A. TOLOCHKO,[1] P. TESELKO,[2] A. LYASHCHOVA,[1] D. FEDORENKO,[1]
G. KLIMUSHEVA,[1] T. MIRNAYA,[3] V. ASAULA [3]

[1] Institute of Physics, Nat. Acad. of Sci. of Ukraine
  (46, Nauky Ave., Kyiv 03680, Ukraine; e-mail: klimush@iop.kiev.ua)
[2] Taras Shevchenko National University of Kyiv
  (2, Academician Glushkov Ave., Kyiv 03022, Ukraine)
[3] Vernadskyi Institute of General and Inorganic Chemistry, Nat. Acad. of Sci. of Ukraine
  (32/34, Academician Palladin Ave., Kyiv 03142, Ukraine)

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STRUCTURE AND SPECTRAL PROPERTIES OF NEW COMPOSITES BASED ON METAL ALKANOATES WITH GOLD NANOPARTICLES

New composites with gold nanoparticles (NPs) have been chemically synthesized in the liquid crystal phase of cadmium and cobalt octanoates. Polymorphism and basic structural characteristics of metal alkanoates and nanocomposites (metal alkanoates with gold NPs) are analyzed, by using the small-angle X-ray scattering method. The structural parameters of gold NPs (their form and dimensions) are estimated by the X-ray spectroscopy and transmission electron microscopy techniques. The dependences of the NP absorption spectra on the spectral properties of cadmium- and cobalt-octanoate matrices are analyzed.

K e y w o r d s: nanocomposites, gold nanoparticles, metal alkanoates, absorption spectra, small-angle X-ray scattering.

1. Introduction

Nanostructured materials draw attention of researchers owing to their considerably enhanced nonlinear optical response resulting from the quantum-dimensional effect in nanoparticles (NPs). Those materials find application in optoelectronics. Namely, they can be used as optical limiters [1], and switches [2], as well as to store optical information [3]. There are a number of methods for the nanocomposite preparation, e.g., the insertion of NPs into a liquid matrix to form a suspension or the creation of NPs in a solid matrix, in particular, by the ionic implantation [4], laser ablation [5, 6], and various chemical methods [7, 8]. In particular, those methods were used to obtain nanocomposites with particles of such metals as Ag, Au, and Cu in organic [6], glass [5], and liquid crystal [9] matrices, as well as in colloid solutions [7, 8].

Nanocomposites on the basis of liquid crystals (LCs) with gold NPs form a separate and rather interesting direction of researches from both the scientific and application viewpoints. Regular researches of surface-functionalized gold NPs in various liquid crystal phases ranging from the one-dimensionally ordered nematic phase through the two-dimensionally ordered smectic one to the three-dimensionally ordered columnar phase were successfully carried out in work [9]. Liquid-crystal-based nanocomposites possess a number of advantages, owing to the combination of unique properties inherent to liquid crystals and nanodimensional particles. In particular, the parameters of a surface plasmon resonance for metal NPs can be changed as a result of the interaction with the liquid crystal matrix. Moreover, the properties of liquid crystals can be changed by introducing NPs into them.

Researches of gold NPs in solid matrices have also demonstrated a considerable nonlinear optical response of those nanocomposites, especially in the interval of their surface plasmon resonance [5]. In particular, an optical restriction of the intensity was found experimentally, when a nanocomposite of Au NPs in a glass matrix was irradiated with nanosecond laser pulses [10]. Let us consider the structural features of nanocomposites on the basis of metal alkanoates. Note that this class of composite materials has a number of advantages from the viewpoint of their synthesis and stability.

Metal alkanoates compose a wide class of ionic liquid crystals. Owing to the Coulomb interaction, the structure of a metal alkanoate corresponds to that of smectic A. In addition, as a result of the strong coupling between molecular layers, the temperature interval of LC phase existence (100–200 °C) is much larger than for ordinary nematic LCs with elongated electrically neutral molecules. The most interesting property of ionic LCs is that the smectic ordering of molecules survives at the cooling of a smectic ionic LC down to room temperature. Hence, at room temperature, the ionic LCs exist in the form of an anisotropic layered glass combining the orientational ordering characteristic of LCs and the spatial arrangement of structural elements typical of solids.

