frequency has been justified. The contributions of two components, namely, skeletal (carbon–carbon) bond stretching and the change (an increase during stretching and a decrease during heating) in the angle between skeletal bonds, to the longitudinal deformation of polyethylene crystals, have been quantitatively estimated. It has been shown that the negative thermal expansion (contraction) of the polymer crystal is caused by the dominant contribution of the decrease in the bond angle.

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1. INTRODUCTION

Polymer crystals consist of straightened segments of chain molecules packed in parallel and regularly relative to each other. The straightened chain molecules of many polymers have a carbon skeleton shaped as a plane zigzag consisting of carbon C–C bonds of length $l_C \approx 1.5$ Å with the bond angle $\theta \approx 110°$ (Fig. 1). Such a skeleton shape results in that the straightened polymer molecule has two parameters:

(i) the contour length $L_c = \sum_n l_C = l_C n$, where n is the number of carbon atoms in the chain;

(ii) the axial length $L_{\mathrm{ax}} = \sum_n l_C \sin\theta/2 = n l_C \sin\theta/2 = n l_{\mathrm{ax}}$, where l_{ax} is the axial length of the C–C bond (projection of the bond contour length l_C on the molecule axis).

Under different mechanical actions on the polymer crystal (on chain molecules in it), caused by loading or heating, the contribution to the total strain is made by stretching (shortening) of C–C bonds and changes in bond angles, which leads to variations in combination with changes in the axial and contour lengths of C–C bonds.

Efficient methods for measuring deformation-induced changes in polymer crystals at the molecular level are X-ray diffraction and Raman spectroscopy. These methods were used to obtain the data on variations in the magnitude and signs of deformation response of polymer crystals to force and temperature influences [1–4], but without sufficient detailing and quantitative information on measured changes. The objective of the present study is the further develop-

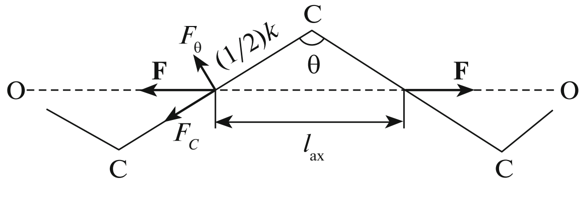

Fig. 1. Schematic representation of the carbon skeleton of the chain polymer molecule, shaped as the plane zigzag. The stretching force F is applied along the O–O molecule axis.

ment of the analysis of experimental results obtained by X-ray diffraction and Raman spectroscopy methods to detail deformation-induced structural changes in polymer crystals during mechanical and thermal influences.

2. OBJECTS OF INVESTIGATION

The main object of study was the simplest crystallizing polymer, i.e., polyethylene (PE). Its long molecules have the form $-CH_2-CH_2-CH_2-$, and the carbon skeleton of straightened PE molecule is a plane zigzag shown in Fig. 1. PE samples were oriented plates and fibers consisting of crystallites with sizes from ~20 to ~100 nm, in which axes of straightened molecules are directed along the single axis, i.e., the axes of the entire sample orientation. In addition to PE, other oriented samples of crystallizing polymers, i.e., flexible-chain (polycaproamide, polypropylene) and rigid-chain (Kevlar-49, polyamide benzimidazole), were studied.

3. METHODS OF INVESTIGATION

3.1. X-ray Diffraction

This method was used to measure angular displacements of meridional, i.e., axial chain molecules in crystals, reflections through variations in tensile loading along the sample orientation axis to stresses of 2–3 GPa and in temperature from 90 to 350 K. Measurements were performed with DRON-1 and DRON-3 setups using filtered CuK_α radiation with wavelength $\lambda = 0.154$ nm. The measurement technique is described in more detail in [5].

3.2. Raman Spectroscopy

This method was used to measure frequency shifts of spectral bands through variations in tensile loading to stresses of 1.5–2.0 GPa and in temperature from 90 to 350 K. The spectra were recorded with a Ramalog 5 Raman spectrometer. The measurement technique is described in more detail in [6].

4. EXPERIMENTAL RESULTS

The choice of temperature conditions of PE studies was based on the PE thermal dynamics characteristics. The PE crystal melting temperature is ~410 K. Therefore, the upper temperature of experiments with PE was $T = 350$ K to which the PE crystalline state was retained.

The PE lattice dynamics in the range from 0 to $T \approx 400$ K is controlled by three types of skeletal vibrations of molecules. The frequency of the first type is $\nu \approx 3.3 \times 10^{13}$ Hz; these are stretching vibrations of carbon–carbon bonds, during which atoms are displaced along the molecule axis. Furthermore, there are bending and torsional vibrations with frequencies $\nu \approx 1.56 \times 10^{13}$ and $\approx 0.72 \times 10^{13}$ Hz at which atoms are displaced across the molecule axis; therefore, in what follows, we refer them to as transverse vibrations [7]. Characteristic temperatures of skeletal vibrations $T_{ch} = h\nu/k$ (h and k are the Planck and Boltzmann constants) are ~1650, ~750, and ~340 K, respectively. Thermal excitation of vibrations becomes appreciable at $T \approx T_{ch}/3$ [8], i.e., at ~550, ~250, and ~ 110 K, respectively. Hence, thermal dynamics of PE molecules is almost absent below 90–100 K (only “zero-point vibrations” take place). We note that transverse vibrations of molecules are sequentially excited as the PE temperature increases to 350 K: first, torsional and then bending vibrations appears. Stretching vibrations remain unexcited.

