




THERMOCHROMIC PROPERTIES OF NANO- AND MICROCOMPOSITES BASED ON $(\text{NH}_2(\text{C}_2\text{H}_5)_2)_2\text{CuCl}_4$ CRYSTALS

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The absorption spectra of $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_2\text{CuCl}_4$ (DEACC) nanocrystals and microcrystals incorporated into the polymer matrices were investigated. The main attention was devoted to the size effects manifestation in the spectral properties of the nano- and microcomposites based on DEACC crystals. It has been found that contrary to the case of the initial bulk crystals undergoing the first order thermochromic phase transition, the composites with the nanocrystals of average size 160 nm are characterized only by continuous change of color. Polymer-based microcomposites with an average microcrystal size of 20 μm were found to possess the thermochromic properties similar to those in a bulk crystal, although their discontinuous thermochromic phase transition was shifted to higher temperatures (316 K) compared to the case of the bulk crystal (311 K). Besides, these microcomposites are characterized by a more diffused hysteresis loop observed on the temperature dependence of the absorption coefficient at the constant wavelength reflecting the hysteresis of the phase transition temperature. The significant effect of the polymer matrix on the phase transition temperature and nature was also detected. Indeed, the polystyrene-based microcomposites with an average microcrystal size of 200 μm were found to possess the thermochromic properties similar to those in a bulk crystal, although their discontinuous thermochromic phase transition was more considerably shifted toward higher temperatures (337 K) compared to the case of the bulk crystal. It was suggested that the “rigid” polystyrene matrix more significantly affects the geometry of the anionic $[\text{CuCl}_4]^{2-}$ complex than the “softer” latex matrix.

Key words: nanostructured materials, phase transitions, optical spectroscopy, thermochromic effect.

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I. INTRODUCTION

The compounds of A_2MeCl_4 and AMeCl_3 ($\text{Me} = \text{Cu}, \text{Co}$) [1–8] groups with an alkylammonium cation have been the subject of considerable attention. Diethylammonium tetrachlorocuprate $(\text{NH}_2(\text{C}_2\text{H}_5)_2)_2\text{CuCl}_4$ (DEACC) crystals grown from a water solution, which belong to this group, undergo a clear discontinuous thermochromic phase transition (PT) at 311 K (at heating) accompanied by a sharp change of the sample color from deep green to pale yellow connected with the change of the copper ion coordination. Such a change manifests itself in the shift of the principal spectral bands corresponding to the internal transitions of Cu^{2+} ion by about 50 nm [4]. DEACC crystals grown from alcohol were found to undergo the thermochromic phase transition at higher temperatures — 323 K (at heating) [1, 4]. It was suggested that the structure of both modifications of DEACC crystals is the same [1, 2, 4].

The crystal structure of DEACC consists of DEA^+ cations and metal-halogen complexes (MHC) connected by the hydrogen bonds. The high-temperature phase is characterized by a distorted tetrahedral environment of the copper ion, whereas in the case of the low-temperature phase, the tetrahedral and planar square coordinations coexist [1, 4, 7, 8]. At the room temperature, a phase crystal belongs to the space group

$P2_1/n$. The parameters of the unit cell are: $a = 7.362 \text{ \AA}$, $b = 15.025 \text{ \AA}$, $c = 45.193 \text{ \AA}$, $\beta = 89.94^\circ$, and $z = 12$. One asymmetrical structural group includes three tetrahedral and nine square planar $[\text{CuCl}_4]^{2-}$ ions in an abnormally large cell. In the first approximation, they can be considered to possess the D_{2d} symmetry. The crystal system in the high-temperature phase is also monoclinic with the space group $P2_1/c$ ($a = 25.055 \text{ \AA}$, $b = 10.531 \text{ \AA}$, $c = 15.455 \text{ \AA}$, $\beta = 100.6^\circ$, and $z = 8$) [1, 4]. In this phase, two independent crystallographic $[\text{CuCl}_4]^{2-}$ ions have the shape of a distorted tetrahedron.

