Electronics and Information Technologies, 2025, 30, 163–176
http://publications.lnu.edu.ua/collections/index.php/electronics/index

UDC: 538.975, 539.2, 621.382

MAGNETO- AND PHOTO-CONTROLLED SUPRAMOLECULAR CLATRATES BASED ON GALLIUM SELENIDE

***Vitalii Maksymych*[1]*, *Oleksii Korchev*[2], *Nadiia Pokladok*[2], *Roman Shvets*[2], *Oleh Bordun*[1], *Fedir Ivashchyshyn*[3]**

[1]Faculty of Electronics and Computer Technologies,
Ivan Franko National University of Lviv,
50 Dragomanov Str., 79005 Lviv, Ukraine
[2]Institute of Applied Mathematics and Fundamental Sciences,
Lviv Polytechnic National University,
12 Stepan Bandera Str., 79013 Lviv, Ukraine
[3]Faculty of Electrical Engineering, Czestochowa University of Technology,
ul. J.H. Dąbrowskiego 69, 42-201 Częstochowa, Poland

Maksymych, V., Korchev, O., Pokladok, N. et al. (2025). Magneto- and Photo-Controlled Supramolecular Clatrates Based on Gallium Selenide. *Electronics and Information Technologies*, 30, 163–176. https://doi.org/10.30970/eli.30.13

ABSTRACT

Background. The development of modern nanoelectronics and sensor technologies necessitates the creation of new functional materials with tunable electrical, optical, and magnetic properties. One promising approach involves the formation of supramolecular clathrates based on layered A^3B^6 group semiconductors. This paper presents the results of electrophysical analysis of GaSe-based clathrate systems intercalated with a β-cyclodextrin<ferrocene> (β-CD<FC>) complex, synthesized both under normal conditions and in a constant magnetic field.

Materials and Methods. A GaSe single crystal was used as the host matrix. The β-CD<FC> guest complex was intercalated under two different conditions: normal conditions and a constant magnetic field with a strength of 220 kA/m. Electrophysical properties were studied using impedance spectroscopy over a frequency range of 10^{-3}–10^{6} Hz and thermally stimulated discharge analysis.

Results and Discussion. Intercalation of β-CD<FC> into the expanded GaSe structure results in increased resistance in the low-frequency range and a non-monotonic behaviour of ReZ(ω). In samples synthesized in a magnetic field, a decrease in ReZ(ω) is observed, indicating a change in the electronic character of the guest complex from acceptor to donor type. Thermally stimulated discharge spectra reveal a transition from a quasi-continuous energy level distribution to a mini-zone structure, with homocharge relaxation dominating in the clathrate phase. Furthermore, samples synthesized in a magnetic field exhibit a fivefold increase in the magnetoresistive effect and a twofold enhancement in photosensitivity.

Conclusion. The study demonstrates that intercalation of the supramolecular β-CD<FC> complex into the expanded GaSe matrix enables targeted modification of the impurity structure, resulting in changes in electrical conductivity and sensory behaviour of the clathrate. It was established that synthesis conditions, particularly the presence of a constant magnetic field, significantly influence the electronic nature of the guest component, the type of charge carriers, trap level parameters, and the manifestation of quantum effects during charge transport.

Keywords: Intercalation, impedance spectroscopy, magnetoresistive effect, photoresistive effect, supramolecular complex, hierarchical architecture.

INTRODUCTION

The rapid advancement of modern electronics and sensor technologies necessitates the development of new functional materials with tunable electrical and physical characteristics. Such materials can be designed based on nanostructured systems capable of exhibiting novel physical phenomena due to their internal architecture, engineered at the atomic and molecular levels. Particularly noteworthy in this context are hybrid nanostructured systems that demonstrate complex sensitivity to external fields, thereby opening new avenues for their integration into multifunctional device components.

One promising direction in this field involves the formation of clathrates–supramolecular compounds in which guest molecules or complexes are incorporated into the cavities of a host matrix [1–3]. In particular, the intercalation of functionalized organic complexes into layered semiconducting materials offers a versatile approach to tailoring the electronic, magnetic, and optical properties of the resulting systems.

