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Abstract. *The structure of the mesophases and mesomorphic glasses of cobalt alkanoates homologous series was obtained. It is shown, that typical for ITLC smectic A packing of molecules (cation-anion layer between layers alkanoate chains) preserves also in a glass phase (at room temperature).*

Keywords: cobalt alkanoates; ionic thermotropic liquid crystals; mesomorphic glasses; mesophase structure; method of X-ray small-angle scattering.

1. Introduction

Searching for and investigation of new materials, which can be perspective for developing and establishing of information storage and processing devices, is one of the important areas of modern science.

As a result, much attention is paid to the investigation of alternative classes of Liquid Crystals (LC) recently.

Unusual properties of these materials open up new opportunities for a variety of practical applications.

The melting point and mesophase existence interval are very important because of practical application which require LC materials with low melting points and ability to exist at room temperature in the LC glass state.

2. Analysis of research and publications

Salts of alkane acids $C_nH_{2n+1}COOM$ form Thermotropic Ionic LC (TILC) during melting.

TILC exhibit high ionic conductivity, wide interval of mesophase existence, high thermal stability and ability to vitrification [7].

However, their use as new functional materials is often limited by high melting points [3, 7].

Decrease the melting temperature is observed for multicomponent LC systems, which include two, three or more individual compounds of approximately the same chemical nature.

Aim of the work is:

- investigation of the cobalt alkanoates structure depending on temperature and phase state;
- development of molecules packing model in the crystal, liquid crystal and glass states.

3. Methods and objects of research

The X-ray small-angle scattering study was conducted for establishing the nature of the molecules arrangement and its changes during phase transformations for samples of cobalt octanoate

$(C_7H_{15}COO^-)_2Co^{2+}$ ($T_{melt} = 93^\circ C$, $T_{clar} \approx 164^\circ C$),
cobalt decanoate

$(C_9H_{19}COO^-)_2Co^{2+}$ ($T_{melt} = 82^\circ C$, $T_{clar} > 300^\circ C$)
and lead decanoate

$(C_9H_{19}COO^-)_2Pb^{2+}$ ($T_{melt} = 87^\circ C$, $T_{clar} = 114^\circ C$),
binary mixture

$Pb^{2+}, Co^{2+} | (C_9H_{19}COO^-)_2$ (60:40 mol. % correspondingly, $T_{melt} = 83^\circ C$, $T_{clar} = 92^\circ C$),
cobalt laurate

$(C_{11}H_{21}COO^-)_2Co^{2+}$ ($T_{melt}=88C$, $T_{clar}>300^\circ C$).

Measurements were carried out with small-angle diffractometer with a slit collimation system.

The studies were carried out on the experimental setup with monochromated $CuK\alpha$ -radiation of X-ray tube with capacity of 1,2 kV, monochromator - nickel foil, focused spot size of 0,4x8 mm.

Range of 2θ angles – from $0,1^\circ$ to 20° , resolution of collimation system was $0,02^\circ$.

The temperature was measured by copper-constantan thermocouple, with an accuracy of $0,2^\circ C$. Measurements were carried out in the direction of growth temperature and towards its reduction.

**4. X-ray investigation of lead decanoate
 $(C_9H_{19}COO^-)_2Pb^{2+}$**

Research of lead decanoate compound in the crystalline state (temperature range $30-80^\circ C$)

showed that in the range of $2\vartheta \approx 2,85^\circ$ there is intense diffraction maximum (Fig. 1).

