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ABSORBANCE SPECTRA OF Co^{2+} ALKANOATE LIQUID CRYSTALS AND SMECTIC GLASSES

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Abstract**—***The work is devoted to the study of the optical properties of ionic thermotropic liquid crystals of the homologous series of cobalt alkanoates and their smectic glasses using methods of electronic spectroscopy. The aim of the study was to determine the dominant coordination of cobalt cations in the alkanoate matrix and the nature of the matrix's influence on the absorption of samples. It is shown that the dominant coordination of cobalt ions in the studied media is the octahedron. A significant decrease in the absorption coefficient with the increase in the length of the aliphatic chain in the homologous series of cobalt alkanoates is due to a decrease in both the volume concentration of the cobalt cation complexes and the values of the dipole moments of the d-d transitions.*

Index Terms—Ionic thermotropoic liquid crystals; smectic glasses; cobalt alkanoates; optical absorption spectra.

I. INTRODUCTION

The ability of liquid crystals to reveal small temperature gradients has resulted in studies of their utility in the thermal testing of aerospace materials and components. These studies led to successful application of liquid crystals in low-cost techniques for performing thermal mapping on large areas in avionics [1]. Also, it is well known that first liquid crystals displays were created and tested for aviation [2]. The development of these technologies and further research into new types of liquid crystals led to the creation Active-Matrix Liquid-Crystal Display (AMLCD) – type of display technology commonly used in aviation [3]. Nowadays, research into the properties and characteristics of liquid crystals led to their wide applications – not only in display technologies, but also in photonics, laser beam steering, information storage, non-destructive testing, developing adaptive optical elements for space applications, creation of tunable lenses for augmented reality, Bragg gratings for sensors, etc. [4], [5].

Modern tendencies in holographic recording of information mostly associated with the developing of new multifunctional materials. One of such materials is metalalkanoates which form TILC during their melt. TILC are the universal matrixes for great number of organic and nonorganic materials. In particular, they are used for introduction of the different dyes in order to create medium for holographic grating recording.

II. PROBLEM STATEMENT

Cobalt alkanoates are standing out of metalalkanoates series due their ability to absorb light in visible spectral region. Also, the important feature of these materials is ability to overcool with vitrification. Received glass state is characterized by preserving liquid crystal (LC) structure. Materials with preassigned characteristics can be established by varying length of cobalt alcanoates hydrocarbon chains.

Aim of the work is:

- development of preparation methods of liquid crystal cells and mesomorphic glasses based on cobalt alkanoates;
- determination of cobalt ions coordination, it’s possible change depending on the temperature and physical state of matter (mesophase, mesomorphic glass).

III. ANALYSIS OF RESEARCH AND PUBLICATIONS

Recently metalalkanoates are used for developing of new optical and nonlinear-optical materials [6] – [8]. In particular, metalalkanoates serve as matrixes in composites for dyes and photosensitive impurities with great and fast nonlinear response.

Another perspective way of developing materials with improved nonlinear-optical characteristics on the basis of metalalkanoates is establishing of LC compounds with ions of *d*- and *f*-metals [8] – [10]. It is common knowledge that ions of *d*- and *f*-metals are widely used for developing of nonlinear-optical materials [8], [9]. Therefore it is necessary to study optical properties of cobalt alkanoates TILC and mesomorphic glasses.

IV. METHODS AND OBJECTS OF RESEARCH

Electronic spectroscopy was used to study optical properties of cobalt alkanoates. Measurements were taken in the temperature range 20–150° C, towards increase and decrease of the temperature, with measurement pitch 3° C. Temperature was regulated by using specially constructed oven, which was situated in the monochromator chamber on the light path.

Electronic absorption spectra of cobalt alkanoates samples were studied in visible optical wavelengths diapason (400–700 nm) using automatic spectral setup CSOS-6 on the basis of monochromator MDG-6. As the radiation detector for wavelength range λ = 650–1200 nm was used PED-62. Scanning of the spectrum was carried out using step engine, scanning pitch – 2.00 nm. Number of averaging was 1000.

Obtained spectrum of the intensity-transmittance wavelength relation was converted to the optical density wavelength relation using expression $D = \lg(I_0 / I)$, where D is the optical density, I_0 is the intensity of incident beam, I is the intensity of the beam after passing the sample.