The liquid crystal phase of a thermotropic ionic LC can be used as a nanoreactor for the synthesis and the stabilization of various particles. In so doing, by changing metal ions and the length of alkanoate chains in the matrices, we can modify the dimensions and the shape of synthesized NPs [11]. Since the parameters of the obtained nanocomposite appreciably depend on the synthesis conditions, it is necessary that the structure of obtained nanocomposites and the influence of the synthesized gold nanoparticles on the spectral and nonlinear optical properties of matrices (in particular, cadmium and cobalt octanoates) be studied in detail.

2. Nanocomposite Synthesis and Matrix Polymorphism

Gold nanoparticles were synthesized in matrices of cobalt octanoate $Co^{+2}(C_7H_{15}COO^{-2})$ – in brief, CoC_8 – and cadmium octanoate $Cd^{+2}(C_7H_{15}COO^2)$ – in brief, CdC_8 – by reducing hydrogen tetrachloroaurate(III) $H[AuCl_4] \cdot 3H_2O$ [11].

The synthesis procedure was performed in one stage in an inert atmosphere for 2 h by maintaining the reaction mixture at a temperature in the interval of the smectic A liquid crystal phase existence (100–150 °C). In the course of synthesis, the cadmium octanoate matrix simultaneously plays the roles of a reducing agent and a stabilizer. According to rough estimates (by the expense of reagents), the molar concentration of Au in the obtained nanocomposite specimens amounted to about 4%. At the next synthesis stage, the ionic smectic mesophase of the synthesized nanocomposite was slowly cooled down to room temperature. As a result, a polycrystalline powder of cadmium octanoate with gold NPs was obtained.

Gold NPs in the cobalt octanoate matrix were synthesized in a similar way.

3. Small-Angle X-ray Scattering

The structure of nanocomposites on the basis of cobalt and cadmium octanoates with gold NPs was studied using the method of small-angle X-ray scattering.

3.1. Specimen fabrication

Nanocomposite specimens fabricated in the form of a fine-dispersed powder were put, as densely as possible, into thin-walled (0.01 mm) Lindemann capillary tubes 1 mm in diameter. When studying the nanocomposites in the mesomorphic state, the capillary tubes with specimens were arranged in a the temperature chamber with thin Dacron windows for X-ray irradiation. The specimen temperature was measured with the help of a copper-constantan thermocouple with an accuracy of 0.2 °C.

3.2. Small-angle X-ray scattering technique

In the course of experiments, we used an automatic small-angle X-ray diffractometer created on the basis of an AMUR-1 goniometer with a slit collimator. As a radiation source, we used a fine-focus X-ray tube with a copper anode (a line focus 0.4×8 mm^2 in dimensions). The experimental conditions were selected as follows: the voltage $U = 40$ kV, the current $I = 20$ mA, a nickel monochromator, a distance of 500 mm between the tube and the specimen, and a distance of 350 mm between the specimen and the detector. The intensity of scattered radiation was mea-
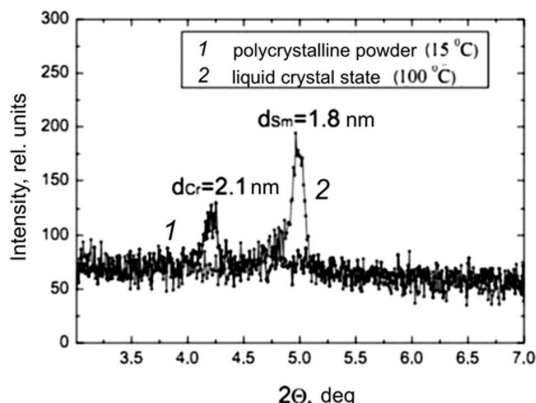
Fig. 1. Small-angle roentgenograms of Co(C₇H₁₅COO)₂ + + Au nanocomposite in the crystalline and smectic phases
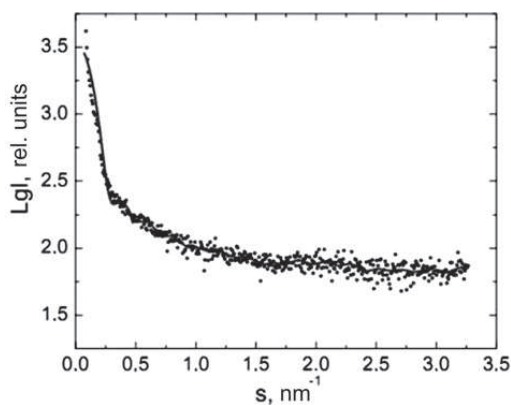
Fig. 2. Experimental and calculated scattering intensities in the interval of small scattering angles (Co(C₇H₁₅COO)₂ + Au nanocomposite in the smectic phase)