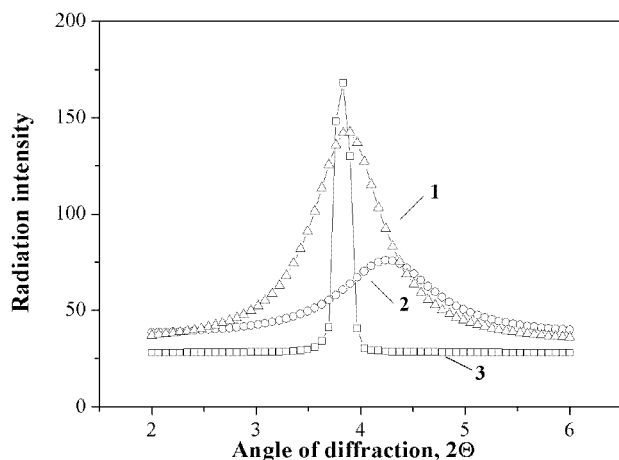


Fig. 1. Dependence of X-ray scattering intensity on angles 2θ :

- 1 – $\text{Pb}^{2+}, \text{Co}^{2+} | (\text{C}_9\text{H}_{19}\text{COO}^-)_2$ for binary mixture (88°C) (60:40 mol. %);
 2 – for sample $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Co}^{2+}$ (85°C);
 3 – for sample $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Pb}^{2+}$ (102°C)

Calculated by the Wolf-Bragg formula

$$2d\sin\vartheta = m\lambda \quad (m=1) \quad \text{bilayer distance didn't}$$

change throughout a specified temperature range and amounts to $d_{cr} \sim 31 \text{ \AA}$.

The bilayer distance decrease $\Delta d \sim 1,5 \text{ \AA}$ is observed at the temperature $\sim 86^\circ\text{C}$ (Fig. 2, A), which can be explained by the transition to a different polymorphic crystalline modification of a classical mesogenic crystal disordering of alkyl chains of molecules [2, 6, 7].

In temperatures $\sim 94^\circ\text{C}$ there is a sharp reduction of bilayer distance to $d_{\text{mesoph}} \sim 23 \text{ \AA}$ (Fig. 2, A).

Thus the nature of roentgenogram indicates (Fig. 1, curve 1), that even for nonoriented LC sample very intense and narrow diffraction maximum is observed.

This is typical for Smectic A and indicates a very high quality of molecules interlayer ordering.

This is confirmed by the fact that calculated by the Debye-Scherrer formula

$$\zeta_{\parallel} = \lambda / \beta \cos\vartheta$$

(λ – X-ray wavelength, β – diffraction peak width at half height in radians, θ – angle of diffraction) interlayer correlation length is $\zeta_{\parallel} \approx 1000 \text{ \AA}$.

To clarify the nature of the molecules packing in the crystal and mesophase the CS Chem3D molecular modeling was used.

The length of the molecule in its most elongated state was calculated.

In the calculations we take into account the ionic radius of lead $r_{\text{ion}}^{\text{Pb}} = 1,19 \text{ \AA}$ [1] and Van der Waals

radius of the hydrogen atoms $r_{\text{H}} = 1,2 \text{ \AA}$ [1] of finite methyl groups in the molecule alkyl chain.

Found that the experimental value of interlayer distance $d_{cr} \sim 31 \text{ \AA}$ may correspond to the bilayer allocation of elongated molecules axes $l_{\text{theor}} \sim 31,2 \text{ \AA}$ with approximately perpendicular orientation of the molecule to the plane between the layers.

Since according to optical data (conoscopic picture as uniaxial crosses) $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Pb}^{2+}$ compound form smectic mesophase type A, the sharp decrease in the periodic distance of mesophase means that there is an abrupt contraction of cation-anion layers during the phase transformation.

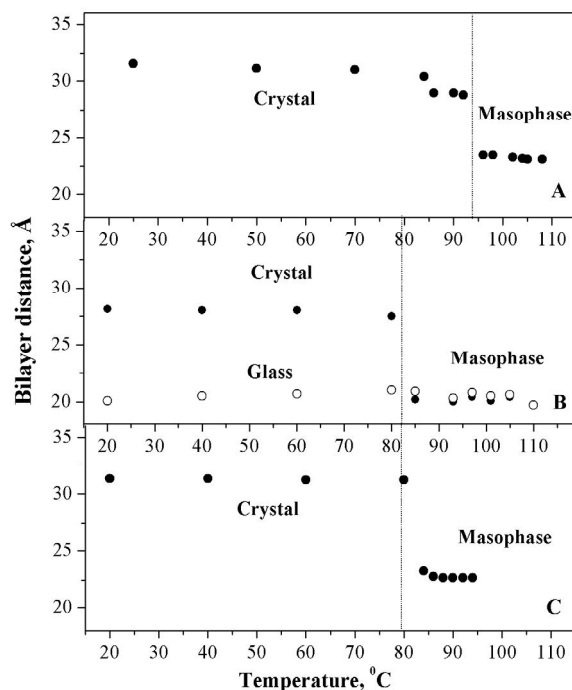


Fig. 2. Temperature dependence of bilayer distance of polycrystalline samples:

