

# PECULIARITIES OF THE THERMAL MOTION IN CRYSTALS FORMED BY CETYLTRIMETHYLAMMONIUM BROMIDE MOLECULES

O.M. ALEKSEEV,<sup>1</sup> M.M. LAZARENKO,<sup>1</sup> G.O. PUCHKOV'S'KA,<sup>2</sup>  
T.V. BEZRODNAYA,<sup>2</sup> A.A. SENDZYUK<sup>1</sup>

<sup>1</sup>Taras Shevchenko National University of Kyiv, Faculty of Physics

(2, Academician Glushkov Ave., Kyiv 03680, Ukraine; e-mail: *maks@univ.kiev.ua*)

<sup>2</sup>Institute of Physics, Nat. Acad. of Sci. of Ukraine

(46, Nauky Ave., Kyiv 03022, Ukraine)

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Phase transformations in CTAB polycrystals are investigated with the use of the thermophysical, dielectric, and spectroscopic techniques. A molecular model of these transformations is proposed. According to this model, the free volume in the intercrystalline layer of CTAB polycrystals starts to grow at 10 °C, and Br<sup>-</sup> ions bound with the -N(CH<sub>3</sub>)<sub>3</sub> terminal groups increase their mobility. At 55 °C, topological solitons of the “one-unit constriction with 180° reorientation” type appear. They arise at terminal methyl groups, pass by the molecules, and are reflected from -N(CH<sub>3</sub>)<sub>3</sub> groups. In this case, CTAB crystals pass to the orthorhombic rotation-crystalline phase. At 92 °C, topological solitons change the orientation of the terminal -N(CH<sub>3</sub>)<sub>3</sub> groups, which results in the melting of nonpolar aliphatic layers.

of phase transformations in molecular crystals. In [6], the differential scanning calorimetry (DSC), gravimetry, X-ray, and optical methods were used to show that, in a vicinity of 103°C, there exists a first-order phase transition in the solid state. It was also established that CTAB crystals consist of polar and nonpolar layers, which was confirmed in [7]. As was supposed in [6], the phase transition close to 103°C is related to the “melting” in nonpolar layers formed by carbon chains. But the mechanisms of molecular motion in CTAB under phase transformations have not been studied. In our previous work [8], we shortly reviewed the available molecular mechanisms of reorientation of molecules with a carbon chain. Recently, new ideas of the mechanism of azimuthal reorientation of such molecules in crystals were developed. This mechanism can be related to the formation and motion of specific conformational defects, topological solitons (TS), which can change the orientation of a molecule, by passing near it [9–12]. In particular, the creation of local topological defects in an infinite chain of polycrystalline polyethylene at an increase in the temperature due to thermal oscillations of the chain was studied in works [13, 14] by the method of molecular dynamics. It is shown that thermal oscillations cause the formation of defects of only a single type (TS) which correspond to a compression (tension) by a half-period of the chain with a simultaneous twisting by 180°. This model considered the infinite chain, whereas a CTAB molecule is linear and has only 16 carbon atoms. It was assumed in [15] that solitons can be excited by a local external action. The probability of the creation of a soliton is maximum, if such an action is realized just at the end of a molecular chain. This assertion is based on the consideration of the topological stability of a soliton. Therefore, it is possible to assume that, in the oligomer systems composed of a carbon

## 1. Introduction

Surface-active substances (SAS) are important components of numerous practically important processes and technologies. Depending on their chemical properties, they can be divided into ionogenic and nonionogenic ones. The former are presented by molecules having either positive charge — cation SASs (quaternary ammonium groups) or negative charge — anion SASs (basic oil soaps). SASs usually represent complex many-component mixtures consisting of SAS homologs and admixtures of primary substances. That is why the analysis of their composition consisting of SASs of different classes is a complicated task. Such an analysis is performed with the use of various physical methods.