Mentioned below representatives of homologous series of cobalt alkanoates Co^{2+} were used for spectral studies: cobalt caprylate $(C_7H_{15}COO^-)_2Co^{2+}$ (T_{melt} = 93° C, $T_{\text{clar}} \approx$ 164° C), cobalt decanoate $(C_9H_{19}COO^-)_2Co^{2+}$ (T_{melt} = 82° C, $T_{\text{clar}} >$ 300° C), cobalt laurate $(C_{11}H_{21}COO^-)_2Co^{2+}$ (T_{melt} = 88° C, $T_{\text{clar}} >$ 300° C).

To obtain spectra were used optical quartz cuvettes with a thickness of 30 μm. Samples in the form of polycrystalline powder were placed in the cuvette and heated to the temperature of mesophase formation. Orientation of the samples was examined in polarized light using a microscope with a warm stage. In the liquid crystal state samples were mainly homeotropic orientation. In the case of slow cooling the liquid crystal went into a state of smectic glass that obtain at the room temperature for a quite long time (one year), keeping the structure of the liquid crystal.

V. RESULTS AND DISCUSSION

The absorption spectra both of cobalt caprilate mesophase $(C_7H_{15}COO^-)_2Co^{2+}$ (in the temperature range 115° C – 150° C) and mesomorphic glass (room temperature 25° C) are shown in the Fig. 1. The spectra of cobalt caprylate consist of a broad absorption band with a maximum at 565 nm and clearly marked shoulder at 530 nm due to electronic transitions in complexes of cobalt ions and their coordinating ligands. With increase of the mesophase temperature from 100° C up to 135° C shape and position of the absorption spectrum bands of Co^{2+} ions remained practically constant. But a change of the intensities of the absorption maxima was observed (Fig. 2). This is caused by the change of Co^{2+} ions coordination symmetry – they become less centrosymmetric, which is indicated by a decrease of the optical absorption intensity with increasing of the temperature $\Delta D / \Delta T < 0$ [11]. With the further increase of temperature (up to 150° C) an increase in the intensity of optical absorption $\Delta D / \Delta T > 0$ is observed. That is complexes of cobalt ions Co^{2+} become a centrosymmetric again.

The absorption spectra of cobalt decanoate mesophase $(C_9H_{19}COO^-)_2Co^{2+}$ (90° C – 130° C) and cobalt decanoate mesomorphic glass (25° C) are shown in the Fig. 3. The spectra of cobalt decanoate consist of a broad absorption band with a maximum at 560 nm and clearly marked shoulder at 530 nm due to electronic transitions in complexes of cobalt ions with the surrounding ligands. As for the sample of cobalt caprylate, with increasing of the temperature shape and position of the absorption spectrum bands of Co^{2+} ions remain almost unchanged.

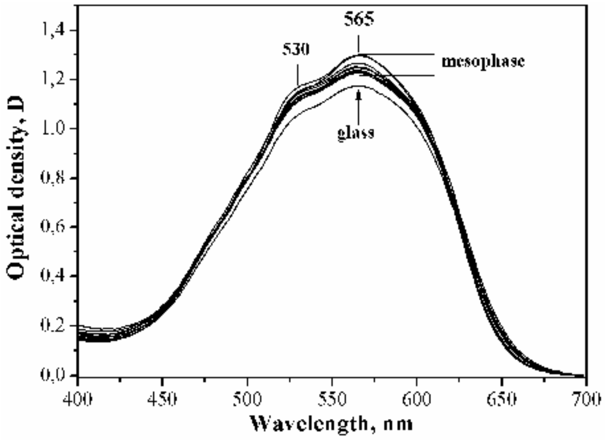

Fig. 1. The absorption spectra of Co^{2+} ions in the mesophase (100° C – 150° C) and mesomorphic glass (25° C) of cobalt caprylate $(C_7H_{15}COO^-)_2Co^{2+}$