A – $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Pb}^{2+}$;

B – $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Co}^{2+}$;

C – binary mixture $\text{Pb}^{2+}, \text{Co}^{2+} | (\text{C}_9\text{H}_{19}\text{COO}^-)_2$

(60:40 mol. %);

● – under heating;

○ – under cooling

The value of contraction $\sim 8 \text{ \AA}$ corresponds to the mutual bilayer penetration of the decanoate molecules “tails” approximately on $\sim 4 \text{ \AA}$.

Reduction of interlayer distance during the phase transformation “crystal - smectic phase” is observed for thermotropic molecular [8] and ionic [5] LC.

Such contraction is explained by the conformational disorder of molecules alkyl “tails” with the increasing of the temperature, their interpenetration and statistical tilt of the molecules to the plane of layers.

However, for thermotropic ionic liquid crystals the significant additional factor of contraction is the long-range electrostatic interaction.

It is on one hand distend the layers due to the repulsion along them, and on the other hand trying to compress the layers, due to the mutual attraction, in the direction perpendicular to their plain.

5. X-ray investigation of cobalt decanoate $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Co}^{2+}$

In contrast to $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Pb}^{2+}$ for the $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Co}^{2+}$ compound in the mesophase is observed broad diffraction maximum (Fig. 1, curve 2).

The correlation length for mesophase calculated using the diffraction maximum is only $\xi_{||} \approx 50 \text{ \AA}$.

The $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Co}^{2+}$ compound is also characterized by bilayer arrangement of molecules in the crystalline state and in the mesophase (smectic A).

Bilayer period is about $d_{\text{cr}} \sim 28 \text{ \AA}$ – in the crystal and $d_{\text{mesoph}} \sim 20 \text{ \AA}$ – in the mesophase (Fig. 2, B).

Value of the compression ($\sim 8 \text{ \AA}$) during the phase transformation “crystal – mesophase” is the same as for $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Pb}^{2+}$ compound.

According to calculations the length of the molecule of $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Co}^{2+}$ (ionic radius of cobalt $r_{\text{ion}}^{\text{Co}} = 0,74 \text{ \AA}$ [1]) in the most elongated state is $l_{\text{theor}} \sim 30,7 \text{ \AA}$ and in the crystal is $d_{\text{cr}} \sim 28 \text{ \AA}$.

This means that the molecules in the crystalline state either don't have the maximum anisometric shape, or their long axis slightly inclined to the plane of the interlayer (maximum angle of deviation from the normal to the plane is $\sim 24^\circ$), or a combination of above-listed.

Should be noted that angle of deflection $\sim 24^\circ$ is not great.

Usually classical mesogenic molecular crystals that form smectic A phase, it can reach $\sim 50\text{-}60^\circ$ [8].

The inclination of the molecules in the crystalline state is energy-optimal and this is consistent with the principle of dense packing of molecules by type hump – depression [4].

As the cobalt decanoate $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Co}^{2+}$ during the cooling is able to vitrification, the study of its vitrified state was conducted.

For this purpose the thermostat was turned off and the change in value of the bilayer period depending on temperature was monitored up to the room temperature.

Then, the sample was taken out and checked for vitrified state.

As shown in Fig. 2, B, the magnitude of bilayer period does not change during cooling and is approximately equal $d_{\text{glass}} \sim 21 \text{ \AA}$.

Correlation length in the glass state at room temperature is the same as in the mesophase ($\xi_{||} \approx 50 \text{ \AA}$).