sured in the interval of scattering angles $2\theta = 0.08 \div 7°$ with the scanning step $\Delta 2\theta = 0.01°$. The time of pulse accumulation at every point was $t = 30$ s.

3.3. Nanocomposite $Co^{+2}(C_7H_{15}COO^{-2})$ with Au nanoparticles

In the small-angle roentgenogram of the CoC₈ + + Au NPs nanocomposite obtained at a temperature of 100 °C, a maximum of scattering from the cobalt alkanoate matrix in the smectic state is observed. It corresponds to the bilayer period $d_{Sm} = 1.8$ nm (Fig. 1). At room temperature of the nanocomposite, when the matrix is in the crystalline state, the lattice period $d_{Cr} = 2.1$ nm. The indicated d_{Sm} and d_{Cr} values coincide very well with the periods obtained by us earlier for pure cobalt octanoate [12]. This fact con-

firms that no structural changes occur in the matrix concerned during the synthesis of gold NPs.

Information on the size and the shape of Au NPs can be obtained by analyzing the dependence of the scattered radiation intensity on the scattering angle in the interval of smallest angles $2\theta = 0.08 \div 4°$. For this purpose, we used the Guinier approximation, provided that the magnitude of scattering vector $s = 4\pi \sin \theta / \lambda \to 0$, and an approach on the basis of the correlation function, which is calculated with the help of the indirect Fourier transform (the program GNOM [13] of the software package AT-SAS 2.5 [14]). The analysis of the small-angle X-ray scattering curve in the Guinier coordinates showed that the examined nanosystem was not monodisperse enough. Therefore, the error for the radius of inertia R_g determined from the Guinier approximation can be rather considerable as a result of the deviation from a linear dependence in the plot $\lg I(s^2)$ and the violation of the condition $sR_g < 1.5$. Taking this circumstance into account, we calculated the particle distribution function over the particle radius, $D_v(R)$, using the program GNOM and the integral equation

$$I(s) = \int_{R_{\min}}^{R_{\max}} D_\nu(R) m^2(R) i_0(sR) dR. \qquad (1)$$

Here, R is the particle radius; $R_{\min}$ and $R_{\max}$ are its minimum and maximum values, respectively; and $i_0(sR)$ and $m^2(R)$ are the form factor and the volume of the particle, respectively. For the analyzed system, we used the approximation of hard polydisperse spherical particles, so that the value of $R_{\min}$ was considered to equal zero, and $R_{\max}$ was selected to provide the best fitting of experimental data by the theoretical curve for the scattering intensity. The calculation by Eq. (1) is more stable to the influence of the polydispersion character and the aggregation of particles, because it includes the whole angular interval of measured intensities. As one can see from Fig. 2, the experimental data for the intensities are in rather a good agreement with the results calculated in the framework of the model of polydisperse spherical particles (the solid curve).

The solution with the program GNOM was found with the help of the regularization method. The reliability of the obtained numerical solution, according to the general criterion TOTAL, was higher than

0.75, which we consider as a rather confident result. It should be noted that a higher accuracy of calculations could not be achieved because of the small intensity of scattered radiation owing to its high absorption by heavy metals in the specimens and to the complications at the consideration of the effect of breaking of the experimental curve at the minimum, $s_{\min}$, and maximum, $s_{\max}$, values of scattering vectors.