In the experiments described, PE samples were mechanically loaded at $T = 90$ K and heated in the range from 90 to 350 K.

Thus, deformation-induced changes in PE crystals could be compared proceeding from the same state of unloaded samples (at 90 K) but at different influence types, i.e., loading and heating.

4.1. Effect of Elastic Tensile Loading

The tensile force P was applied along the sample orientation axis and caused the stress $\sigma = P/S$, where S is the sample cross section area. It is known that the stresses S_M on the sample cross section and on the polymer molecule cross section SM in crystals are almost identical in sufficiently highly oriented polymer samples [9]. Therefore, the force stretching the molecule in the crystal (Fig. 1) is

$$F = \sigma S_M = P\frac{S_M}{S}.$$

4.1.1. X-ray diffraction. For PE samples, the change in the angular position φ_m of the meridional 002 reflection under load was measured. According to the Bragg equation, the angle φ_m corresponds to the distance between skeletal carbon atoms along the chain molecule axis in the PE lattice, i.e., to the axial length of the C–C bond: $l_{ax} = \lambda(2\sin(\varphi_m/2))^{-1} = 0.127$ nm at $T = 90$ K. Under tensile loading, the reflection shift to the smaller angle ($\Delta\varphi < 0$) [10] was measured, which meant the increase in the axial length of the C–C bond

$$\Delta l_{ax} = -(1/2)l_{ax}\cot(\varphi_m/2)\Delta\varphi_m$$

or, in relative measurements,

$$\varepsilon_{ax} = \Delta l_{ax}/l_{ax} = -0.65\Delta\varphi_m.$$

Based on the measured dependence of the reflection shift on the applied stress $\Delta\varphi_m(\sigma)$, we find the dependence of Δl_{ax} and ε_{ax} on σ and $F = \sigma S_M$, shown in Fig. 2.

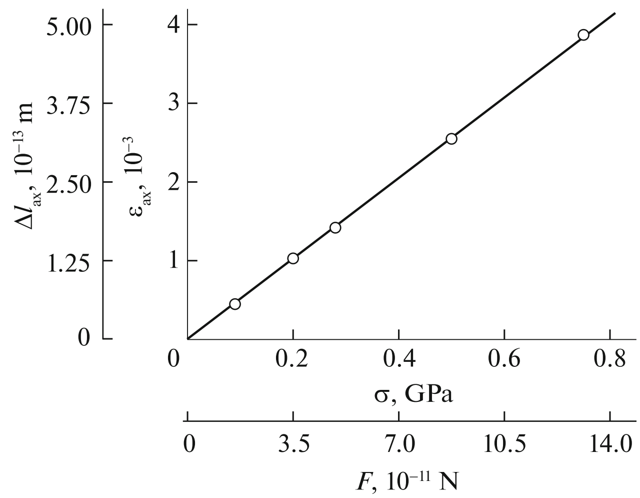

Fig. 2. Dependence of the increase in the axial length of the skeletal C–C bond in the PE molecule on the longitudinal tensile load of the PE crystal.

The proportionality of the axial stretching of PE chain molecules to the applied longitudinal load follows from Fig. 2. From this, we determine Young's modulus of the longitudinal elasticity of the crystal, $E_{\|} = \sigma/\varepsilon_{ax} = 19.3$ GPa, and the force constant of axial stretching of the C–C bond, $f_{ax} = F/\Delta l_{ax} = 280$ N/m (we note that the relation between $E_{\|}$ and f_{ax} is written as $f_{ax} = E_{\|}S_M/l_{ax}$).

The found values of $E_{\|}$ and f_{ax} are close to the same PE characteristics obtained in experimental studies [1, 9].

4.1.2. Raman spectroscopy. In the same PE samples under loading, we measured the change in the frequency of the band in the Raman spectrum, which at $T = 90$ K has the frequency $\nu = 1130\ \mathrm{cm}^{-1} \approx 3.4 \times 10^{13}$ Hz at $T = 90$ K. This band corresponds to stretching vibrations of the carbon skeleton of the PE molecule. In this case, the change in the frequency of these vibrations is defined only by the change in the C–C bond length without the effect of changes in the bond angle [11].

The measured dependence of the relative change in the frequency $\varepsilon_\nu = \Delta\nu(\sigma)/\nu(\sigma = 0) = (\nu(\sigma) - \nu(\sigma = 0))/\nu(\sigma = 0)$ on the tensile stress σ is shown in Fig. 3.

The decrease in the vibration frequency of PE molecule skeleton units during elastic tension is caused by the vibration anharmonicity due to the nonlinearity of interatomic interaction forces (see below). It is important to emphasize that exactly the frequency decrease indicates C–C bond lengthening, hence, contour stretching of PE molecule axes. The quantitative determination of this contour stretching is a subject of further analysis.