This means that the nature of the molecules bilayer arrangement in smectic A and in the glass is equal.

So it can be concluded that we obtained smectic glass.

This state of matter is stable and persists a long time – up to several months.

6. X-ray investigation of binary mixture $\text{Pb}^{2+}, \text{Co}^{2+} | (\text{C}_9\text{H}_{19}\text{COO}^-)_2$

Small-angle X-ray investigation of two-component system $\text{Pb}^{2+}, \text{Co}^{2+} | (\text{C}_9\text{H}_{19}\text{COO}^-)_2$ with content 40 mol. % of $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Co}^{2+}$ showed that the X-ray diffraction pattern (Fig. 1, curve 3) for the mesophase is close to the individual compound $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Pb}^{2+}$.

Correlation length of the smectic ordering for the binary system is $\xi_{||} \approx 200 \text{ \AA}$.

And the bilayer periods in the crystalline state ($d_{\text{cr}} \sim 31 \text{ \AA}$) and smectic A mesophase ($d_{\text{mesoph}} \sim 23 \text{ \AA}$) (Fig. 2, C) coincide with similar magnitudes of individual compound $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Pb}^{2+}$.

Thus, investigation of binary system showed that the diffraction pattern has characteristics of both individual compounds included in the composition.

And the compound $(C_9H_{19}COO^-)_2Pb^{2+}$ acts as an orienting matrix.

In particular, the correlation length in the binary system has quadrupled in comparison with the individual compound $(C_9H_{19}COO^-)_2Co^{2+}$.

This indicates higher quality smectic bilayer ordering in binary system than in $(C_9H_{19}COO^-)_2Co^{2+}$.

However, it should be noted that for the binary system melting temperature remained high ($\sim 82^\circ C$).

In addition, as actually and lead decanoate, binary mixture is unable to vitrification, which significantly limits its use.

7. X-ray investigation of cobalt laurate $(C_{11}H_{21}COO^-)_2Co^{2+}$

Ability to vitrification exhibits compound of cobalt laurate $(C_{11}H_{21}COO^-)_2Co^{2+}$.

In the diffraction pattern of the investigated sample at temperatures ranging from room temperature to $\sim 82^\circ C$ the clear intense diffraction maximum of the crystal is observed (Fig. 3, curve 1).

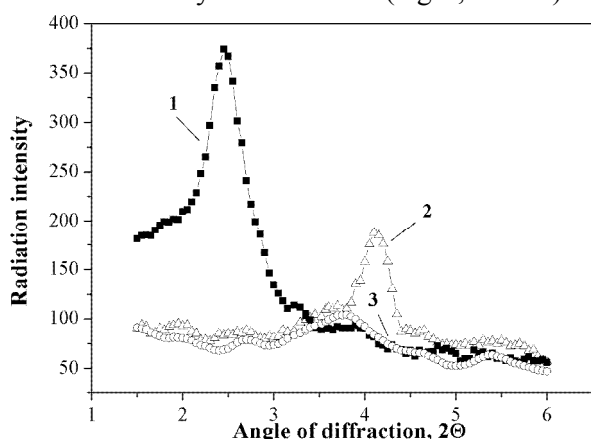


Fig. 3. X-ray diffraction patterns of the sample $(C_{11}H_{21}COO^-)_2Co^{2+}$:
1 – crystalline state ($25^\circ C$);
2 – mesomorphic state ($160^\circ C$);
3 – glass state ($25^\circ C$)

Its angular positions indicate that bilayer distance in the crystal decreases from $d_{cr} \sim 36 \text{ \AA}$ (according to calculations $l_{theor} \sim 35,8 \text{ \AA}$) to $d_{cr} \sim 33 \text{ \AA}$ (Fig. 4) during heating.

This is typical for most LC compounds, especially those with long alkyl chains [7, 8], and connected with their disordering with temperature increasing.