Intercalation into A^3B^6-type layered semiconductor crystals, such as gallium selenide (GaSe), represents an effective method for modifying their electronic structure, impurity spectrum, and physicochemical characteristics. Owing to the presence of weak interlayer van der Waals interactions, these crystals can accommodate guest species—particles, molecules, or complexes—within their interlayer spaces without disrupting the integrity of the internal crystal lattice [4, 5]. This enables the formation of stable intercalated systems that preserve their layered morphology while acquiring novel functional properties, including enhanced electrical conductivity, magnetic responsiveness, and photoelectric behaviour.

Of particular scientific interest is the formation of clathrates with a hierarchical architecture of the subhost<host<guest>> type. In this regard, the intercalation of supramolecular complexes such as β-cyclodextrin with ferrocene (β-CD) appears especially promising, as these components can serve not only as carriers of functional properties (e.g., photo- or magneto-sensitivity) but also as modulators of electronic state ordering due to their specific geometry and inherent self-assembly capabilities.

This work presents the results of a study on clathrates formed by two approaches: intercalation of the β-CD complex into the GaSe matrix under normal conditions and intercalation performed in the presence of a constant magnetic field.

MATERIALS AND METHODS

In the experiments, a semiconductor single crystal of gallium selenide (GaSe) (Fig. 1) was used as the subhost material. Grown by the Bridgman–Stockbarger method, the single crystal exhibits a multilayer hexagonal structure and p-type conductivity. GaSe is particularly well-suited for intercalation owing to its wide band gap (2.02 eV, as determined from optical data), high anisotropy of electrical conductivity, and resistance to chemical modification. It is also characterised by the presence of so-called guest-accessible sites — regions of weak van der Waals forces oriented perpendicular to the crystallographic C-axis [5].

β-cyclodextrin ($C_{42}H_{70}O_{35}$) (β-CD) [6] was selected as the host. This compound is a cyclic oligosaccharide with a well-defined toroidal geometry (see Fig. 2), featuring a hydrophilic outer surface and a hydrophobic inner cavity. Such a structure enables the formation of inclusion complexes with hydrophobic guest molecules via weak non-covalent interactions, particularly van der Waals forces. Owing to its rigid geometry and propensity for forming ordered supramolecular assemblies, β-CD serves as a structural platform for the spatial organisation of guest species within the interlayer regions of host materials [7-9].

Ferrocene (FC) (Fig. 3) was used as the guest molecule. Ferrocene is an organometallic compound with well-characterised donor–acceptor and electrochemical properties and exhibits high stability in a wide range of chemical environments. Its molecular structure consists of an iron atom sandwiched between two cyclopentadienyl rings, forming a delocalized π-system that facilitates interaction with the electronic states of the sub-host material [10-12].

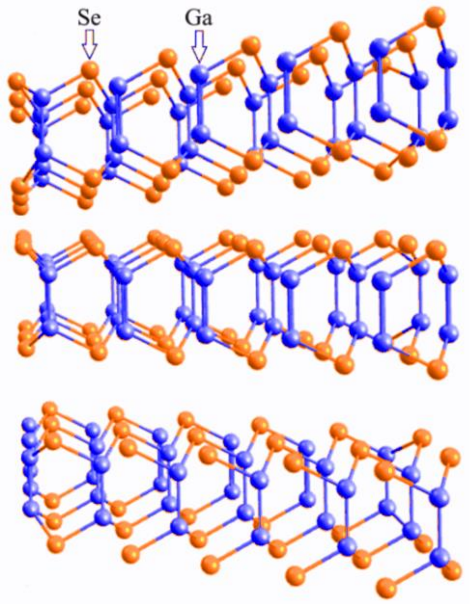

Fig. 1. Spatial representation of the GaSe structure.

Ferrocene (FC) (Fig. 3) was used as the guest molecule. Ferrocene is an organometallic compound with well-characterised donor–acceptor and electrochemical properties and exhibits high stability in a wide range of chemical environments. Its molecular structure consists of an iron atom sandwiched between two cyclopentadienyl rings, forming a delocalized π-system that facilitates interaction with the electronic states of the sub-host material [10-12].

Since ferrocene is insoluble in water, the supramolecular complex β-CD<FC> was prepared using a method described in [13]. A fine powder of ferrocene was added to an aqueous solution of β-CD at 60 °C under continuous stirring. The molar ratio of β-CD to ferrocene was maintained at 1:1.

