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Electro-conductive properties of cadmium octanoate composites with CdS nanoparticles

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Abstract. Electrical properties of mesogenic cadmium octanoate composites containing CdS nanoparticles (NPs) have been studied for the first time. Semiconductor CdS spherical NPs (sizes of 2.5 nm) were chemically synthesized in the thermotropic ionic liquid crystalline phase (smectic A) of cadmium octanoate that was used as nanoreactor. We compared the electrical properties of both clean matrix and nanocomposite to clarify the role of semiconductor CdS NPs with different concentrations. We have investigated electrical characteristics at different temperatures, which correspond to the different phases of the composites. The conductivity of nanocomposites has an activation nature both in anisotropic glassy and smectic A phase. The conductivity of the nanocomposite along the cation-anion layers is by two orders of magnitude higher than that across the cation-anion layers, which confirms anisotropy of the nanocomposite regardless of the phase of material. In the glassy phase, the electronic type conductivity is observed. Increasing the nanoparticles concentration brings additional free charge carriers or increases their mobility. For the smectic A phase, increasing the CdS NPs concentration brings additional traps for the carriers that travel in plane of the cation-anion layers. On the other hand, the nanoparticles deform the cation-anion layers and increase the mobility of carriers across the layers.

Keywords: octanoate, CdS nanoparticles, ionic liquid crystal, nanocomposite, electrical properties.

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1. Introduction

The new class of ionic liquid crystals based on metal alkanoates possesses a number of unique properties, such as intrinsic ionic conductivity, high solvating power and ability to form time-stable mesomorphic glasses [1]. The mesophase of metal alkanoates can be used as a nanoreactor for chemical synthesis and stabilization of semiconductor nanoparticles (NPs). Earlier, the electrical conductivity of lyotropic and thermotropic ionic liquid crystals of different metal alkanoates was studied [2]. High electrical conductivity was observed in the potassium caproate lyotropic ionic liquid crystals (LILC). It appeared to be higher than that in isotropic water electrolytes [3], which arises from ordering the structure of lyotropic smectic A liquid crystals. On applying an electric field, the potassium cations can easily migrate along the cation-anion layers with water of LILC. The electrical conductivity of the cobalt decanoate mesophase along the cation-anion layers is by four orders of magnitude larger than that in the perpendicular direction due to the homeotropic layer alignment of the thermotropic smectic A phase [2].

In the present work, we investigate electrical properties of both pure cadmium octanoate matrix and cadmium octanoate composites with different concentration of synthesized CdS NPs.

2. Sample preparation and experimental techniques

Cadmium octanoate ($\mathrm{Cd}^{+2}(\mathrm{C_7H_{15}COO})^{-2}$, abbreviation – CdC_8) exists in the form of the polycrystalline powder at room temperature. Within the temperature range 98…180 °C, cadmium octanoate forms the smectic A mesophase (Fig. 1) that can be used for chemical synthesis of semiconductor nanoparticles (NPs) [4]. The smectic A phase of CdC_8 can be frozen by quick cooling to room temperature.

We study cadmium octanoate composites containing CdS NPs, which were synthesized directly in the CdC_8 matrix by the template-controlled method [1]: a cadmium octanoate polycrystalline powder impregnated with a saturated aqueous-alcoholic solution of thiourea was put in a furnace at 150 °C (the temperature of the mesophase of cadmium alkanoates) in argon atmosphere for one hour. Under these conditions, CdS NPs grow in the matrix. After cooling the mesophase of composite to room temperature, the nanocomposite contained CdS NPs (Fig. 2). The starting concentrations of thiourea for preparation of composites were 2, 4, 6 mol.%. It was shown that increasing the concentration of sulphide ions in the matrix does not affect the size of CdS NPs but increases their concentration in the matrix [4].

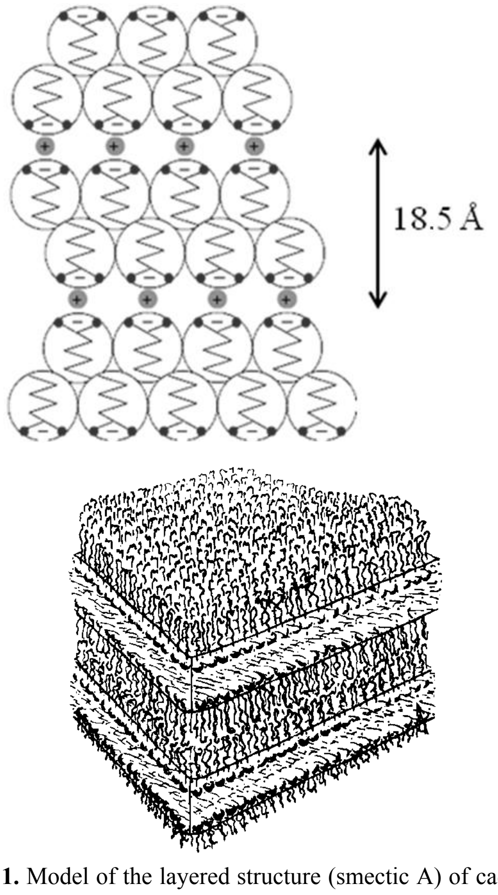


Fig. 1. Model of the layered structure (smectic A) of cadmium octanoate CdC_8.