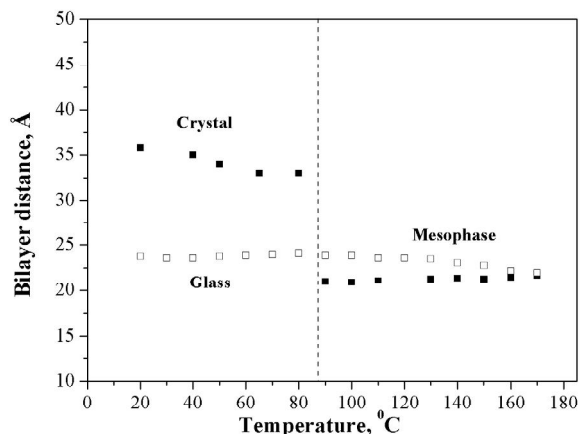


Fig. 4. Temperature dependence of bilayer distance of polycrystalline sample $(C_{11}H_{21}COO^-)_2Co^{2+}$:
■ – under heating;
□ – under cooling.

Phase transition to the mesophase (Fig. 3, curve 2) is accompanied by a sharp reduction of bilayer distance $d_{mesoph} \sim 21 \text{ \AA}$, which practically does not change in mesophase up to $170-180^\circ C$ (Fig. 4).

The value of reduction is the largest of all investigated compounds and amounts to $\sim (12-15) \text{ \AA}$ that also applies to LC compounds with the longest alkyl chains [7, 8].

The vitrified state is formed during the cooling of the sample (Fig. 3, curve 3) with the value of bilayer distance $d_{glass} \sim 23 \text{ \AA}$ close to its magnitude in smectic A mesophase (Fig. 4).

Correlation length in the mesophase $\xi_{||} \approx 220 \text{ \AA}$ is significantly higher than the glass state $\xi_{||} \approx 130 \text{ \AA}$, which indicates a lower ordering in the vitreous state, but this state is stable and long-term at room temperature.

8. X-ray investigation of cobalt octanoate $(C_7H_{15}COO^-)_2Co^{2+}$

Small angle X-ray investigation of cobalt oktanoate $(C_7H_{15}COO^-)_2Co^{2+}$ showed that the crystal, smectic A phase and smectic glass phase also have bilayer nature of molecules packing.

In the diffraction pattern of the crystal diffraction maximum is observed.

Intensity of the maximum decreases during the phase transition to the mesophase and the glass state (Fig. 5).

The value of bilayer period in the crystalline state $d_{cr} \sim 21,5 \text{ \AA}$ (Fig. 6) was significantly lower than expected.

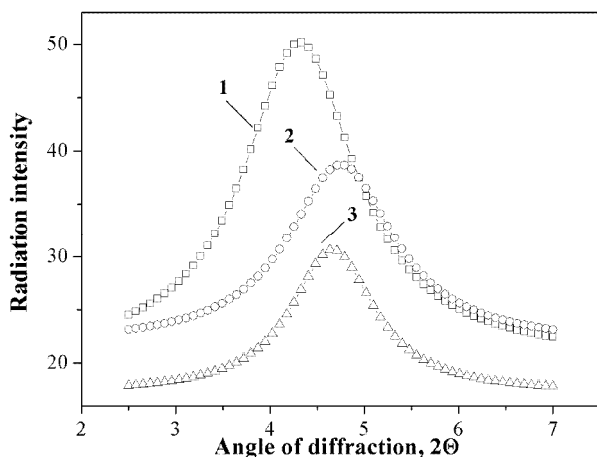


Fig. 5. X-ray diffraction patterns of the sample $(C_7H_{15}COO^-)_2Co^{2+}$
 1 – crystalline state (40°C);
 2 – mesomorphic state (100°C);
 3 – glass state (40°C)