The performed analysis shows that the key effect responsible for the thermochromic first order phase transition consists in the transformation of the square planar MHC to the tetrahedral shape at heating [1, 2, 4]. Indeed, the low temperature “green” phase is characterized by the coexistence of the tetrahedral and square planar coordinations of the copper ion, whereas the structure of the high temperature “yellow phase” contains only the tetrahedral copper-halogen complexes [1, 4]. Due to their specific thermochromic properties, DEACC crystals are considered to be the prospective materials for sensor technique, in particular, for thermography as well as for the optical data storage. Unfortunately, their technical application is restrained because of the hygroscopicity and instability of their spectral parameters after repeated thermal cycling near the PT [2, 4]. It is expected that the incorporation of



the nanocrystals (NCs) of the mentioned substances into the polymer matrix could resolve this problem. Besides, in such a case one can observe manifestations of the quantum confinement effects and related phenomena in the absorption spectra of such a type of materials [9–12].

It has been shown that the absorption spectra of DEACC are considerably modified at the transition from bulk crystals to a nanostructural state in the range of 12 000–28 000 cm^{-1} [13]. Such a change is connected with the specific symbiosis of the quantum confinement effects and specific surface phenomena. The quantum confinement effect in the NCs with sizes limited by 10 nm clearly manifested itself in the considerable narrowing of the absorption band corresponding to the internal transition of Cu^{2+} ion. It was shown that the lateral tension arising on the surface of NC suppresses the square planar coordination characteristic of the low temperature phase of the bulk crystal. As a result, the thermochromic phase transition was not observed in the nanocrystals of DEACC [13].

Incorporation of the NCs of DEACC into the polymer matrix allowed us to identify clearly the charge transfer (CT) bands of ligand-metal types $\text{Cl } 3p \rightarrow \text{Cu } 3d_{x^2-y^2}$ in the spectral range of 21 000–26 500 cm^{-1} that could not be observed in the absorption spectra of the bulk crystal. The theoretically calculated oscillator strengths for the allowed CT bands agree fairly well with the oscillator strengths of the corresponding bands in the experimentally observed absorption spectra of DEACC NCs [13].

In any case, on the basis of the obtained spectra of the nanocomposites an opportunity appears to estimate the approximate energy of the CT transitions which is impossible for the bulk crystals due to the very high absorption.

This work is devoted to a detailed study of the size effects manifestation in the spectral properties of the nano- and microcrystals (MCs) of DEACC embedded into the polymer matrices. The works [10–12] show that the incorporation of NCs into the polymer matrix opens new opportunities for using nanocomposites. First of all, it is important to check how the thermochromic effect would manifests itself in the parameters of the CT bands observed in the nanocomposites. On the other hand, from the practical point of view, possible thermochromic properties of the microcomposites based on DEACC demand a detailed study. The main reason for this type of investigations consists in the elaboration of the nonhygroscopic thermochromic material for thermography and optical storage devices. It is also important to investigate the impact of the polymer matrices on the properties of these MCs.

II. EXPERIMENTAL

The DEACC crystals were grown from an aqueous solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $[(\text{C}_2\text{H}_5)_2\text{NH}_2]\text{Cl}$ salts, taken in a stoichiometric ratio, using the method of slow evaporation at room temperature [13].

On the basis of the grown single crystals, we prepared three types of composites: nanocrystals in polycarbonate and microcrystals in latex and polystyrene, respectively.

The preparation of the nanocomposites consisted in the dispersion of DEACC nanocrystals in the polymer. Polycarbonate (PC) was used as a polymer matrix.

At the first stage, DEACC single crystals were mechanically milled into fine particles. Then the mixture of the obtained particles in the liquid polymer was treated by an acoustic field during one hour. The prepared composition was filtered and deposited on the BK7 glass substrate using the spin coating method. Nanocrystals of a certain size were selected using the membrane filter. As it follows from the SEM microscopy data, the average size of the NCs in this case was 160 nm. The use of such polymer matrices allows us to avoid the influence of significant mechanical stresses on NCs, which are commonly observed when using traditional “rigid” polymers [14, 15].

The preparation of the microcomposites consisted in the dispersion of DEACC microcrystals in a polymer. Latex and polystyrene (PS) were used as polymer matrices.