On the basis of X-ray measurements, the size of synthesized CdS NPs was estimated ≈2.5 nm. Our results show that NPs have a small dispersion of their sizes, and their shape is spherical. The nanocomposites are stable over a long period of time (years) and ordered in a layered matrix (Fig. 2) [5].

The cadmium octanoate composites with CdS NPs placed in flat cell form smectic A domains with homeotropic orientation. The cells were prepared using nickel electrodes and glass supports. Two geometric configurations of samples were used to investigate anisotropy of electrical properties of matrix and composites (Fig. 3). We placed the electrodes in such a way to direct the current perpendicular (Fig. 3a) and parallel (Fig. 3b) to the ionic layers of the nanocomposite. The spacers in the case 3a adjust the thicknesses of the samples. In the case 3b, the thickness is given by the thickness of the electrodes. The thicknesses of samples are chosen to be 30 μm in the case 3a and 1 mm for the case 3b.

The electric conductivity was measured using the oscilloscopic technique (Fig. 4) [6, 7]. The voltage signal had a triangular shape with the pick amplitude 0.25 V. The signal frequency was changed within the range from 50 up to 10^6 Hz. It was found that the resistance of the samples had no dispersion at frequencies above 5×10^3 Hz. Therefore, the electric conductivity was measured at the frequency 10^4 Hz.

The bulk resistance was directly measured in our experiments. Thus, the geometric parameter, k, must be known for each sample to make the calculation of the possible conductivity, $\sigma = k/R$. The geometric parameter, $k = l/(d \cdot z)$, depends on the sample thickness d, the length of the metal electrode z , and the distance between electrodes l.

To make the temperature measurements available, the samples were placed into a thermostat. The temperature was changed from 20 °C up to 200 °C.

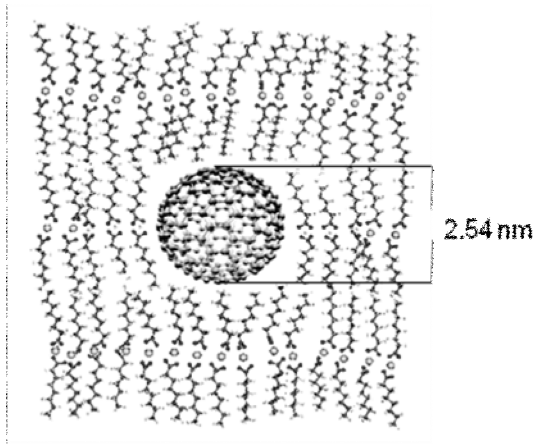
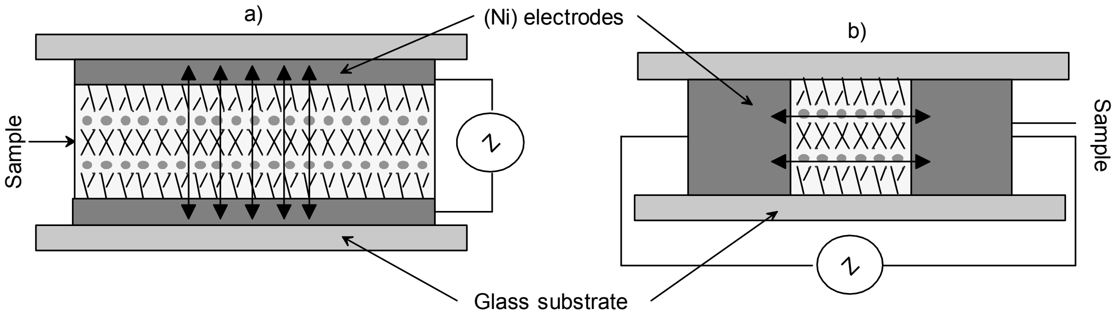


Fig. 2. Model of the nanocomposite with incorporated nanoparticles.



a) Charge transfer across cation-anion layer

b) Charge transfer along the cation-anion layer

Fig. 3. Configuration of the cells used in experiments.