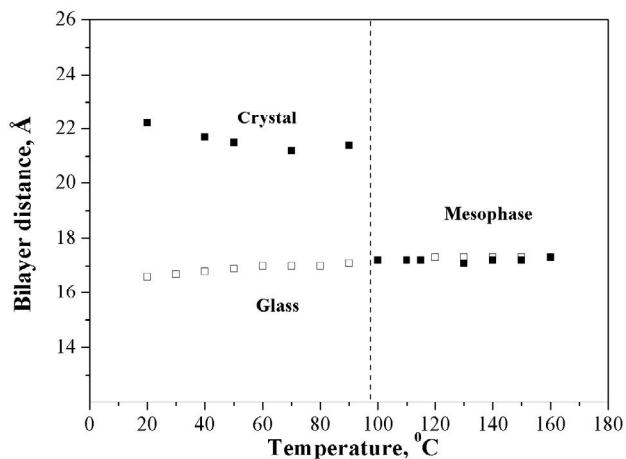


Fig. 6. Temperature dependence of bilayer distance of polycrystalline sample $(C_7H_{15}COO^-)_2Co^{2+}$:
 ■ – under heating;
 □ – under cooling

According to the calculations the length of the molecule of $(C_7H_{15}COO^-)_2Co^{2+}$ in the most elongated state must be equal to $l_{theor} \sim 25,7 \text{ \AA}$.

This means that unlike homolog $(C_9H_{19}COO^-)_2Co^{2+}$ elongated axis of the molecules $(C_7H_{15}COO^-)_2Co^{2+}$ in crystal are more inclined to the interlayer plane (maximum deviation from the normal to the plane ($\sim 33^\circ$)).

At the phase transition from the crystalline state to the smectic A phase this inclination disappears, and at the same time at the expense of interpenetration of

molecules alkyl chains decreases the periodicity of the bilayer from $d_{cr} \sim 21,5 \text{ \AA}$ – in the crystal to $d_{mesoph} \sim 17 \text{ \AA}$ – in the mesophase.

Considering that the maximum length of the molecule $l_{theor} \sim 25,7 \text{ \AA}$, and bilayer thickness in the smectic A phase and in the glass $\sim 17 \text{ \AA}$ (Fig. 6), the maximum mutual penetration of molecules tails is approximately equal to $\sim 4,4 \text{ \AA}$.

Periodicities in the mesophase and glass (Fig. 6) and the correlation lengths ($\xi_{||} \approx 65 \text{ \AA}$ and $\xi_{\perp} \approx 75 \text{ \AA}$, respectively) are close.

This gives the reason to assert that the mesophase and glass are identical nature of molecules ordering.

9. Conclusions

Small-angle X-ray studies of TILC have shown that during the phase transition from the crystalline state to the mesophase there is a sharp reduction in interlayer periodicity that preserve in the glass state up to room temperature.

This abrupt contraction of smectic layers is caused by conformational disorder of molecules alkyl chains and long-range electrostatic interaction.

The model of bilayer allocation of the molecules in the crystal, mesophase and in the vitreous state is constructed.

The characteristic feature of molecules ordering in mesophase and glass is interlayer interpenetration of disordered alkyl chains of molecules on $\sim (4-7) \text{ \AA}$.

The value of the correlation lengths in the vitreous state show that the glass has a smectic structure with a clear orientation of molecules elongated axes in the range of two to six bilayer distances.

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Наведено результати досліджень структурних характеристик термотропних іонних рідких кристалів алканоатів кобальту та їх мезоморфних стекел. Показано, що двошарове пакування молекул (катион-аніонний прошарок між шарами алканоатних ланцюгів), властиве смектичній А фазі, зберігається в склоподібному стані при кімнатній температурі.

Ключові слова: алканоати кобальту; іонні термотропні рідкі кристали; мезоморфні стекла; метод малокутового розсіювання рентгенівських променів; структура мезофаз.

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Приведены результаты исследований структурных характеристик термотропных ионных жидких кристаллов алканоатов кобальта и их мезоморфных стекел. Показано, что двухслойная упаковка молекул (катион-анионная прослойка между слоями алканоатных цепей), характерная для смектической А фазы, сохраняется в стеклоподобном состоянии при комнатной температуре.

Ключевые слова: алканоаты кобальта; ионные термотропные жидкие кристаллы; мезоморфные стекла; метод малоуглового рассеяния рентгеновских лучей; структура мезофаз.

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