One of the representatives of cation SASs is cetyltrimethylammonium bromide (CTAB) [N(CH<sub>3</sub>)<sub>3</sub>(C<sub>16</sub>H<sub>32</sub>)]Br [1–5]. In addition to the high importance of CTAB as a representative of SASs, the study of its phase transformations in the solid state is important for the construction of microscopic models

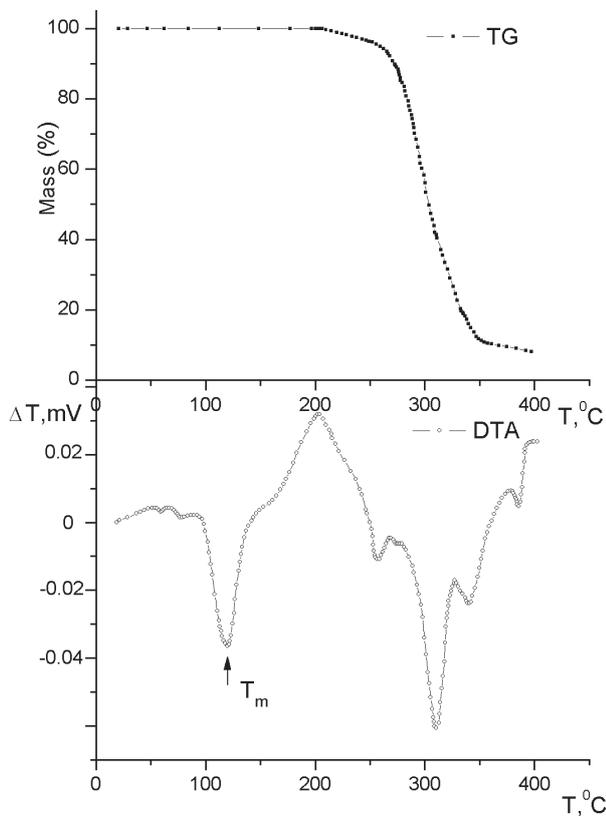


Fig. 1. Temperature dependence of the mass loss (TG) and differential thermal analysis (DTA) of CTAB

chain, the solitons are excited at the terminal methyl group  $-\text{CH}_3$ . As known from the studies of NMR spectra [16], this group in crystals of alkanes can be reoriented and can serve a source of perturbations under the action of thermal oscillations. That is why this work aims at the investigation of the mechanisms of molecular motion in CTAB in a wide temperature range including the regions of phase transitions.

## 2. Experiment

We used a number of experimental techniques for studying the mechanisms of molecular motion in CTAB polycrystals with a purity of 99% (produced by Fluka (Germany)).

### 2.1. Gravimetry and differential-thermal analysis

We used a Q-1500D derivatograph that allowed us to obtain the temperature dependence of the mass loss (TG)

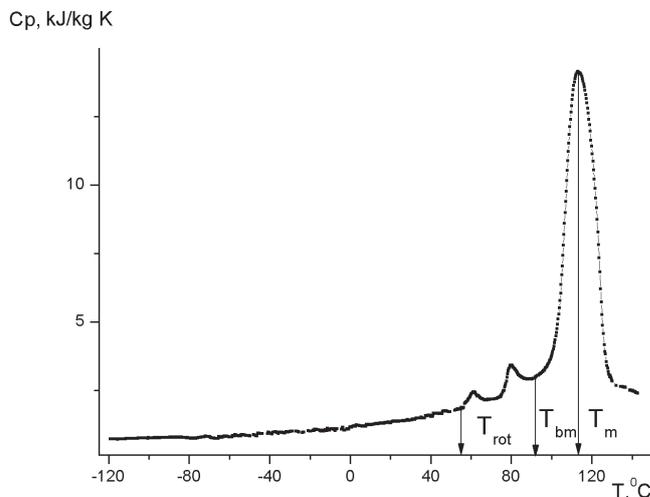


Fig. 2. Temperature dependence of the specific heat capacity of CTAB ( $T_{\text{rot}} = 55$  °C is the phase transition temperature in the solid state,  $T_{\text{bm}} = 92$  °C is the melting temperature of nonpolar aliphatic chains)

and perform the differential-thermal analysis (DTA) for CTAB (Fig. 1).