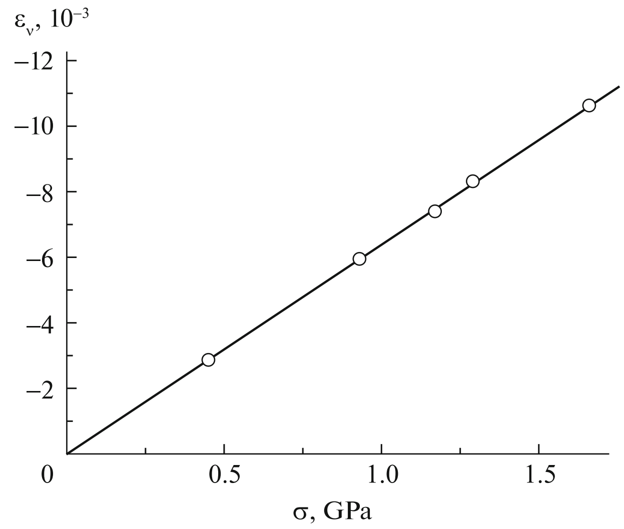

Fig. 3. Dependence of the decrease in the stretching vibration frequency of the PE molecule on the longitudinal tensile load of the PE crystal.

Thus, both axial and contour lengths of the PE molecule in crystals increase during longitudinal elastic tension.

4.2. Effect of Temperature Change (Increase)

The same PE samples in the free (unloaded) state were heated at temperatures from 90 to 350 K. The temperature was increased in steps with holding at each temperature for some time sufficient to reach thermal equilibrium and to perform X-ray and Raman measurements.

4.2.1. X-ray diffractometry. The angular position of the 002 reflection was measured upon PE heating, from which the temperature dependence of the reflection shift $\Delta\varphi_m(T)$ was determined. In contrast to the reflection shift toward decreasing the diffraction angle φ_m during longitudinal tensile loading of PE samples, the reflection shift during heating of the same samples was oppositely directed, i.e., toward increasing the angle φ_m, i.e., $\Delta\varphi_m > 0$ [10].

This meant that the axial length of the C–C bond decreases (!) with increasing temperature. Based on the dependence $\Delta\varphi_m(T)$, we find the temperature dependence $\varepsilon_{ax} = \Delta l_{ax}/l_{ax}$ shown in Fig. 4. We can see well-known shortening of the polymer crystal length upon heating, referred to as a negative thermal expansion [12]. The cause of such an anomaly in comparison with thermal expansion of most low-molecular solids with positive thermal expansion coefficients is the dominance of transverse thermal vibrations in the polymer crystal lattice [13]. This effect will play a crucial role in further analysis.

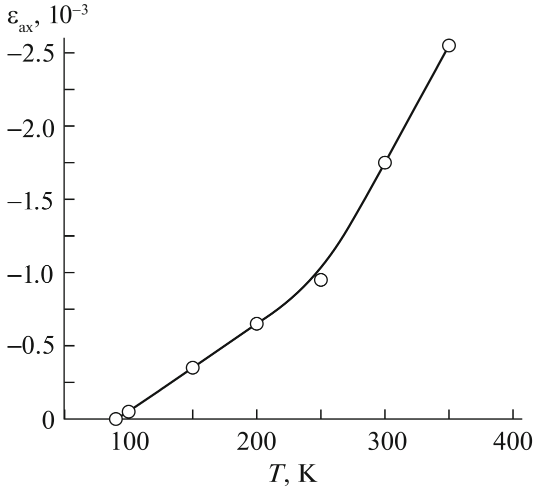

Fig. 4. Decrease in the axial length of the skeletal C–C bond in the PE molecule during heating of the PE crystal.

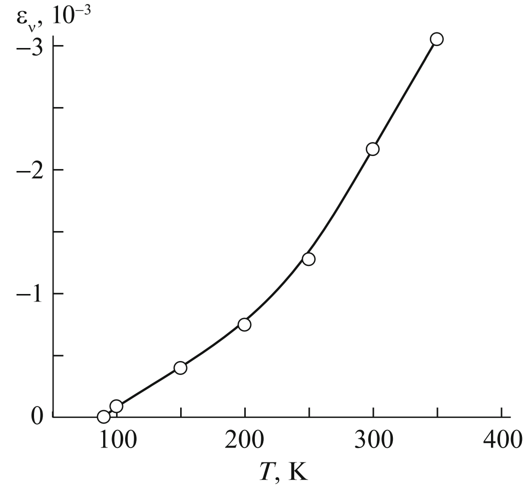

Fig. 5. Decrease in the skeletal vibration frequency of PE molecules during heating of the PE crystal.

4.2.2. Raman spectroscopy. The change in the frequency of the $\Delta\nu$ maximum of the band at 1130 cm^{-1} ($\sim 3.4 \times 10^{13}$ Hz) in the Raman spectrum was measured as the temperature was increased from 90 to 350 K, and the temperature dependence of the relative change $\varepsilon_\nu = \Delta\nu/\nu$ shown in Fig. 5 was determined. We can see that the change in the vibration frequency of the PE molecule with increasing temperature has the same sign as during tensile loading (Fig. 3). This suggests that the C–C bond contour length increases as during PE loading.

Thus, opposite signs of changes in axial and contour lengths of C–C bonds are observed during heating of the PE crystal in contrast to the same sign of changes in axial and contour lengths of C–C bonds under longitudinal tensile loading of PE crystals.