Firstly, DEACC single crystals were crashed into a “powder” mechanically. Microcrystals of a certain size were selected using the filter and dispersed in the liquid polymer. The prepared composition was deposited on the BK7 glass substrate using the spin coating method. A thin latex film with the evenly distributed microcrystals inside was formed upon drying. As it follows from the optical microscopy data, the average sizes of the MCs in latex were close to 20 μm and in PS — close to 200 μm . The samples produced this way were of a good quality and stability for the surrounding environment background.

The samples of nano- and microcomposites were not hygroscopic, contrary to the bulk crystals. They were semitransparent and the microcomposites were of a light green color.

The nonpolarized absorption spectra of the single crystals and nanocomposites were investigated at different temperatures in the spectral region from 250 nm up to 850 nm using a computerized ZMR-3 monochromator with a spectral resolution of 1 nm. The absorption spectra of the microcomposites were recorded in the spectral range from 300 nm up to 850 nm using a computerized AvaSpec-2048L spectrometer with the CCD linear detector.

III. RESULTS AND DISCUSSIONS

Taking into account, that contrary to the case of DEACC bulk crystals, the corresponding composites based on the nanocrystals (NCs) did not manifest any changes in the crystal field spectral bands parameters characteristic of the sharp thermochromic effect [13], we decided to investigate the temperature evolution of their CT bands. Moreover, in this case we used a composite with larger NCs (160 nm).

The absorption spectrum of DEACC NCs incorporated into the PC polymer matrix is shown in Fig. 1. The clear band observed at $25\,200\text{ cm}^{-1}$ has to be related to the CT transition of a ligand-metal type ($\text{Cl } 3p \rightarrow \text{Cu } 3d_{x^2-y^2}$) [13].

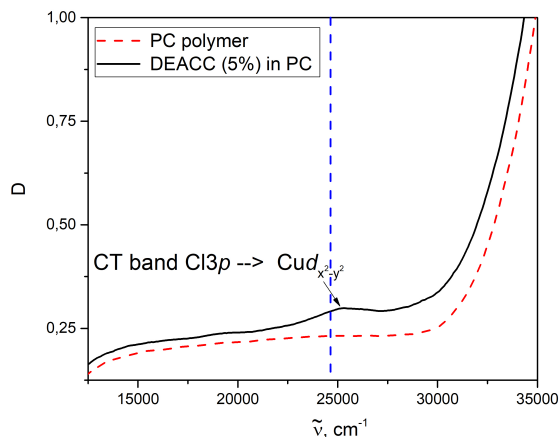


Fig. 1. Absorption spectra of DEACC (5%)-PC nanocomposite and PC polymer matrix

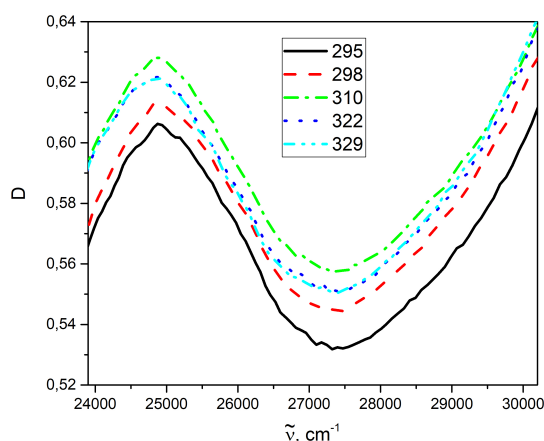


Fig. 2. The temperature evolution of the absorption spectra of DEACC (7%)-PC nanocomposite

The temperature dependence of the absorption spectra of DEACC NCs+PC composite with a higher concentration of NCs is depicted in Fig. 2. They are characterized by the same single CT band of higher intensity in comparison with those presented in Fig. 1. Moreover, its intensity increases at heating, reflecting a decrease in the sample transparency. At the same time, the band position practically does not depend on the temperature in the vicinity of the expected thermochromic phase transition.

The temperature dependence of the optical density at $\lambda = 406\text{ nm}$ ($24\,630\text{ cm}^{-1}$) corresponding to the maximum of the CT band in DEACC (5%)-PC nanocomposite manifests a noticeable but continuous change in the vicinity of $T = 313\text{ K}$ (Fig. 3), which would be considered a thermochromic effect. On the other hand, we did

not observe any noticeable hysteresis of this dependence characteristic of the first order thermochromic phase transitions. Moreover, the sample's color is practically independent of the temperature contrary to the case of a bulk crystal, which correlates with the conclusions made in [13] concerning the temperature changes of the crystal field bands.