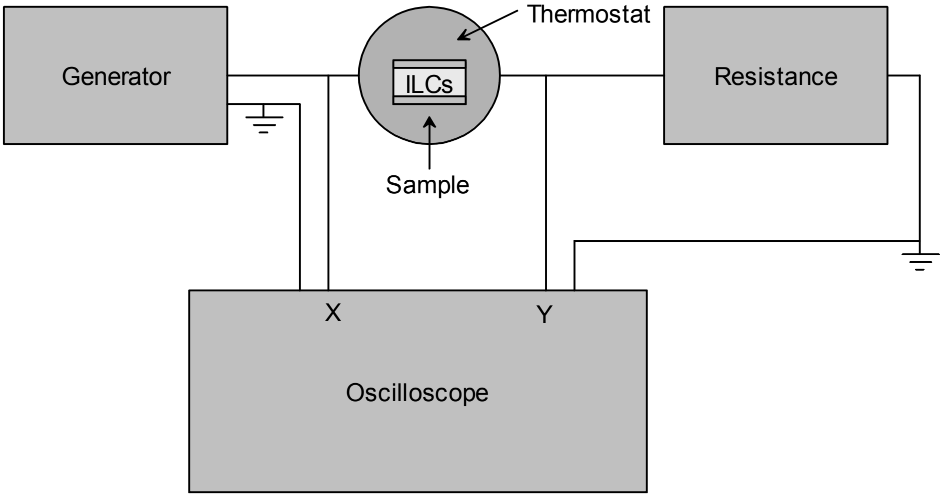


Fig. 4. Setup for measuring the electric conductivity.

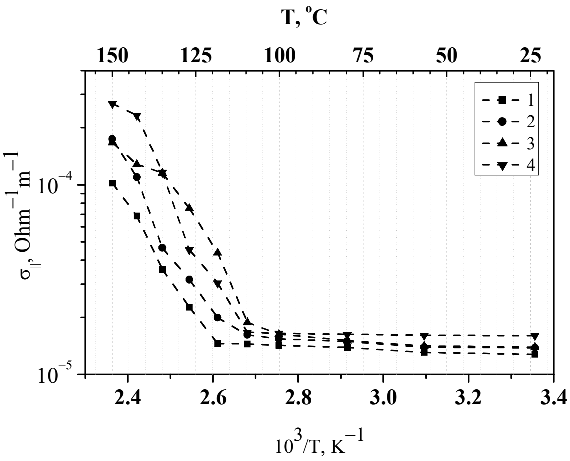


Fig. 5. Electric conductivity $\sigma_{||}$ of matrices CdC_8 (*1*), CdC_8 + 2% CdS (*2*), CdC_8 + 4% CdS (*3*) and CdC_8 + 6% CdS (*4*) versus inverse temperature.

3. Experimental results and discussion

The temperature dependence of the conductivity $\sigma_{||}$ along the cation-anion layers (see Fig. 3b) is shown in Fig. 5. Different symbols and lines correspond to the conductivity of the nanocomposites with a different concentration of NPs: matrix CdC_8 (*1*), CdC_8 + 2% CdS (*2*), CdC_8 + 4% CdS (*3*) and CdC_8 + 6% CdS (*4*). Their analysis shows that the temperature dependences $\sigma(T)$, plotted in the Arrhenius coordinates $\ln\sigma(1/T)$, can be approximated by straight lines for both investigated phases (glass and ionic liquid crystals). Thus, like for the majority of liquid crystals, the temperature dependence of nanocomposite conductivity can be represented as:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \qquad (1)$$

where σ_0 is the parameter depending on the phase of liquid crystal, E_a – activation energy of conduction, k_B – Boltzmann constant.

Similar dependences were measured for $\sigma_\perp(1/T)$, see Fig. 6.

Comparison of the values of $\sigma_\parallel(1/T)$ in Fig. 5 and $\sigma_\perp(1/T)$ in Fig. 6 confirms anisotropy of our materials. The difference by two orders of magnitude arises from the large difference in the mobility of charge carriers along and across the cation-anion layers. Each dependence $\sigma_\parallel(1/T)$ and $\sigma_\perp(1/T)$ can be approximated by two straight lines. Thus, the activation energy, E_a, can be established for both phases and for each concentration of the nanoparticles by using formula (1).

Let us describe the glassy phase first. The dependence of the activation energy, E_a, on the concentration of NPs is presented as the following plot (Fig. 7).

The values of the activation energy are indicative of the electronic nature of conductivity. As stated above, the mobility of electrons in the cation-anion layers is higher than that perpendicular to them. With increasing the nanoparticle concentration, the activation energy decreases. The increase of the number of free charge carriers or their mobility may cause this decrease.