On the DTA dependence, one observes endothermic peaks at 59, 80, and 113 °C taking place without mass loss (Fig. 1). We think that the former two peaks are related to phase transformations in the solid state, while the third peak corresponds to the melting in nonpolar layers of CTAB crystals ( $T_m = 113$  °C). At the temperature  $T = 204$  °C, the sample starts to lose its mass. This is caused by the evaporation of CTAB molecules or their destruction followed by the evaporation of formed low-molecular compounds. The DTA dependence contains five endothermic peaks at temperatures of 248, 261, 303, 353, and 390 °C accompanied by the mass loss. This fact testifies to the destruction and the evaporation of low-molecular compounds at the heating of CTAB polycrystals to temperatures exceeding 204 °C.

### 2.2. Calorimetry

The phase transformations were investigated with the help of a dynamic calorimeter that registered a change of the heat flow that entered into the sample during the heating [17]. Our measurements yielded the temperature dependence of the specific heat capacity  $C_p(T)$  in the temperature interval ( $-125 \div 140$ ) °C. In this dependence (Fig. 2), one observes the phase transformations in the solid state at 59 °C and 80 °C and the melting of nonpolar aliphatic chains at  $T_m = 113$  °C.

### 2.3. Dielectric Spectroscopy

We used the technique of studying the temperature-frequency dependences of the complex dielectric permittivity  $\varepsilon(T, f)$  of the CTAB sample. The used automated set-up included a P5083 ac bridge coupled with a personal computer. The sample was placed into a four-electrode temperature-controlled measuring cell that allowed us to measure the relative deformation of the sample [18]. These experiments yielded the dependences of the real and imaginary parts of the complex dielectric permittivity in the temperature range  $(-150 \div 130)^\circ\text{C}$  at the frequencies  $f = 5, 10, 20,$  and  $50$  kHz and the temperature dependence of a relative deformation.

The dependences  $\varepsilon'(T)$  contain the shoulders of  $\varepsilon'$  and  $\varepsilon''$  in the temperature range  $(10 \div 55)^\circ\text{C}$ , whose heights fall with increase in the frequency (Fig. 3). At the higher temperatures  $(55 \div 92)^\circ\text{C}$ , there appear other maxima, whose intensities also decrease with increase in the frequency. Above  $92^\circ\text{C}$ , one registers the increase of  $\varepsilon'$  and  $\varepsilon''$  inversely proportional to the frequency.

Works [19–24] dealt with the study of the dielectric relaxation at  $20^\circ\text{C}$  in the frequency range from 1 MHz to 20 GHz for water micellar CTAB systems in the range of concentrations  $C_D = (2 \div 1000)$  mmole/kg. The surface structure of CTAB micelles in a water solution is similar to the structure of its lamellar crystals in the solid state. The authors have demonstrated that such a system has three relaxation modes. The second relaxation mode (whose intensity falls with decrease in  $C_D$ , while the contact area of micelles, respectively, grows) is referred to the migration of electrically coupled  $\text{Br}^-$  ions. The intensity of the first mode depends on the concentration at  $C_D < 100$  mmole/kg; at  $C_D > 100$  mmole/kg, it is independent on the concentration. The authors believe that this mode is related to the rotation relaxation of ion pairs formed between  $\text{CTA}^+$  and  $\text{Br}^-$ . In spherical micelles, it is considerably suppressed in the contact regions of surfaces of two neighboring micelles at  $C_D > 100$  mmole/kg. This fact results in the limitation of the highest relaxation rate at large  $C_D$  and in the appearance of the third relaxation mode, whose intensity grows with  $C_D$ . At  $C_D > 100$  mmole/kg, the water micellar CTAB system becomes a liquid-crystal one, i.e., it passes to the hexagonal liquid-crystal phase, and the third relaxation mode is related to the formation of a polar layer in the contact region of micelles similar to the polar layer in CTAB crystals.