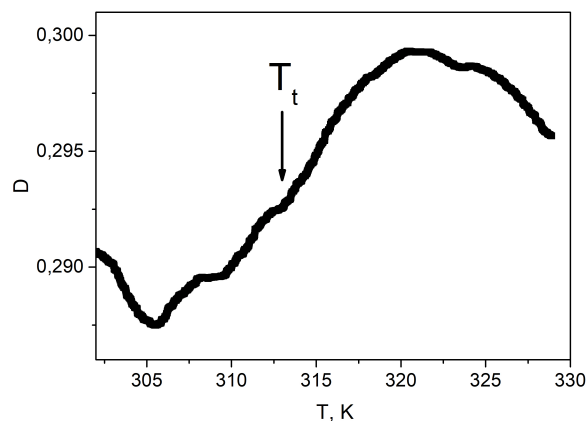


Fig. 3. The temperature dependence of the optical density of DEACC (5%)-PC nanocomposite at the fixed wavelength $\lambda = 406\text{ nm}$ ($24\,630\text{ cm}^{-1}$)

Taking into account that the considered CT band corresponds to the electronic transition on the $\text{Cu } 3d_{x^2-y^2}$ level, the continuous PT in the nanocomposite does not affect considerably Cu^{2+} ion coordination. Both low and high temperature phases are characterized only by tetrahedral copper-halogen complexes. The square planar complexes characteristic of the low temperature phase in the bulk single crystals are eliminated from NCs due to the size effect connected with the surface phenomena. According to the supposition made in [13], such a phenomenon is connected with the distortion of the square planar metal-halogen complexes within the surface layers of the nanocrystal due to the surface tension. One can expect that the ratio of these distorted surface complexes increases when the cluster sizes diminish. The arising of the lateral tension is a characteristic feature of the NCs of a different type [16]. It can be expected that the fraction of the distorted surface complexes will increase as the size of the nanocrystals decreases due to the increase in the surface/volume ratio. In our case, due to the effect of such a tension, of the two possible forms of MHC only a tetrahedral environment remains in the surface layer of a given crystal [13]. At the same time, it is necessary to mention the difference between the composites with NCs of small and larger sizes. Indeed, as it follows from the data of a previous study [13], the composites with small NCs (10 nm) do not show any changes that have to be linked to the thermochromic effect. In our case, the composite with the considerably larger sizes (160 nm) of the NCs undergoes a continuous thermochromic PT. It is clear that in this case the surface/volume ratio is much smaller and the properties of the NCs become closer to those in the bulk crystal.

1	2	3	4	5	6	7	8	9	10
Band	Transition energy, [eV] (cm^{-1})							Transitions	
	Calculated energy levels (ECM data) [9]		T , K					from $3d_{x^2-y^2}$ on:	from d_{xy} on:
	T_d	O_h	DEACC bulk		Microcrystals 20 [μm] DEACC (latex matrix)		Nano-crystals 10 [nm] DEACC PC matrix	O_h	T_d
			293 [K]	314 [K]	290 [K]	318 [K]	293 [K]		
<i>A</i>	1.461 (11 778), 1.508 (12 161)	1.564 (12611)	—	—				d_{xy}	$d_{yz,xz}$
<i>B</i>	1.678 (13 522)		1.735 (13 980)	1.623 (13 080)	1.630 (13 155)	1.612 (13 005)	1.599 (12 890)		$d_{x^2-y^2}$
<i>C</i>	2.038 (16 426)	1.915 (15 430)	1.902 (15 325)	1.805 (14 560)	1.735 (14 000)	—		d_{z^2}	d_{z^2}
<i>D</i>		2.183 (17 607)	2.103 (16 945)	— (16000)	1.983			d_{xz}	
<i>E</i>		2.187 (17 640)	2.191 (17 655)	—				d_{yz}	