The intercalation of the β-CD<FC> supramolecular complex into GaSe crystals involved several stages and has been described in detail in our previous works [14, 15]. First, sodium nitrite ($NaNO_2$) was introduced into the GaSe matrix until a 5-fold expansion was achieved. Following this, the $NaNO_2$ was washed out, and the crystals were dried in a vacuum oven at 100 °C for 24 hours.

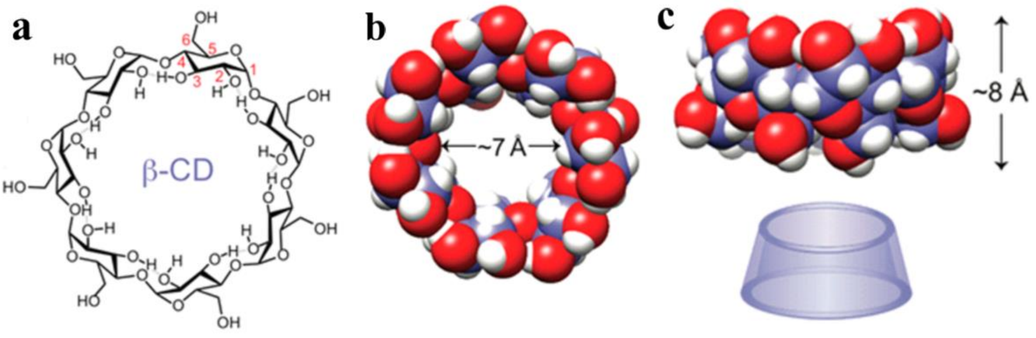

Fig. 2. Structure of β-cyclodextrin (β-CD): schematic representation of the molecule with atom numbering of the glucopyranose units (a); space-filling model showing the inner cavity (b); truncated cone-like shape of β-CD (c).

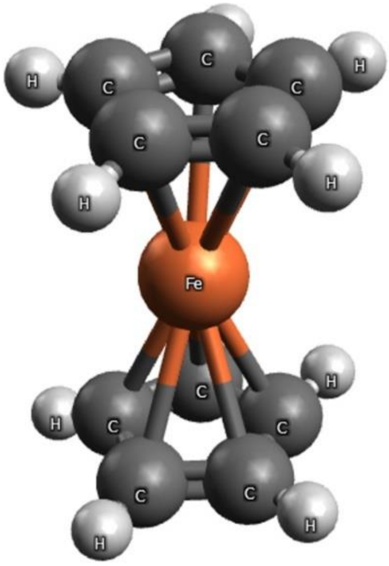

Fig. 3. Molecular structure of ferrocene.

The intercalation of β-CD<FC> was performed in two modes. In the first mode, the GaSe crystal was immersed in an aqueous solution containing β-CD and ferrocene under normal conditions. In the second mode, to control the spatial ordering of the magnetically sensitive guest during intercalation, the GaSe crystal was placed in the same solution while exposed to a constant magnetic field with a strength of 220 kA/m. During the intercalation of the supramolecular complex β-CD<FC>, the GaSe crystal was positioned so that the magnetic induction vector was oriented parallel to the crystallographic axis C, i.e., perpendicular to the plane of the layers. This orientation ensures maximum influence of the magnetic field on the ordering of magnetosensitive ferrocene molecules along the interlayer voids of the crystal. Upon completion, the intercalated GaSe<β-CD<FC>> clathrate samples were dried at 45 °C for 24 hours in a vacuum oven.

As a result, the obtained experimental sample represents a stage-wise ordered layered structure in which unexpanded GaSe layers alternate with expanded layers containing the intercalated β-CD<FC> supramolecular complex.

The studies using impedance spectroscopy were carried out along the crystallographic axis C in a $10^{-3}..10^{6}$ Hz frequency range using the AUTOLAB measurement system (ECO CHEMIE, the Netherlands), equipped with FRA-2 and GPES software packages. The uncertain points were removed using the Dirichlet filter [16]. The impedance measurements were made under normal conditions, in a constant magnetic field of 220 kA/m lighted by a 65W solar simulator. The external fields were applied along the impedance spectra measurements. This geometry of measurements was chosen in order to dismiss the Lorentz force.

The studies were also carried out using the thermally stimulated discharge in the temperature range of –25..+70°C with a constant heating rate of 5 degrees/min.