We believe that the similarity of CTAB crystals and water-micellar CTAB systems in the liquid-crystal state results in the similar mechanisms of thermal motion in

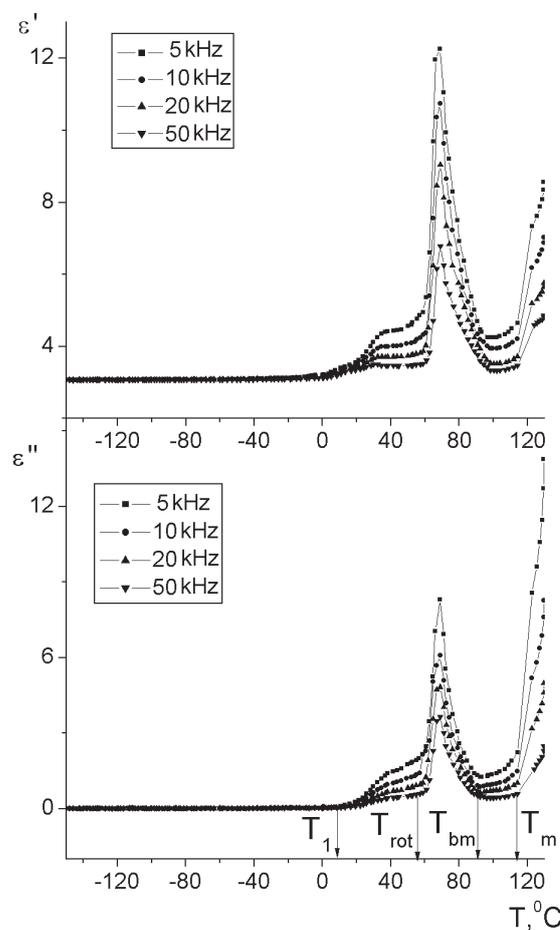


Fig. 3. Temperature dependences of the real and imaginary parts of the dielectric permittivity of CTAB ( $T_1 = 10^\circ\text{C}$ )

the both cases. That is why the peculiarity in the range  $(10 \div 50)^\circ\text{C}$  (Fig. 3) is caused, to our mind, by the motion of  $\text{Br}^-$  ions. The peculiarity in the temperature range  $(55 \div 92)^\circ\text{C}$  (Fig. 3) is associated with the third relaxation mode, whereas that registered above  $T_{\text{bm}} = 92^\circ\text{C}$  (Fig. 3) is related to the rotation relaxation mode of ion pairs formed by  $\text{CTA}^+$  and  $\text{Br}^-$ .

On the temperature dependence of the relative deformation  $\Delta h/h_0$ , one observes a sharp increase in the range  $(-14 \div 10)^\circ\text{C}$  (Fig. 4). After that, in the interval from  $30^\circ\text{C}$  to  $65^\circ\text{C}$ ,  $\Delta h/h_0$  falls in two stages. The anomalous behavior of the relative thickness of the sample in the temperature interval  $(45 \div 65)^\circ\text{C}$  is a macroscopic effect induced by a decrease of the elasticity modulus of the sample and, consequently, its deformation under the action of spring-loaded measuring electrodes of the cell. In the interval  $(65 \div 92)^\circ\text{C}$ , one registers an increase. The fall at  $T_{\text{bm}} > 92^\circ\text{C}$  is caused by the melt-