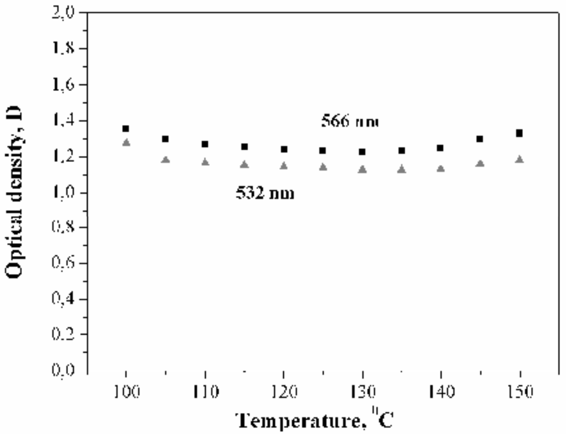

Fig. 2. Temperature dependence of the absorption maxima of Co^{2+} ions in the mesophase (100° C – 150° C) of cobalt caprylate $(C_7H_{15}COO^-)_2Co^{2+}$

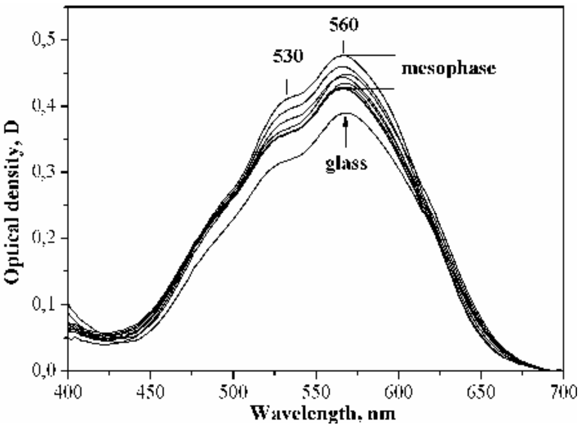

Fig. 3. The absorption spectra of Co^{2+} ions in the mesophase (90° C – 130° C) and mesomorphic glass (25° C) of cobalt decanoate $(C_9H_{19}COO^-)_2Co^{2+}$

The intensity of absorption maxima changes with increase of the temperature from 90° C up to 125° C (Fig. 4). As in the previous case, reduce of the optical absorption intensity with temperature increase ($\Delta D / \Delta T < 0$) indicates that cobalt ion complexes surrounded by decanoate ligands undergo a coordination distortion, becoming less centrosymmetric with temperature increase up to 125° C. The reverse process takes place at the temperature 130° C. The increase of optical absorption intensity with the temperature $\Delta D / \Delta T > 0$ denotes the restoration of cobalt Co^{2+} ion complexes to more centrosymmetrical coordination.

Absorption spectra of cobalt laurate $(C_{11}H_{21}COO^-)_2Co^{2+}$ at the temperature of mesophase existence (100° C – 130° C) and at the room temperature (25° C – mesomorphic glass) are shown in the Fig. 5. As for previous samples the spectrum is characterized by a broad absorption band with a maximum at 565 nm and clearly marked shoulder at 530 nm. With temperature increase the shape and position of the absorption spectrum bands of Co^{2+} ions in observed samples remain practically unchanged. But there is a change in the intensities of the absorption maxima (Fig. 6). The typical decrease in absorption intensity with increasing temperature ($\Delta D / \Delta T < 0$) indicates that complexes of cobalt ions undergo conformational distortion becoming less centrosymmetric in the case of temperature increase [6].

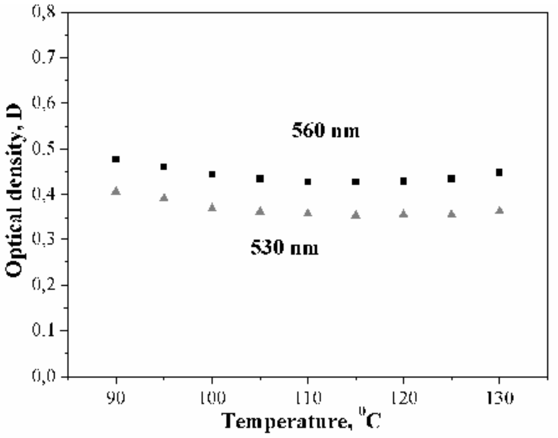

Fig. 4. Temperature dependence of the absorption maxima of Co^{2+} ions in the mesophase (90° C – 130° C) of cobalt decanoate $(C_9H_{19}COO^-)_2Co^{2+}$.