In the study of the effect of tensile loading and heating on other polymeric objects, the experimental results were similar to those obtained for PE crystals.

We can see from the presented experimental results that quite definite quantitative data on changes in the C–C bond axial length in the skeleton of chain PE molecules were obtained under both the longitudinal tensile stress and heating of PE crystals.

For the behavior of the contour length Δl_C, the data on the increase in this length during both influence types were obtained, but without quantitative determination of Δl_C or $\varepsilon_C = \Delta l_C/l_C$.

The determination of the change in the intrinsic length (i.e., the contour length) of C–C bonds and, hence, the entire contour length of the PE molecule in the crystal is a subject of further analysis.

5. ANALYSIS OF EXPERIMENTAL RESULTS

5.1. Longitudinal Tensile Loading of the PE Molecule

In this case, the main role is played by the initial zigzag shape of the carbon skeleton of the PE molecule. The schematic representation of the plane zigzag, i.e., the straightened region of the PE molecule with the molecule axis (O–O line), is shown in Fig. 1. The intrinsic (contour) length of the C–C bond is denoted by l_C; the axial length of the C–C bond is $l_{ax} = l_C \sin\theta/2$.

Then the change in the axial bond length (l_C projection on the O–O axis in Fig. 1) is given by

$$\Delta l_{ax} = \Delta l_C \sin\frac{\theta}{2} + \left[l_C \Delta\left(\frac{\theta}{2}\right)\right]\cos\frac{\theta}{2}.$$

The situation when the change in the axial length of the C–C bond was caused by the tensile force F along the polymer molecule axis (Fig. 1) was analyzed in [14]. In the analysis, the effective force F was expanded in two components (Fig. 1). The first one ($F_C = F\sin\theta/2$) directed along the C–C bond (zigzag side) causes bond stretching. The second one ($F_\theta = F\cos\theta/2$) orthogonal to the C–C bond causes a torque at the $l_C/2$ shoulder, which leads to a change (increase) in the bond angle θ.

The dependence of the axial stretching of the C–C bond on the force, including the force dependences of axial stretching components due to C–C bond lengthening and bond angle widening, was obtained in the form

$$\Delta l_{ax}(F) = F\frac{\sin^2\theta/2}{f_C} + F\frac{l_C^2\cos^2\theta/2}{4f_\theta}, \qquad (1)$$

where f_C is the force constant of the C–C bond stretching and f_θ is the force constant of bond angle widening. We recall that the value of $\Delta l_{ax}(F)$ is measured by X-ray diffraction. According to Eq. (1), the fraction of this value, caused by C–C bond stretching, is written as

$$\frac{F(\sin^2\theta/2)/f_C}{\Delta l_{ax}} = \frac{1}{1+l_C^2(f_C/4f_\theta)\cot^2\theta/2}. \qquad (2)$$

Since the C–C bond lengthening $\Delta l_C = F_C/f_C = (F\sin\theta/2)/f_C$, it follows from Eq. (2) that elastic lengthening of the C–C bond under the axial force F is given by

$$\Delta l_C(F) = \Delta l_{ex}(F)\left[\sin\frac{\theta}{2}\left(1+l_C^2\frac{f_C}{4f_\theta}\cot^2\theta/2\right)\right]^{-1}. \qquad (3)$$

We can see that expression (3), in addition to the well determined values $l_C = 1.53 \times 10^{-10}$ m and $\theta = 109°28'$, includes the force constants f_C and f_θ whose ratio does play the crucial role in determining the C–C bond stretching.

For C–C bonds in the PE molecule, the values of f_C and f_θ are given in [15]: $f_C = 440$ N/m and $f_\theta = 8.2 \times 10^{-19}$ N m. Based on these values, let us calculate the force constant of the PE molecule stretching $f_{ax} = F/\Delta l_{ax}(F)$ and compare the obtained value with the experimental value $f_{ax} \approx 2.8 \times 10^2$ N/m determined by the measured dependence of Δl_{ax} on F (Fig. 2).

It follows from Eq. (1) that $f_{ax} = [(\sin^2\theta/2)/f_C + (l_C^2\cos^2\theta/2)/4f_\theta]^{-1}$ at the found values of f_C and f_θ this leads to the value $f_{ax} \approx 2.6 \times 10^2$ N/m. We can see that the calculated and experimental values of f_{ax} are close enough (the difference is a few percent). This indicates the validity of the values of f_C and f_θ and, hence, the validity of the values of elastic lengthening of C–C bonds determined by the measured axial lengthening of the PE molecule at given values of the longitudinal tensile loading stress.

From Eq. (3), using the values of l_C, θ, f_C, and f_θ, we find the simple relation between changes in the contour $\Delta l_C(F)$ and axial $\Delta l_{ax}(F)$ lengths of the C–C bond

$$\Delta l_C(F) \approx 0.48\Delta l_{ax}(F). \qquad (4)$$

For relative values, we obtain

$$\begin{aligned}\varepsilon_C(F) &= \frac{\Delta l_C}{l_C} = 0.48\frac{\Delta l_{ax}}{l_C} = 0.48\frac{\Delta l_{ax}}{l_{ax}}\frac{l_{ax}}{l_C} \\ &= 0.48\varepsilon_{ax}\sin\frac{\theta}{2} \approx 0.4\varepsilon_{ax}(F).\end{aligned} \qquad (5)$$

Thus, proceeding from the results of X-ray diffraction measurements and determined values of the axial stretching of the PE molecule, we find the intrinsic stretching of skeletal C–C bonds.