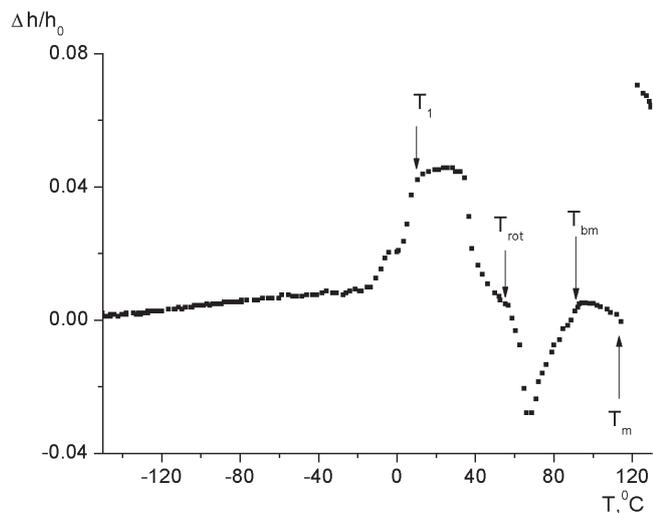


Fig. 4. Temperature dependence of the relative deformation of CTAB

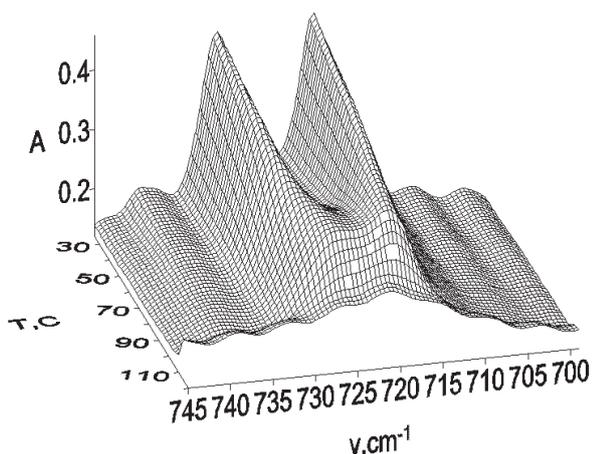


Fig. 5. Intensity of IR-spectra of CTAB as a function of the temperature and the wave number  $\nu$  in a neighborhood of  $\nu = 720 \text{ cm}^{-1}$

ing of nonpolar aliphatic layers, which is seen in the temperature dependence of the specific heat capacity (Fig. 2). A change of the type of subcells of CTAB molecular crystals under phase transformations can be registered by X-ray diffractograms measured at various temperatures, but it is a difficult problem for the polycrystals under study [25].

#### 2.4. IR-spectroscopy

In order to clarify the CTAB structure and the molecular nature of the processes in detail, we obtained the IR-spectra with the help of an IFS-88 Bruker Fourier spectrometer. The structurally sensitive band in the IR

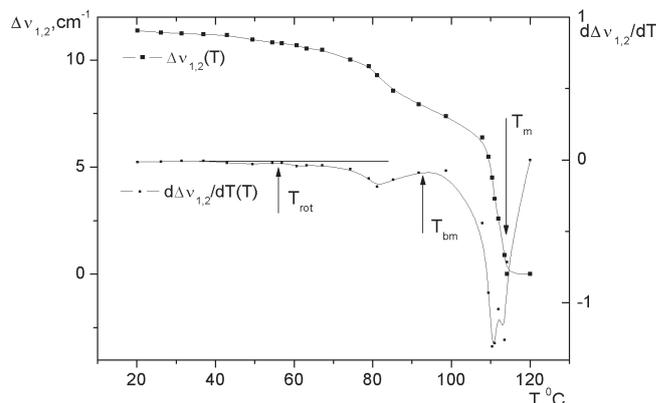


Fig. 6. Temperature dependences of the Davydov splitting  $\Delta\nu_{1,2}(T)$  and the derivative  $d(\Delta\nu_{1,2})/d(T)$  for CTAB

spectrum of such samples is that related to pendular oscillations of  $\text{CH}_2$  groups in aliphatic chains in a neighborhood of  $\nu = 720 \text{ cm}^{-1}$ . Below the melting temperature, one observes the so-called Davydov splitting of this band (inherent only to orthorhombic crystal cells) [26].

Figure 5 shows the intensities of the IR-spectra for CTAB as functions of the temperature and the wave number  $\nu$  in a neighborhood of  $\nu = 720 \text{ cm}^{-1}$ . With increase in the temperature, the registered two peaks approach each other and unite into a single one in a vicinity of the phase transition region. In order to separate these two maxima and to determine the value of  $\Delta\nu_{1,2}$  in the region  $\nu = 720 \text{ cm}^{-1}$ , we approximated the profiles of the peaks with the help of the Voigt distribution according to [26] and determined the temperature dependences of the Davydov splitting  $\Delta\nu_{1,2}(T)$  and the first derivative  $d(\Delta\nu_{1,2})/d(T)$  for CTAB, which are given in Fig. 6.