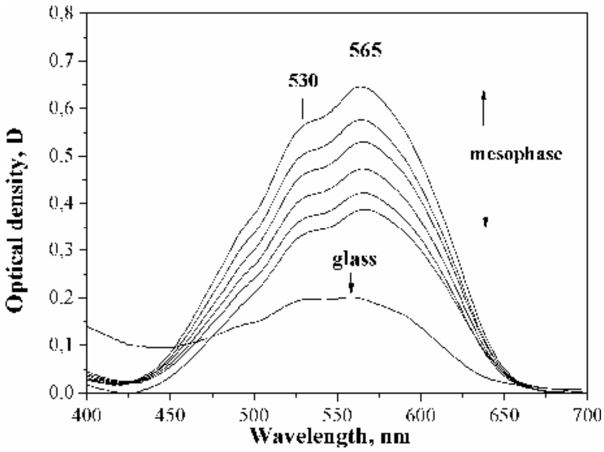

Fig. 5. The absorption spectra of Co^{2+} ions in the mesophase (100° C – 130° C) and mesomorphic glass (25° C) of cobalt laurate $(C_{11}H_{21}COO^-)_2Co^{2+}$

Spectra of cobalt alkanoates homologous series can be considered in terms of ligand field theory [6], [7], as excitation display of the octahedral coordination (coordination number = 6) of cobalt ions. Two characteristic electronic transitions were observed for this coordination. Maximum on 535 nm corresponds to an electronic transition $^4T_{1g}(^4F) \to {}^4T_{1g}(^4P)$ [6], [8], and maximum on 565 nm – $^4T_{1g}(^4F) \to {}^4A_{2g}(^4F)$ [6], [8].

Thus, studies of the homologous series of cobalt Co^{2+} alkanoates in the mesophase and in the mesomorphic glass revealed the presence of octahedral Co^{2+} ions. The decrease of the intensity of optical absorption with increasing temperature of the mesophase $\Delta D / \Delta T < 0$ indicates that the octahedral coordination of cobalt ions undergo certain distortions, becoming less centrosymmetric, especially for the longest homolog $Co(C_{12})$ (Fig. 6). It is known that for d-metal alkanoates extinction coefficient decreases with increasing number of carbon atoms in the aliphatic chain of the ligand [11]. This is because the increase of alkanoate ligand size promotes the increase of the coordination distortion. We can assume that the larger ligand is located in the coordination sphere of a transition metal cation, the less is centrosymmetric complex. Alkanoate-anions with short chains are able to form more symmetrical surroundings around the cobalt cation unlike the alkanoate-anions with long chains, since they have more spatial barriers. For the studied homologous series modulo the value of $\Delta D / \Delta T$ increases monotonically from short aliphatic chain $Co(C_8)$ to the long $Co(C_{12})$, i.e. homologues with longer chain are less centrosymmetric.

Also, for the studied homologous series found that the change of the aliphatic chain length of alkanoate anions does not affect form and position of the absorption bands. But there is a significant decrease in the intensity of absorption. The absorption coefficient α decreases monotonically from 450 cm^{-1} to 200 cm^{-1}: $\alpha (CoC_8) > \alpha (CoC_{10}) > \alpha (CoC_{12})$ (Fig. 7).

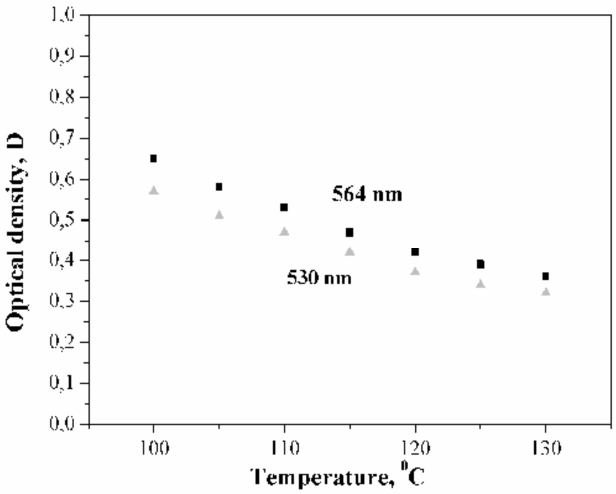

Fig. 6. Temperature dependence of the absorption maxima of Co^{2+} ions in the mesophase (100° C – 130° C) of cobalt laurate $(C_{11}H_{21}COO^-)_2Co^{2+}$