We now turn to spectroscopic (Raman) measurements of the change in the frequency of skeletal vibrations of molecules during tensile loading of PE crystals. The physical cause of the change in the atomic vibration frequency during loading of solids is the nonlinearity of interatomic interaction forces, leading to vibration anharmonicity [16].

The simplest approximate description of this nonlinearity is the dependence of the elastic force F_{el} on the bond lengthening Δl_C in the form of the quadratic binomial at small Δl_C ($\Delta l_C/l_C \ll 1$),

$$F_{el} \approx f_C\Delta l_C - g(\Delta l_C)^2,$$

where f_C is the linear elasticity coefficient of the C–C bond and g is the first-order anharmonicity coefficient. We note that at small Δl_C, the coefficient f_C is approximately the force constant of the elastic stretching of the C–C bond.

Then the dependence of the elasticity $f_{\Delta l_C}$ on the bond stretching has the form

$$f_{\Delta l_C} = \frac{dF_{el}}{d(\Delta l_C)} \approx f_C - 2g\Delta l_C \approx f_C\left(1-\frac{2g}{f_C}\Delta l_C\right).$$

The frequency of stretching (along the C–C bond) vibrations of the CH_2 unit in PE molecules at small Δl_C is given by

$$\begin{aligned}\nu_{\Delta l_C} &= \frac{1}{2\pi}\sqrt{\frac{f_{\Delta l_C}}{m^*_{CH_2}}} \approx \frac{1}{2\pi}\sqrt{\frac{f_C}{m^*_{CH_2}}\left(1-\frac{2g}{f_C}\Delta l_C\right)} \\ &\approx \nu(\Delta l_C = 0)\left(1-\frac{g}{f_C}\Delta l_C\right),\end{aligned}$$

where $m^*_{CH_2}$ is the reduced mass of the CH_2 unit, $\nu(\Delta l_C = 0) = \nu_0$ is the vibration frequency of the undeformed bond.

From this, we have

$$\varepsilon_\nu = \frac{\Delta\nu}{\nu} = \frac{\nu_{\Delta l_C} - \nu_0}{\nu_0} \approx -\frac{g}{f_C}\Delta l_C \approx -\frac{g}{f_C}l_C\varepsilon_C, \qquad (6)$$

where $\varepsilon_C = \frac{\Delta l_C}{l_C}$ is the relative stretching of the C–C bond.

Let us approximately estimate the value of $\frac{g}{f_C}l_C$.

In describing the C–C bond potential by the Morse formula [17], the expression for the binding energy is written as [18]

$$D_C \approx \frac{9}{8}\frac{f_C^3}{g^2}.$$

For PE, $D_C \approx 3.6$ eV $\approx 5.8 \times 10^{-19}$ J [19]. Then, at known $f_C = 440$ N/m and $l_C = 1.53 \times 10^{-10}$ m, we obtain $\frac{g}{f_C}l_C \approx 4.5$. From this, according to Eq. (6), it follows that

$$\varepsilon_\nu \approx -4.5\varepsilon_C. \qquad (7)$$

Thus, we can see that the C–C bond vibration frequency decreases with increasing C–C bond length ($\varepsilon_C > 0$).

Hence, if a decrease in the vibration frequency is measured, this does mean C–C bond stretching (which was indicated above) and, according to Eq. (7), the approximate estimate of the stretching is given by

$$\varepsilon_C \approx -0.23\varepsilon_\nu. \tag{8}$$

We now should ascertain the degree of agreement of calculated (by Eq. (8)) and experimental (determined from the measured dependence $\varepsilon_\nu(\sigma)$) C–C bond lengthening.

Let us consider the experimental data on the change in the vibration frequency during tensile loading of PE (Fig. 3).

The expression $\varepsilon_\nu(\sigma) = -6.7 \times 10^{-3}\sigma$ (σ is given in GPa) follows from the proportional dependence $\varepsilon_\nu(\sigma) = \Delta\nu(\sigma)/\nu(\sigma = 0)$ on σ.

The expression $\varepsilon_{ax} = 5.1 \times 10^{-3}\sigma$ (σ is given in GPa) follows from the proportional dependence of the axial stretching of the C–C bond ε_{ax} on σ (Fig. 2).

Comparing the dependences $\varepsilon_\nu(\sigma)$ and $\varepsilon_{ax}(\sigma)$, we find the relation between ε_ν and ε_{ax}: $\varepsilon_\nu = -1.3\,\varepsilon_{ax}$.

Using the relation between axial and contour lengthening of the C–C bond (5), we obtain $\varepsilon_{ax} = 2.5\varepsilon_C$.

Then we obtain the direct dependence of the change in the PE skeletal vibration frequency on the C–C bond stretching

$$\varepsilon_\nu \approx -3.3\varepsilon_C. \tag{9}$$

We can see that the experimental dependence of the frequency change on the bond stretching $\varepsilon_\nu(\varepsilon_C)$ is quantitatively in a reasonable closeness (taking into account all approximations and admissions) with the estimated calculated value (7).