One can see that  $\Delta\nu_{1,2}(T)$  practically does not vary in the temperature interval from  $20 \text{ }^\circ\text{C}$  to  $55 \text{ }^\circ\text{C}$ . Reaching the beginning of the phase transition ( $T_{\text{rot}} = 55 \text{ }^\circ\text{C}$ ), the splitting sharply decreases in two stages – from  $T_{\text{rot}} = 55 \text{ }^\circ\text{C}$  to  $T_{\text{bm}} = 92 \text{ }^\circ\text{C}$  and from  $T_{\text{bm}} = 92 \text{ }^\circ\text{C}$  to  $T_m = 113 \text{ }^\circ\text{C}$ . One can conclude that nonpolar aliphatic CTAB layers have the orthorhombic symmetry of the subcell  $\text{Or}_{\text{cryst}}$  below  $55 \text{ }^\circ\text{C}$ . The splitting  $\Delta\nu_{1,2}$  is inversely proportional to  $R^3$ , where  $R$  is the distance between the axes of the molecules in an orthorhombic subcell [26]. That is why the behavior of  $\Delta\nu_{1,2}(T)$  (Fig. 6) gives grounds to state that, in a neighborhood of the phase transition ( $T_{\text{rot}} = 55 \text{ }^\circ\text{C}$ ), the distance between the axes of molecules considerably decreases in two stages, and the azimuthal reorientation of chain molecules becomes possible. This statement is confirmed by the existence of the orthorhombic

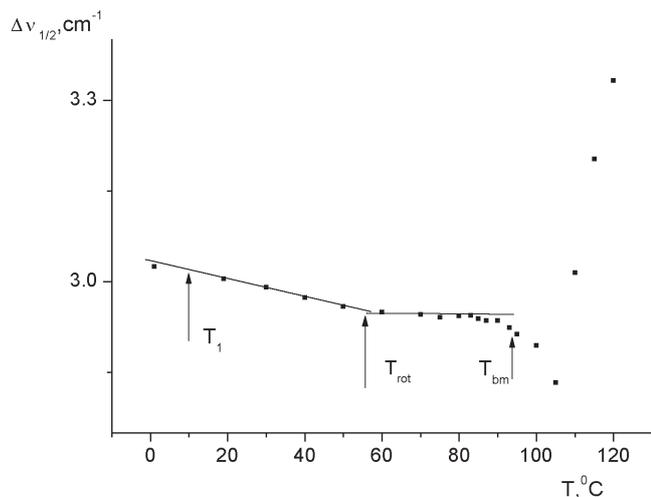


Fig. 7. Temperature dependence of the half-width of the 1480- $\text{cm}^{-1}$  band for CTAB

rotation-crystalline phase  $\text{Or}_{\text{rot}}$  in CTAB in the region ( $92 \div 113$ )  $^{\circ}\text{C}$ . The splitting disappears at  $T_m = 113$   $^{\circ}\text{C}$ , which testifies to the absence of the azimuthal correlation between molecules in the melt. The dependence  $d(\Delta\nu_{1,2})/d(T)$  allows one to determine the region of the temperature variation of the Davydov splitting more accurately.

In the IR-spectra of CTAB, there exists the band in a neighborhood of  $1480 \text{ cm}^{-1}$  related to the stretching vibrations  $\text{Q}(\text{C}-\text{N})$ , whose half-width depends on the temperature (Fig. 7).

One can see from Fig. 7 that the half-width of the  $1480\text{-cm}^{-1}$  band linearly decreases with increase in the temperature in the interval ( $10 \div 55$ )  $^{\circ}\text{C}$ , practically does not depend on it in the range ( $55 \div 92$ )  $^{\circ}\text{C}$ , sharply decreases in the region ( $92 \div 105$ )  $^{\circ}\text{C}$ , and starts to grow above  $105$   $^{\circ}\text{C}$ .