Second, the conductivity significantly grows at temperatures above 100 °C when the glassy nanocomposite turns to the smectic A phase. The anisotropy of conductivity is still as high as in the glassy phase. But the values of the activation energy get much higher (approximately by two orders of magnitude), which states a different type of conductivity. Therefore, we suggest that Cd^{2+} cations are main charge carriers in the smectic A phase of the nanocomposite. The dependences of the activation energy in the smectic A phase of nanocomposites on the concentration of CdS NPs are presented in Fig. 8.

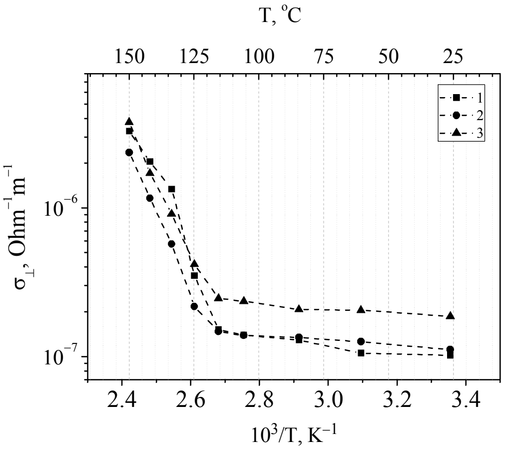


Fig. 6. Electric conductivity $\sigma_\perp$ of matrices CdC_8 (*1*), CdC_8 + 2% CdS (*2*), CdC_8 + 4% CdS (*3*) versus inverse temperature.

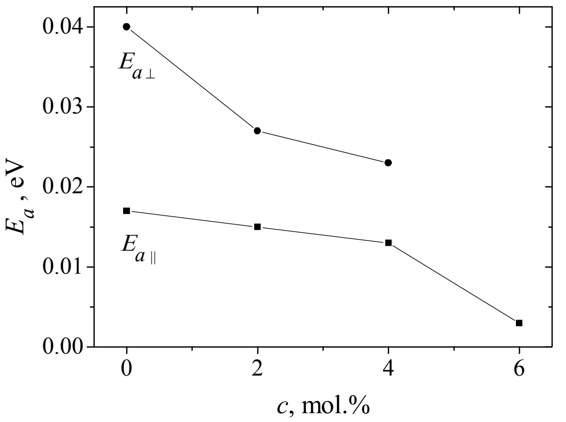


Fig. 7. Conductivity activation energy on the concentration of CdS NPs in glassy nanocomposites across and along the cation-anion layers.

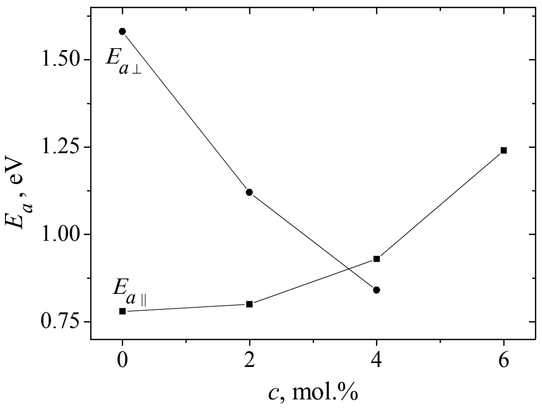


Fig. 8. Conductivity activation energy on the concentration of CdS NPs for the smectic A phase of nanocomposites across and along the cation-anion layers.

Here we can see that the activation energies behave principally different when charge carriers occur either across or along the cation-anion layers. When the carriers move inside the cation-anion layers, $E_{a\parallel}$ grows with the concentration of NPs. This non-evident result can be explained by appearance of new traps due to increasing the number of nanoparticles on the way of carriers. Thus, we have to state that the nanoparticles not only increase the number of charge carriers or mobility, but also create “potential wells” for moving ions, thereby increasing the height of energetic barriers on the way of ions. On the other hand, the nanoparticles deform the alkanoate chains and increase the mobility of carriers across the layers.

4. Conclusions

The conductivity of nanocomposites has an activation dependence both in glassy and smectic A phases. The conductivity of the nanocomposite along the cation-anion layers is by two orders of magnitude higher than that across the cation-anion layers, which confirms anisotropy of the nanocomposite regardless of the phase of materials. In the glassy phase, electrons carry the charge. The increase of the nanoparticle concentration brings additional free charge carriers or increases their mobility. For the smectic phase, increasing the nanoparticle concentration brings additional traps for the carriers that travel in plane of the cation-anion layers. On the other hand, the nanoparticles deform the alkanoate chains and increase the mobility of carriers across the layers. In general, we can conclude that the new nanocomposites based on metal alkanoates with synthesized CdS nanoparticles have very interesting electric properties and are promising for applications in electro-optical devices.

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