This circumstance increases confidence to the values of PE skeletal C–C bond stretching obtained from measured changes in the skeletal vibration frequency using the relation

$$\varepsilon_C \approx -0.3\varepsilon_\nu, \tag{10}$$

following from Eq. (9).

5.2. Heating of the PE Crystal

The feature of the polymer crystal response to heating is as follows: the negative longitudinal thermal expansion (i.e., compression) is caused by the dominant role of transverse skeletal vibrations (displacement of skeletal atoms orthogonally to the polymer molecule axis [13]). The active effect of transverse vibrations is indicated by the positive in sign and large in magnitude coefficient of transverse thermal expansion of the polymer crystal for PE in the region of $T = 300$ K: $\alpha \approx +2.0 \times 10^{-4}$ K^{-1} [20].

Certainly, the effect of thermal dynamics on polymer molecules in the crystal is complex and differs from the effect of concentrated constant forces. Therefore, to analyze the changes in molecules upon heating, we choose a simplified model similar to the model (considered in Subsection 5.1) of the action of the longitudinal stretching force, but with a significant difference in modeling of the shape of the chain molecule itself.

Transverse vibrations of straightened chain molecules are characterized by the fact that skeletal atom displacements during vibrations are orthogonal to the polymer molecule axis. Then, it seems possible to model the thermal generation of transverse vibrations by "impacts" of forces on skeletal atoms, directed orthogonally to the molecule axis. In this case, due to thermal dynamics randomness, impacts can occur from any azimuthal direction (both in the zigzag plane and orthogonally to this plane and at other arbitrary angles). Certainly, the responses of changes in the molecule shape to different transverse impacts will be different. Therefore, we turn to averaging and we will represent the ensemble of real skeletal zigzag molecules in the crystal by parallel straight atomic chains without initial zigzag shape of the skeleton, similarly to the model of [21]. In such a model, transverse impacts on skeletal atoms lead to the appearance of a specific zigzag distortion of the axial line of the molecule, rather than the contour line (Fig. 6). Then, the impact force can be expanded in components (similarly to the expansion when considering the stretching force in Subsection 5.1). Figure 6 shows the expansion of the transverse impact force $F_\perp$ in the same components: $F_\perp^C$ is the component along the zigzag side (cause an increase in the axial length of skeletal interatomic bonds), $F_\perp^\theta$ is that orthogonal to the first component (creates the torque at the shoulder (axial length of the C–C bond), which results in a change in the bond angle θ). In this case, this angle is initially $\theta = \pi$, and decreases in response to impacts. This results in the tilt angle of zigzag sides to the molecule axis: $\beta = (\pi - \theta)/2$ (Fig. 6).

Let us estimate the angle β. As noted above, the entire thermal energy is in fact the transverse vibration

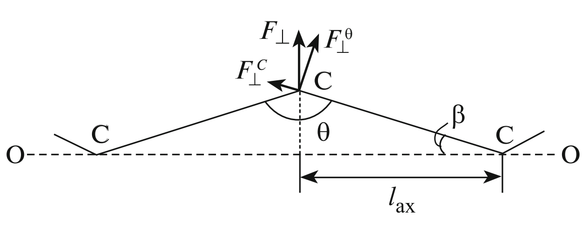

Fig. 6. Schematic diagram of imparting the zigzag shape to the O–O molecule axis due to impacts (transverse to the axis) of the force $F_\perp$ caused by thermal dynamics in the PE crystal.

energy in PE to $T = 350$ K. The average thermal energy of the vibrating CH_2 group at 350 K is $Q = 8.1 \times 10^{-21}$ J [13]. Based on the above transverse vibration frequencies of 0.72×10^{13} and 1.56×10^{13} Hz, the average frequency can be taken as $\nu_\perp \approx 1.2 \times 10^{13}$ Hz.

The force constant for such vibrations is $f_\perp = 4\pi^2\nu_\perp^2 m^*_{CH_2} \approx 60$ N/m ($m^*_{CH_2}$ is the reduced mass of the CH_2 group). Then the transverse vibration amplitude is $\delta_\perp \approx (2Q/f_\perp)^{1/2} \approx 10^{-11}$ m. According to the data of Fig. 6, the angle $\beta \approx \delta_\perp/l_{ax}$; at $T = 350$ K, $\beta \lesssim 10^{-1}$. Thus, changes in the angle β (at $T = 90$ K, $\beta \approx 0$), hence, in the angle θ are small to the temperature $T = 350$ K.

The expansion of the "thermal impact force" $F_\perp$ (Fig. 2), taking into account the smallness of the tilt angle β, allows the following approximate conclusions.

(i) The axial tension force of the C–C bond is $F_\perp^C = F_\perp \sin\beta \approx F_\perp\beta$.

(ii) The axial stretching of the C–C bond is $\delta l_{ax} \approx F_\perp\beta/f_{ax}$, where the force constant of axial stretching of the C–C bond is $f_{ax} = 2.8 \times 10^2$ N/m (according to Fig. 2).