As is known from the literature, the stretching vibrations  $\text{Q}(\text{C}-\text{N})$  are influenced by  $\text{Br}^-$  ion bound with  $\text{N}^+$  one by the ionic bond. In [7], it was shown that the bond radius  $\text{Br}^- \dots \text{N}^+$  in CTAB crystals amounts to  $0.42 \text{ nm}$ , whereas it was established in [10] that this the bond radius in the case of the CTAB solution is equal to  $0.37 \text{ nm}$ . One can state that, both in the solution and in the melt,  $\text{Br}^-$  ions appear closer to  $\text{N}^+$  ions than in the crystal, that is why it stronger affects the stretching vibrations  $\text{Q}(\text{C}-\text{N})$  and results in the growth of the half-width of the indicated band (Fig. 7), which is related to the conformational, orientational, and translational disorder in CTAB under the melting of methylene chains of its molecules.

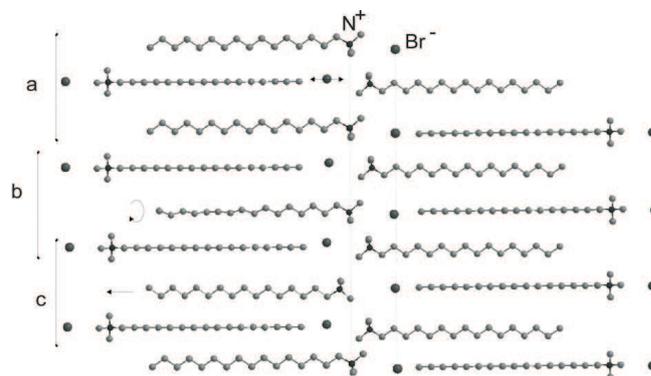


Fig. 8. Diagram of the CTAB crystal: *a* – motion of  $\text{Br}^-$  ion; *b* – passage of a topological soliton along the molecule; *c* – translation of a CTAB molecule from the crystal by a half-period with its reorientation by  $180^{\circ}$

### 3. Discussion of the Results

The obtained experimental results allow us to propose a model of phase transformations taking place in CTAB polycrystals.

The heating of CTAB polycrystals results in the thermal expansion (Fig. 4) that sharply increases in the temperature interval ( $-14 \div 10$ )  $^{\circ}\text{C}$ . In the same temperature interval, we observed a shoulders of  $\varepsilon'(T)$  and  $\varepsilon''(T)$ , whose height decreased with increase in the frequency. To our mind, it is related to an increase of the free volume in the intercrystalline layer, which results in the appearance of a possibility of the translation of  $\text{Br}^-$  ions (Fig. 8,*a*).

Due to the mobility of  $\text{Br}^-$  ions, the bond radius  $\text{Br}^- \dots \text{N}^+$  grows, and the half-width of the  $\text{Q}(\text{C}-\text{N})$  band decreases, respectively (Fig. 7). The further heating results in the phase transition (in the neighborhood of the temperature  $T_{\text{rot}} = 55$   $^{\circ}\text{C}$ ) from the orthorhombic crystalline phase to the orthorhombic rotation-crystalline phase in nonpolar aliphatic layers, where one observes an increase of the distance between the molecules' axes, which manifests itself in a decrease of the Davydov splitting (Fig. 6). In this phase, there appear topological solitons corresponding to the tension (compression) of the chain by a half-period with a rotation by  $180^{\circ}$  [13, 14]. We assume that the solitons are generated on a methyl group in oligomer systems composed of a carbon chain. As known from studies of NMR spectra [16], this group can be reoriented in crystals of alkanes and can serve a source of perturbations under the action of thermal vibrations. Being generated on the terminal methyl group, the TS moves along the aliphatic chain of the CTAB molecule (Fig. 8,*a*) and changes