Based on the obtained impedance spectroscopy data according to the Geballe-Pollack theory [17], the following parameters of the impurity energy spectrum were calculated: density of states at the Fermi level N_F, hopping radius R, spread of traps near the Fermi level J and real density of deep traps N_t.

RESULTS AND DISCUSSION

To investigate the influence of the guest molecule on the electrical conductivity of the GaSe<β-CD<FC>> clathrate, impedance spectroscopy was employed. The analysis begins with a comparison of the real part of the complex impedance (ReZ) for the pristine GaSe single crystal, the 5-fold expanded GaSe matrix, and the GaSe<β-CD<FC>> clathrate synthesized under both normal conditions and in a constant magnetic field with an intensity of 220 kA/m. The frequency dependencies of ReZ are shown in Fig. 4.

The unmodified GaSe single crystal (curve 1, Fig. 4) exhibits frequency-independent behaviour of ReZ in the 10^{-2}..10^{2} Hz range, indicating conductivity governed by equilibrium charge carriers at the given temperature. This conductivity is of the activation type and can be described as follows:

$$\sigma_0 = en\mu, \tag{1}$$

where e is the elementary charge, n is the carrier concentration, and μ is their mobility.

A further increase in frequency (ω>10^{2} Hz) leads to a monotonic decrease in the real part of the impedance (ReZ) of the GaSe single crystal due to the dominance of hopping conductivity. This conductivity arises from the hopping of nonequilibrium charge carriers between localised states near the Fermi level. In this process, the carriers hop from one centre localised in the forbidden band of the semiconductor to another, accompanied by the emission or absorption of a phonon. This type of conductivity is of the activation type, meaning that:

$$\sigma \sim \exp\left[-\frac{\Delta W}{kT}\right]. \tag{2}$$

In the case of alternating current, the hopping conductivity becomes frequency-dependent:

$$\sigma_j(\omega) \sim \omega^n, \tag{3}$$

where n the exponent typically ranges from 0.64 to 1.0.

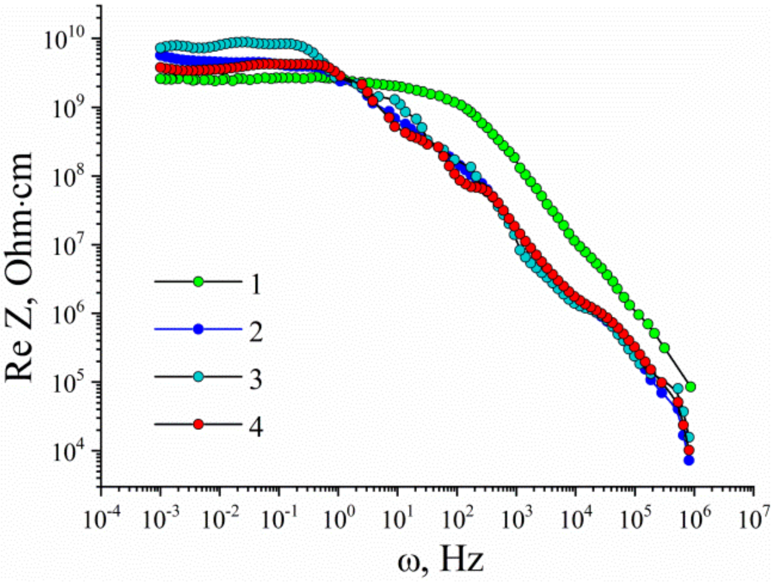

Fig. 4. Real part of complex impedance measured for the initial unexpanded GaSe crystal (1), 5-fold expanded GaSe matrix (2), and GaSe<β-CD<FC>> clathrate synthesized under normal conditions (3) and in a constant magnetic field (4).

As a result, the total conductivity of the GaSe single crystal can be expressed as a sum of equilibrium and hopping contributions:

$$\sigma'(\omega) = en\mu + A\omega^n. \quad (4)$$

Following the 5-fold expansion of the GaSe single crystal (curve 2, Fig. 4), significant changes in ReZ(ω) are observed. The resistance increases by more than a factor of two, attributed to a reduction in the concentration of equilibrium charge carriers due to the formation of additional recombination centres caused by the expansion of the crystal layers. The low-frequency branch of ReZ(ω) loses its frequency independence and begins to decrease monotonically within the 10^{-2}–0.6 Hz range, followed by a sharp and non-monotonic decline with increasing frequency. This deviation from the behaviour predicted by Eq. (3) suggests that, in addition to band and hopping transport mechanisms, charge transfer also involves capture–retention–release processes associated with quantum wells, which are most likely formed in the regions of expanded layers.