(iii) The projection of the axial stretching extension of the C–C bond on the primary molecule axis is

$$\Delta l_{ax} = \delta l_{ax}\cos\beta \approx \delta l_{ax}\left(1 - \frac{1}{2}\beta^2\right) \approx \delta l_{ax} \approx \frac{F_\perp\beta}{f_{ax}}.$$

We note that exactly Δl_{ax} is the component of the change in the axial length of the PE molecule with varying temperature, measured by X-ray diffraction.

(iv) The force creating the torque at the Δl_{ax} shoulder leads to the change in the bond angle θ: $F_\theta = F_\perp\cos\beta \approx F_\perp(1 - \beta^2/2) \simeq F_\perp$. Then the torque $M \cong -F_\theta l_{ax} \approx -F_\perp l_{ax}$. The change in the bond angle θ, caused by the torque M, is $\delta\theta = M/f_\theta$, where f_θ is the force constant of the angle change.

In the used model, the bond angle θ is related to the molecule axis tilt β as $\theta = \pi - 2\beta$. From this, it follows that $\delta\theta = -2\beta$.

Then, for the angle β, we obtain

$$\beta = -\delta\theta/2 = -M/2f_\theta \approx F_\perp l_{ax}/2f_\theta.$$

(v) The displacement of the edge of the axial C–C bond, resulting from its rotation by the angle β is $\delta l_\theta \approx l_{ax}\beta = F_\perp l_{ax}^2/(2f_\theta)$.

(vi) The projection of this displacement on the molecule axis is

$$\Delta l_\theta = -\delta l_\theta \sin\beta \approx -\delta l_\theta\beta \approx -F_\perp\beta\frac{l_{ax}^2}{2f_\theta}.$$

We note that Δl_θ is the second component of the measured change in the axial length of the PE molecule.

Thus, the total change in the projection of the axial length of the PE molecule on the molecule axis, measured with changing temperature, has the form

$$\begin{aligned}\Delta l_\Sigma(T) &= \Delta l_{ax}(T) + \Delta l_\theta(T) \\ &= (F_\perp\beta)(T)\left[\frac{1}{f_{ax}} - \frac{l_{ax}^2}{2f_\theta}\right].\end{aligned} \tag{11}$$

Then the temperature-induced axial stretching of the C–C bond relative to the entire axial displacement $\Delta l_\Sigma(T)$ measured by the X-ray method is written as

$$\Delta l_{ax}(T) = \Delta l_\Sigma(T)\left(1 - \frac{l_{ax}^2}{2}\frac{f_{ax}}{f_\theta}\right)^{-1}. \tag{12}$$

In the used model, thermal transverse impacts give rise to the stretching force $F_\perp^C$ directed along the molecule axis and causing axial stretching of C–C bonds. This force is similar to the stretching force along the molecule axis, caused by external loading, which was considered in Subsection 5.1.

In the case at hand, due to the small tilt angle β, the axial stretching of the C–C bond and its projection on the primary molecule axis are almost identical and equal to Δl_{ax}. Therefore, the quantity $\Delta l_{ax}(T)$ appearing in Eq. (12) can be considered as the axial stretching of the C–C bond under the action of the longitudinal (along the molecule axis) force $F_\perp^C$.

Then, using the relation between the contour length stretching Δl_C of the C–C bond and the increase in its axial length Δl_{ax} (see Eq. (4)), given in Subsection 5.1, we can find the stretching of C–C bonds themselves in the PE molecule skeleton, caused by heating of the PE crystal,

$$\Delta l_C(T) = 0.48\Delta l_{ax}(T) = 0.48\Delta l_\Sigma(T)\left(1 - \frac{l_{ax}^2}{2}\frac{f_{ax}}{f_\theta}\right)^{-1}. \tag{13}$$

As follows from Eq. (13), the determination of $\Delta l_C(T)$ decisively depends on the force constants f_C and f_θ, as well as in the corresponding formula (3) in Subsection 5.1 for the case of the action of the applied longitudinal stretching force.

However, we can also see differences in formulas (3) and (13), caused by the different nature of the force action on PE crystal molecules: l_{ax} and f_{ax} enter formula (13) instead of l_C and f_C, i.e., the transition from certain known quantities (l_C and f_C) to the other known quantities (l_{ax} and f_{ax}) takes place.

However, the situation is more complex for one of characteristics, i.e., the force constant f_θ of the change in the bond angle.

In Subsection 5.1, we used the value of f_θ determined exactly for the change (increase) in the already found bond angle (~2 rad) by a comparatively small value $\Delta\theta \approx 10^{-2}$ rad.

However, the effect of the temperature change on the polymer molecule is described in the model using the initial bond angle of π rad which then changes (decreases (!)) by the same small value (~10^{-2} rad). At the same time, there are no published data on force constants for a similar case. Therefore, taking into account a certain closeness of characteristics in both cases (large bond angles: 110° and 180° and small comparable changes in these angles), we assumed the retention of the same force constant $f_\theta = 8.2 \times 10^{-19}$ N m as in [15] for the thermal case as well.