its orientation in the  $a$ - $b$  plane. Approaching the  $-N(CH_3)_3$  group, the soliton tries to change its orientation. In this case, the amplitude of vibrations of  $N^+$  grows, and a peak appears on the dependences  $\varepsilon'(T)$  and  $\varepsilon''(T)$  in the interval  $(55 \div 92)^\circ\text{C}$  (Fig. 3). The large value of  $\varepsilon'$  is explained by the fact that the motion of topological solitons is correlated [27] and induces the reorientation of many  $N^+$  atoms. Due to the steric hindrances, the topological soliton is reflected from the  $-N(CH_3)_3$  group and turns back. This fact is confirmed by the independence of the half-width of the  $1480\text{-cm}^{-1}$  band on the temperature in the interval  $(55 \div 92)^\circ\text{C}$  (Fig. 7), which testifies to the constant bond radius  $\text{Br}^- \dots \text{N}^+$ . With increase in the temperature, topological solitons, whose energy also grows, continue to reflect from  $-N(CH_3)_3$  until their energy becomes sufficient for the reorientation of these groups (Fig. 8,c). The reorientation of  $-N(CH_3)_3$  groups induces the appearance of a rotationally relaxation mode of the ion pairs formed by  $\text{CTA}^+$  and  $\text{Br}^-$ . As a result, one registers peculiarities on the dependences of the components of the complex dielectric permittivity above  $T_{\text{bm}} = 92^\circ\text{C}$  (Fig. 3). After that, the Davydov splitting abruptly falls in a neighborhood of  $T_{\text{bm}} = 92^\circ\text{C}$  (Fig. 6), and the azimuthal correlation of molecules gets lost. The reorientation of  $-N(CH_3)_3$  groups (and, respectively, aliphatic chains) results in the melting in nonpolar aliphatic layers. A decrease of the half-width of the  $1480\text{-cm}^{-1}$  band in the temperature interval  $(92 \div 105)^\circ\text{C}$  (Fig. 7) is caused by the fact that topological solitons change the orientation of  $-N(CH_3)_3$  groups and increase the mean bond radius  $\text{Br}^- \dots \text{N}^+$ . The reorientation motion of the majority of  $-N(CH_3)_3$  groups results in the growth of the free volume in the polar layer. Due to this fact, there appears a possibility to decrease the distance  $\text{Br}^- \dots \text{N}^+$ , which gives rise to the sharp growth of the half-width of the  $1480\text{-cm}^{-1}$  band above  $105^\circ\text{C}$  (Fig. 7).

#### 4. Conclusions

In our opinion, a change of the structure of the crystal lattice under phase transformations in polycrystal CTAB is related to the formation of topological solitons in molecular trans-chains that appear due to an increase of the amplitude of pendular oscillations of terminal methyl groups with increase in the temperature. The further heating results in the growth of the concentration of these formations, which induces the melting in nonpolar layers created by aliphatic chains.

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#### ОСОБЛИВОСТІ ТЕПЛОВОГО РУХУ В КРИСТАЛАХ, УТВОРЕНИХ МОЛЕКУЛАМИ БРОМІДУ ЦЕТИЛТРИМЕТИЛАМОНІЮ

*О.М. Алексеев, М.М. Лазаренко, Г.О. Пучковська, Т.В. Безродная, А.А. Сендзюк*

#### Резюме

За допомогою теплофізичних, діелектричних та спектроскопічних методів досліджено фазові перетворення в полікристалах ЦТАБ. Запропоновано молекулярну модель цих перетворень. На нашу думку, в полікристалах ЦТАБ при 10 °С починає збільшуватись вільний об'єм в міжкристалітному шарі і іони  $\text{Br}^-$ , зв'язані з кінцевими групами  $-\text{N}(\text{CH}_3)_3$ , збільшують свою рухливість. При досягненні 55 °С з'являються топологічні солітони типу стиснення на одну ланку з переорієнтацією на 180°, які зароджуються на кінцевих метильних групах та, проходячи вздовж молекул, відбиваються від груп  $-\text{N}(\text{CH}_3)_3$ . При цьому кристали ЦТАБ переходять в орторомбічну ротаційно-кристалічну фазу. При 92 °С топологічні солітони переорієнтовують кінцеві групи  $-\text{N}(\text{CH}_3)_3$ , внаслідок чого розпочинається плавлення неполярних аліфатичних шарів.