Table 1. Identification of the absorption bands corresponding to the internal transitions of Cu^{2+} ion for different phases of DEACC: bulk crystal [13] and composites based on micro- and nanocrystals

One can expect that the microcomposites would be much close in their properties to the bulk crystals since the surface phenomena in this case have to be less pronounced. The absorption spectra of DEACC MCs based on the latex in the visible and near infrared region are presented in Fig. 4. The MCs are characterized by considerably broadened asymmetric bands in the low energy part of the spectra. They have to be attributed to the internal transition of Cu^{2+} ion. The corresponding electron transitions could be identified only using the approximation of the observed broad bands by the Gaussian contours. Such a procedure is described fairly well in [4]. The results of the band identification are presented in Table 1 in comparison with those for the bulk single crystal [13].

The spectra of the MCs with a latex matrix (Fig. 4a,b) are very similar to those for the bulk crystals. In the high temperature “yellow” phase, the two bands (*B*, *C*) corresponding to the electron transitions within the tetrahedral metal-halogen complexes are observed. At the same time, as it follows from the obtained data, the low temperature “green” phase is characterized by the coexistence of the tetrahedral and square planar coordinations of copper ion. In the last case the crystalline field is much stronger, which leads to the clear shift of the corresponding band *D* (*D*, *E* for the bulk crystal) toward higher energies in comparison with the case of tetrahedral complexes. Due to this, the transparency window in the low temperature “green” phase manifests a considerable blue shift in comparison with those in the high temperature “yellow” phase. It is necessary to note that the band *C* is common for both types of coordinati-

ons.

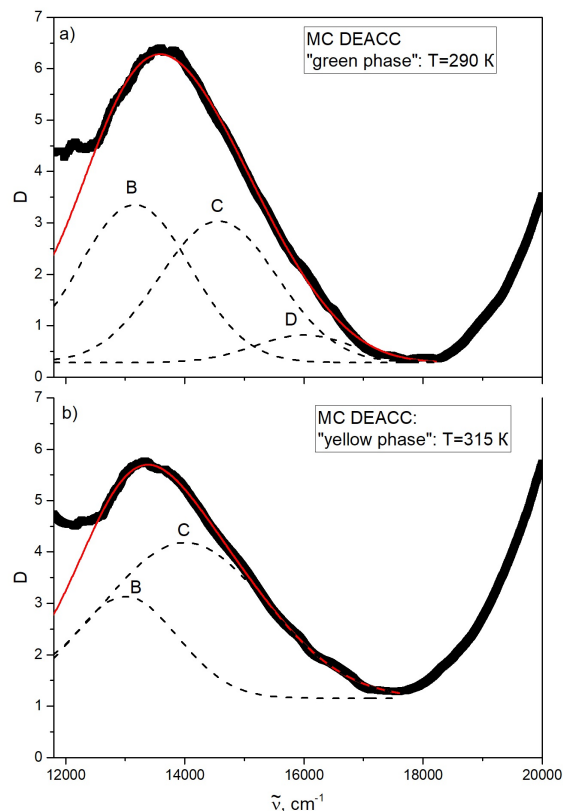


Fig. 4. The absorption spectra of DEACC+latex microcomposite approximated with Gaussians (dashed lines) at: a) 294 K; b) 318 K. The red lines present the sum of the Gaussians

The sharp growth of absorption in the region of higher energies (above $18\,000\text{ cm}^{-1}$) in the spectra of the MCs should be related to the edge of the mentioned CT band observed in the nanocomposite. Unfortunately, the bands of such a type cannot be fully observed due to the very large absorption similarly to the case of the bulk crystal.

The temperature dependences of the optical density of the microcomposites with the latex matrix obtained at the constant wavelength (Fig. 5,b,c: $\lambda = 530\text{ nm}$ and $\lambda = 633\text{ nm}$ respectively) are compared with those for the bulk crystal (Fig. 5,a: $\lambda = 633\text{ nm}$). The latter is characterized by the hysteresis loop of the rectangular shape. The sharp jumps of the absorption coefficient reveal the temperatures of the thermochromic PT at cooling ($T_t^c = 306\text{ K}$) and heating ($T_t^h = 311\text{ K}$) reflecting its first order.