In Fig. 3, the distribution function over the radii of spherical gold NPs in the smectic matrix of cobalt octanoate is depicted. In such a way, we estimated the shape of Au particles in the examined nanocomposite as close to spherical, and the average radius of particles is equal to 6–7 nm.

3.4. Nanocomposite CdC$_8$ with Au NPs

We calculated the electron radius of inertia of gold particles, R_g, using the Guinier extrapolation as $s \to \to 0$. According to our estimations, the average value of R_g amounted to about 10 nm. However, because of a low approximation accuracy, the calculation error is rather considerable and reached 30%.

To visualize the distribution of gold particles in the volume of a polycrystalline nanocomposite powder, the specimens were studied on a transmission electron microscope (TEM) "Selmi PEM-125K". The accelerating voltage was 100 kV. The obtained TEM images of gold particles in the cadmium octanoate matrix and the corresponding distribution histogram for NP diameters are shown in Fig. 4. One can see that the most probable diameter of spherical NPs calculated from the TEM image amounts to 14 ± 3 nm.

4. Spectral Researches of Glassed Nanocomposites

4.1. Specimen fabrication

Specimens of pure cadmium octanoate (CdC$_8$) and cobalt octanoate (CoC$_8$), as well as CdC$_8$ and CoC$_8$ with synthesized Au particles (4 mol.% in both), were prepared for spectral researches as follows. The polycrystalline powder of the nanocomposite (or matrix) was arranged between two plane glass substrates heated up to the mesophase temperature (100 °C). The specimen thickness in the cell was selected with the help of spacers and equaled
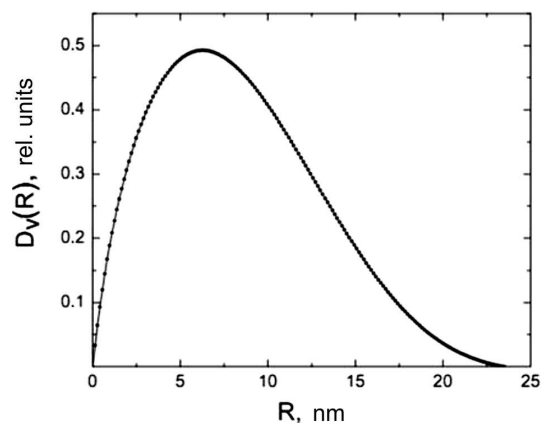

Fig. 3. Distribution function of spherical gold NPs over their radii, $D_v(R)$, in the cobalt octanoate matrix (the smectic phase)

18 μm. Being quickly cooled down to room temperature, the examined substance in the cell acquired the structure of anisotropic glass [15].
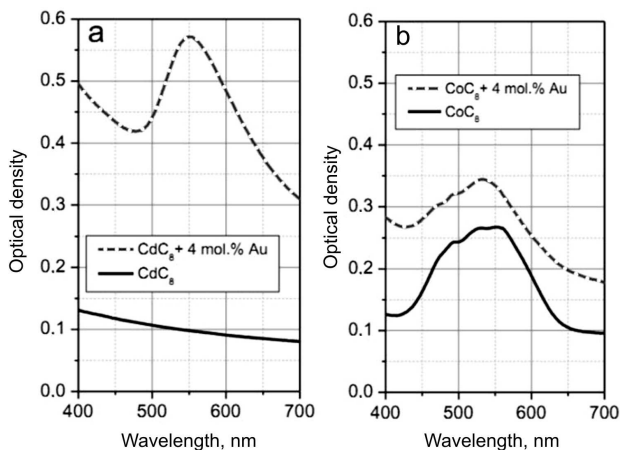
4.2. Absorption spectra

The absorption spectra of gold NPs in two different alkanoate matrices are exhibited in Fig. 5. The absorption spectrum of gold NPs in the cadmium octanoate matrix is characterized by the absorption band with a maximum at a wavelength of 550 nm, which corresponds to the surface plasmon resonance in gold NPs. The cadmium octanoate matrix itself is transparent in the visible spectral range (Fig. 5).