Then, using the values of l_{ax}, f_{ax}, and f_θ from formula (13), we obtain simple relation between Δl_C and Δl_Σ

$$\Delta l_C(T) = -0.28\Delta l_\Sigma(T).$$

For relative values, we obtain

$$\varepsilon_C(T) = \frac{\Delta l_C}{l_C} = -0.28\frac{\Delta l_\Sigma}{l_C} = -0.28\frac{\Delta l_\Sigma}{l_\Sigma}\frac{l_\Sigma}{l_C} = -0.23\varepsilon_\Sigma, \qquad (14)$$

where $\varepsilon_\Sigma = \Delta l_\Sigma / l_\Sigma$.

Thus, from the change ε_Σ in the axial length of the skeletal C–C bond, measured by X-ray diffraction, using relation (14), we can find the change ε_C in the length of the C–C bond during heating of the PE crystal. And the measured change in the vibration frequency ε_ν of skeletal atoms bound by the same bond and the relation determined in Subsection 5.1 for the change in the vibration frequency with variations in the C–C bond length (10) , can be used to find the change in the C–C bond length ε_C during heating of the PE crystal and to ascertain the degree of agreement between quantitative values of ε_C obtained by different methods, i.e., X-ray diffraction and Raman spectroscopy.

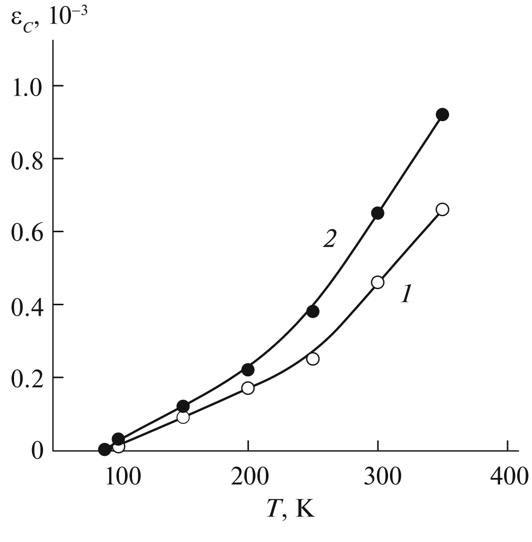

Fig. 7. Comparison of the temperature dependences of the contour C–C bond lengthening in the chain molecule of the PE crystal, obtained from the data of (*1*) X-ray diffraction and (*2*) Raman spectroscopy.

6. COMPARISON OF THE RESULTS OF THE X-RAY DIFFRACTION AND RAMAN STUDIES

The temperature dependence of the axial shortening of the C–C bond in the PE crystal $\varepsilon_\Sigma(T)$, obtained by X-ray diffraction, is shown in Fig. 4. Using relation (14), from the dependence $\varepsilon_\Sigma(T)$, we find the temperature lengthening of the C–C bond: $\varepsilon_C(T) = -0.23\varepsilon_\Sigma$ shown in Fig. 7 (curve *1*).

The temperature dependence of the frequency of skeletal stretching vibrations $\varepsilon_\nu(T)$ in the PE crystal, obtained by Raman spectroscopy, is shown in Fig. 5. Using relation (10), from the dependence $\varepsilon_\nu(T)$, we find the thermal lengthening of the C–C bond $\varepsilon_C(T) \approx -0.3\varepsilon_\nu(T)$ shown in Fig. 7 (curve *2*).

We can see the closeness of dependences *1* and *2* in Fig. 7. The degree of this closeness is satisfactorily explained by the set of admissions and approximations in deriving expressions (10) and (14).

7. CONCLUSIONS

An interesting situation where the influence (mechanical loading or heating) on the polymer crystal results in the application of two forces: one along the axis of interatomic skeletal bonds (which causes a change in their lengths) and the other orthogonal to this axis (which causes a change in the bond angle between skeletal bonds, i.e., the bond tilt angle to the axis of the straightened chain molecule), to the same structural element of the straightened chain molecule (CH_2 group for polyethylene) was considered and explained.

In the case where the mechanical tensile force is applied along the axis of straightened chain molecules in the polymeric crystal at low temperature, the force expansion in orthogonal components, caused by the initial zigzag shape of the chain molecule skeleton, i.e., the zigzag shape of the molecule contour length, was considered.

In the case of polymer crystal heating, the main role is played by excitation of thermal transverse vibrations in chain molecules, which cause effective forces acting as impacts transverse to chain molecule axes. These forces generate a similitude of the zigzag shape of the axial (rather than contour) length of molecules, which results in the expansion of effective forces in orthogonal components in this case as well.

As a result of the analysis of experimental (X-ray and Raman) data in the case of polyethylene, the values of the stretching of skeletal C–C bonds and changes in bond angles (an increase during stretching and a decrease during heating), resulting in opposite-sign changes in the axial length of molecules, are determined for both influence types (tension and heating).

Thus, quantitative detailing of deformation processes during mechanical and temperature influences on PE crystals was implemented for the first time.

The experimental results (X-ray and Raman) for other studied polymers were similar to those for polyethylene. It is complicated to obtain quantitative data about details of deformation processes for these polymers due to the absence of experimental values of such characteristics as force constants of changes in the length and bond angles in molecule skeletons.

However, it can be considered that the similarity of experimental data on changes in the axial molecule length in X-ray studies and changes in the stretching vibration frequency in Raman studies during mechanical and thermal influences suggests that mechanisms of deformation of lattice elements in these polymers are the same as the mechanisms identified for polyethylene.

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