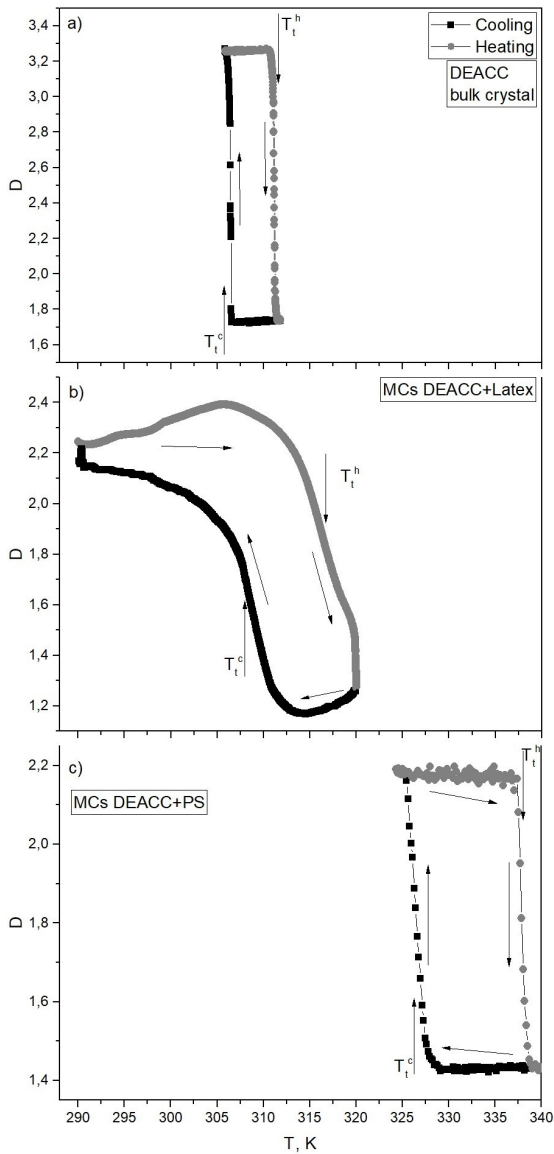


Fig. 5. The temperature dependences of the optical density of DEACC bulk crystal (a) and of MCs in latex (b) at $\lambda = 633\text{ nm}$ ($15\,800\text{ cm}^{-1}$) and in PS matrix (c) at $\lambda = 590\text{ nm}$ ($16\,949\text{ cm}^{-1}$)

As it follows from Fig. 5,b, the microcomposites with the latex matrix also are characterized by the hysteresis loops, but they look broader and more diffused than in the case of DEACC bulk crystal. Nevertheless, one can conclude that the composites based on DEACC MCs undergo a clear but a little diffused thermochromic PT of the first order in the vicinity of 316 K (at heating) accompanied by a considerable change in the sample colour from deep green to pale yellow. The observed shift of the PT temperature in the MCs compared to the case of the bulk crystal as well as the distorted shape of the hysteresis loop would be explained by the influence both of the polymer matrix and surface phenomena that still are important in the microcomposite [12].

The microcomposites with polystyrene matrix also are characterized by the hysteresis loop, very similar to those in DEACC bulk crystal (Fig. 5). These microcomposites undergo the thermochromic PT of the first order in the vicinity of 337 K (at heating) accompanied by a drastic change in the sample colour from deep green to pale yellow. It is clear from the temperature dependence of the optical density of these microcomposite measured at $\lambda = 590\text{ nm}$ ($18\,870\text{ cm}^{-1}$). The shift of the phase transition temperature is associated with the influence of the PS matrix. The clear hysteresis loop observed in this case looks most attractive for the practical application of this microcomposite.