The absorption spectrum of gold NPs in the cadmium octanoate matrix can be used to estimate the size of NPs, because the position, intensity, and width of the absorption band depend on the shape, size, and concentration of Au NPs and the matrix refractive index. On the basis of the Mie theory for spherical NPs and with the use of the Gans model for spheroidal NPs [16], we approximated the experimental absorption curve (Fig. 6). The calculated value of Au NP radius amounted to 7.1 ± 0.6 nm, i.e. the NP diameter equaled 13–15 nm, and the sphericity of those NPs was 0.85. The calculated values agree well with the experimental data obtained with the use of TEM.

From Fig. 5, *b*, one can see that both the cobalt octanoate matrix and gold NPs absorb in the visible spectral interval. The electron absorption spectrum of cobalt octanoate mesomorphic glass was interpreted in work [12].
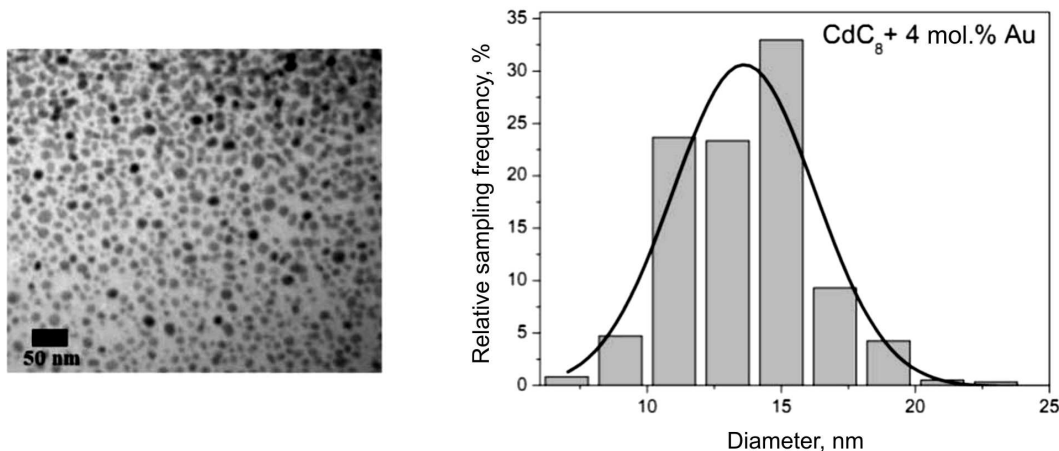
Fig. 4. TEM image of spherical gold particles distributed over the volume of a polycrystalline powder of the CdC$_8$ + 4 mol.% Au nanocomposite (left panel) and the distribution histogram for Au NP sizes (right panel)


Fig. 5. Absorption spectra for the composite of Au NPs in the CdC$_8$ matrix (dashed curve) and the pure CdC$_8$ matrix not absorbing light in the visible spectral interval (solid curve) (*a*); absorption spectra for the pure CoC$_8$ matrix (solid curve) and the CoC$_8$ + Au NPs nanocomposite (dashed curve) (*b*)
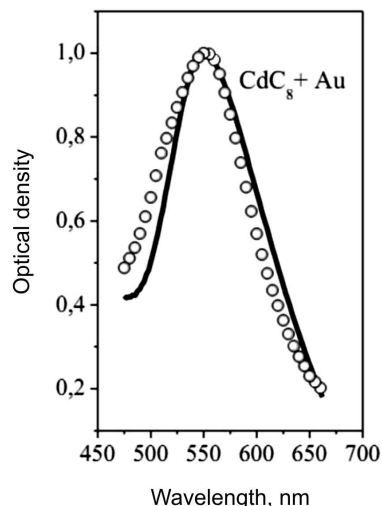
Fig. 6. Normalized absorption spectra of Au NPs in CdC$_8$: experimental (solid curve) and calculated according to the Mie theory (symbols)

The absorption observed in the wavelength interval from 480 to 630 nm is associated with the excitation of *d*–*d* electrons in Co(II) ions. Cobalt ions have a partially filled outer shell with seven *d* electrons, and their excitation is responsible for the absorption by cobalt octanoate. Cobalt alkanoates are coordination compounds. Therefore, cobalt ions can form either an octahedral coordination with six alkanoate ligands or a tetrahedral coordination with four ligands.