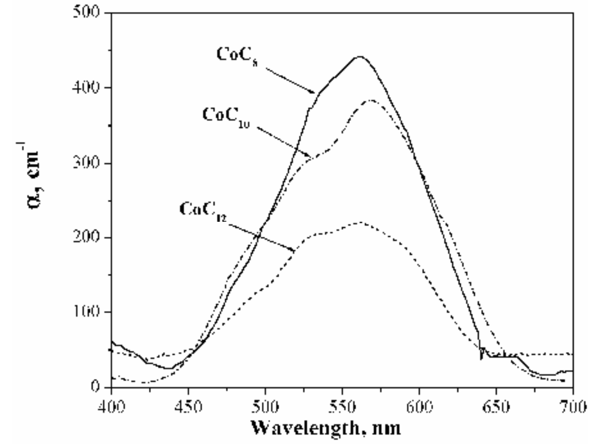

Fig. 7. The absorption spectra of Co^{2+} ions in mesomorphic glasses of homologous series $Co(C_8)$, $Co(C_{10})$, $Co(C_{12})$

Reduction of optical absorption can be caused mainly by two factors:

- decrease of the concentration of cobalt ions complexes in the homologous series $Co(C_8)$, $Co(C_{10})$, $Co(C_{12})$ with increasing of the aliphatic chain length;
- decrease of the d-d transition dipole moments μ_{d-d} with increasing of the aliphatic chain length: $\mu_{d-d}(CoC_8) > \mu_{d-d}(CoC_{10}) > \mu_{d-d}(CoC_{12})$ [14].

It should be noted that observed strong changes in absorbance properties of studied materials can be used for developing of the tunable advanced optical materials. And the main reason for this is the experimental fact that fundamental linear optical properties of the cobalt alkanoates glasses can be tuned by varying of the alkanoate-anion length.

VI. CONCLUSIONS

A detailed study of the electronic absorption spectra of cobalt ion complexes in individual samples of the homologous series of cobalt alkanoates has been carried out.

It is found that octahedral coordination of ions is present in both mesophase and mesomorphic glass of individual compounds of the homologous series of cobalt alkanoates $Co(C_8)$, $Co(C_{10})$, $Co(C_{12})$. It is shown that the octahedral ions become less centrosymmetric with increasing temperature ($\Delta D / \Delta T < 0$) and aliphatic chain length.

It is shown that a significant decrease in the absorption coefficient with increasing aliphatic chain length is caused by a decrease in both the volume concentration of cobalt cation complexes and the magnitude of the dipole moments μ_{d-d} *d-d*-transition in homologous series. $\mu_{d-d}(CoC_8) > \mu_{d-d}(CoC_{10}) > \mu_{d-d}(CoC_{12})$.

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О. В. Грідякіна, А. П. Поліщук, Т. С. Лень. Спектри поглинання алканоатних рідких кристалів Co^{2+} та смектичних стекол

Роботу присвячено дослідженню оптичних властивостей іонних термотропних рідких кристалів гомологічного ряду алканоатів кобальту та їх смектичних стекол методами електронної спектроскопії. Метою дослідження було визначення домінуючої координації катіонів кобальту у алканоатній матриці та характер впливу матриці на поглинання зразків. В ході проведених досліджень показано, що домінуючою координацією іонів кобальту в досліджених середовищах є октаедр. Значне падіння коефіцієнта поглинання при збільшенні довжини аліфатичного ланцюга в гомологічному ряді алканоатів кобальту зумовлено зменшенням як об’ємної концентрації комплексів катіонів кобальту, так і величин дипольних моментів *d*-*d*-переходів.

Ключові слова: іонні термотропні рідкі кристали; смектичні скла; алканоати кобальту; оптичні спектри поглинання.

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