A significant effect of the polymer on the physical and chemical properties of the crystal is noticeable. The shift of the phase transition temperature is much more pronounced in the composite based on polystyrene than in the latex-based microcomposites. Apparently, the phase transition in MCs similarly to the bulk crystal is accompanied by a redistribution of the hydrogen bonds. In the low-temperature phase, the strong hydrogen bonds cause a distortion of the electron cloud of chlorine ions, and this allows a part of the $[\text{CuCl}_4]^{2-}$ anions to acquire the distorted planar form. In the high-temperature phase with the weak hydrogen bonds, the copper ion is in the tetrahedral environment. A change in the anion geometry leads to the thermochromic nature of the phase transition, i.e., the substantial change in the sample color [4]. Because polystyrene is a more “rigid” polymer, it significantly affects the anion geometry of the crystals due to the piezochromic effect, thereby shifting the phase transition temperature to higher values. Latex belongs to more flexible polymers, consequently the influence on the anion complexes’ stiffness was based on the comparison of their Young’s modulus [17,18].

IV. SUMMARY

The detailed study of the size effects manifestation in the spectral properties of the nano- and microcrystals of DEACC embedded into the polymer matrices was performed.

It was known that the thermochromic phase transition was not observed in a composite based on the comparati-

vely small (10 nm) nanocrystals of DEACC. In this work, we found that a composite with considerably larger sizes (160 nm) of the nanocrystals undergoes a continuous thermochromic phase transition, which first of all, affects the CT band. In this case, the surface/volume ratio is much smaller and the properties of the NCs become closer to those in a bulk crystal. In the nanocomposites, the phase transition temperature is shifted to 320 K.

The microcomposites were found to have the thermochromic properties very similar to those of a bulk crystal. They undergo a clear but a little diffused thermochromic PT of the first order in vicinity of 316 K for the case of a latex matrix (at heating). MCs with a polystyrene matrix show a very sharp thermochromic phase transition at a much higher temperature — 337 K. In both cases, PT is accompanied by a considerable change in the sample color from deep green to pale yellow. The observed shift of the PT temperature in

the MCs compared to the case of a bulk crystal as well as the distorted shape of the $D(T)$ hysteresis loop observed in the case of the latex matrix would be explained by the influence both of the polymer type and surface phenomena that are still important in the microcomposite.

The “rigid” polystyrene matrix significantly changes the geometry of the anionic complex $[\text{CuCl}_4]^{2-}$ due to the arising stresses and corresponding piezochromic effect, whereas the influence of a “softer” latex matrix was found to be less pronounced.

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ТЕРМОХРОМНІ ВЛАСТИВОСТІ НАНО- ТА МІКРОКОМПОЗИТІВ НА ОСНОВІ КРИСТАЛІВ $(\text{NH}_2(\text{C}_2\text{H}_5)_2)_2\text{CuCl}_4$

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Досліджено спектри поглинання нанокристалів і мікрокристалів $(\text{NH}_2(\text{C}_2\text{H}_5)_2)_2\text{CuCl}_4$ (DEACC), впроваджених у полімерні матриці. Основну увагу приділено прояву розмірних ефектів у спектральних властивостях нано- та мікрокомпозитів на основі кристалів DEACC. Установлено, що всупереч вихідним об'ємним кристалом, які зазнають термохромного фазового переходу першого порядку, композит із нанокристалом середнього розміру 160 нм характеризується лише плавною зміною

кольору. Мікрокомпозити на основі латексу із середнім розміром мікрочастин 20 мкм мали термохромні властивості, аналогічні до властивостей об'ємного кристала, хоча їхній стрибкоподібний термохромний фазовий перехід змістився до вищих температур (316 К) порівняно з об'ємним кристалом (311 К). Крім того, ці мікрокомпозити характеризуються більш розмитою петлею гістерезису, яка спостерігається на температурній залежності коефіцієнта поглинання на постійній довжині хвилі, що відображає гістерезис температури фазового переходу. Виявлено також істотний вплив полімерної матриці на температуру та характер фазового переходу. Справді, мікрокомпозити на основі полістеролу із середнім розміром мікрочастин 200 мкм мали термохромні властивості, аналогічні властивостям об'ємного кристала, хоча їхній стрибкоподібний термохромний фазовий перехід був істотніше зміщений у бік високих температур (337 К) щодо об'ємного кристала. Висловлено припущення, що "жорстка" полістирольна матриця значно більше впливає на геометрію аніонного $[\text{CuCl}_4]_2^-$ комплексу, ніж "м'якша" латексна матриця.

Ключові слова: наноструктуровані матеріали, фазові переходи, оптична спектроскопія, термохромний ефект.