In order to explain the observed absorption maxima, the electron spectrum was resolved in a standard way into Gaussian components (Fig. 7). The bands with the maxima at wavelengths of 483, 535, and 575 nm emerge as a result of the electron transitions in the octahedral and tetrahedral complexes of cobalt ions [17]. Hence, the synthesized gold particles stimulated changes in the spectral properties of the matrices (Fig. 5, *b*). The most pronounced maximum in the spectrum of composite CoC$_8$ + Au NPs is located

360
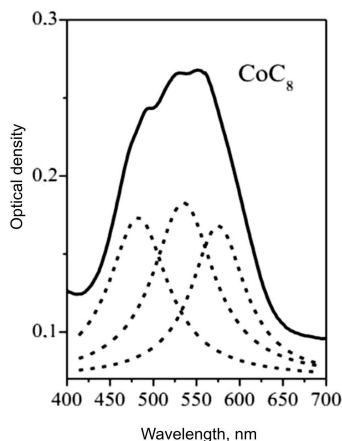
Fig. 7. Absorption spectrum of cobalt octanoate mesomorphic glass resolved into Gaussian components

at a wavelength of 536 nm. The appearance of such intense peak is related not only to the absorption of cobalt ions, but also to the surface plasmon resonance in gold NPs.

5. Conclusions

According to the results of X-ray researches of the polymorphism and the structure of cobalt and cadmium octanoates, as well as new nanocomposites on their basis, the synthesized gold NPs practically do not distort the structure of metal alkanoate matrices. Gold NPs in metal alkanoate matrices have a spherical shape and a small dispersion (the NP diameter amounts to 14 ± 3 nm). They are stable for a long time in both the mesophase and glass states. This conclusion is confirmed by the results of transmission electron microscopy and spectral researches.

In general, the new nanocomposite materials are of great interest for nonlinear optical researches; in addition, they can be applied in optoelectronics. In the case of cadmium octanoate, the optical nonlinearity of the nanocomposite can depend not only on the nonlinear absorption by Au NPs, but also on the variations in the dielectric properties of the matrix. A different situation is observed in cobalt octanoate, whose nonlinear optical properties at the laser influence are not only governed by the intense absorption of Au NPs, but they can be strengthened owing to the matrix absorption in the same spectral interval. Therefore, at the next stage of our research, we intend to consider the nonlinear optical properties of the concerned composite materials.

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А. Толочко, П. Теселько, А. Лящова,
Д. Федоренко, Г. Клімушева, Т. Мирна, В. Асаула

СТРУКТУРА І СПЕКТРАЛЬНІ
ВЛАСТИВОСТІ НОВИХ КОМПОЗИТІВ
НА ОСНОВІ МЕТАЛ-АЛКАНОАТІВ
З НАНОЧАСТИНКАМИ ЗОЛОТА

Р е з ю м е

На основі хімічного синтезу в рідкокристалічній фазі октаноатів кадмію і кобальту отримані нові композитні матеріали, що містять наночастинки (НЧ) золота. За допомогою методики малокутового рентгенівського розсіяння досліджено поліморфізм і основні структурні характеристики метал-алканоатів та нанокомпозитів (метал-алканоатів з НЧ золота). Проведено оцінку структурних параметрів НЧ золота (форма і розміри синтезованих НЧ) з використанням рентгенівського та спектрального методів, а також просвічуючої електронної мікроскопії (ПЕМ). Проаналізовано залежність спектрів поглинання золотих НЧ від спектральних властивостей матриць: кадмій-октаноату і кобальт-октаноату.