Incorporation of the β-CD<FC> supramolecular complex into the interlayer space of the 5-fold expanded GaSe matrix under normal conditions (curve 3, Fig. 4) leads to an increase in ReZ(ω) in the low-frequency range and a further enhancement of the non-monotonic behaviour. This indicates the formation of additional quantum wells due to the presence of the guest component, which likely exhibits an acceptor-type nature.

When the same supramolecular complex is introduced under a constant magnetic field (curve 4, Fig. 4), ReZ(ω) decreases in the low-frequency range, although the non-monotonic behaviour remains pronounced. This also indicates the formation of additional quantum wells, but in this case, the guest molecule likely demonstrates a donor-type character. Given the opposite trends in the low-frequency behaviour of ReZ(ω) depending on the synthesis conditions, we can assume that the nature of the guest molecule differs: acceptor-like under normal conditions and donor-like under the influence of a magnetic field.

For a more detailed interpretation of the ReZ(ω) variations depending on the synthesis conditions, Fig. 5 presents the ratio of the real part of the complex impedance of the clathrate (ReZ_{Clat}) to that of the 5-fold expanded GaSe matrix ($ReZ_{Exp.mat}$). As can be seen, depending on the synthesis conditions, the $ReZ_{Clat}/ReZ_{Exp.mat}$ (ω) dependence exhibits

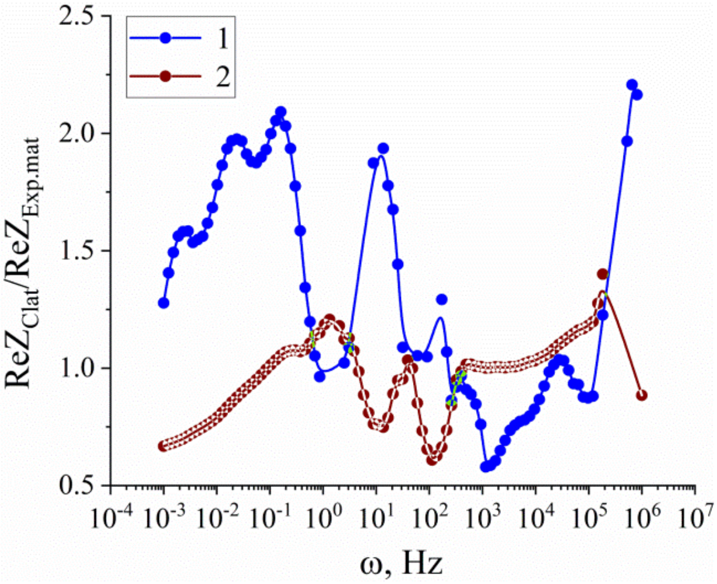

Fig. 5. Change in the real part of the complex impedance for GaSe<β-CD<FC>> clathrate synthesized under normal conditions (1) and in a constant magnetic field (2).

opposite frequency trends, most likely due to different types of conductivity exhibited by the guest component.

To elucidate the structure of impurity energy spectra in the initial GaSe single crystal, the 5-fold expanded GaSe matrix, and the GaSe<β-CD<FC>> clathrates synthesized under normal conditions and in a constant magnetic field, thermally stimulated discharge current spectra were measured, as shown in Fig. 6. For the initial GaSe single crystal, thermally stimulated discharge current signals begin to appear at 283 K. The spectrum initially displays a distinctly miniband-like character, which gradually transitions to a quasi-continuous form with increasing temperature. It is important to note that heterocharge relaxation is observed in this case. For the 5-fold expanded GaSe matrix, the TSDC spectrum exhibits a strongly pronounced miniband-like structure (Fig. 6), with a higher density of states concentrated in the low-temperature region—where the initial GaSe crystal had virtually no detectable thermally stimulated discharge current response. Homocharge relaxation is predominant in this case. The crystal expansion clearly leads to the formation of trap centres localised in narrow bands within the forbidden gap. This result supports the ReZ(ω) behaviour previously observed for the 5-fold expanded GaSe matrix (Fig. 4).

In the case of the GaSe<β-CD<FC>> clathrate, regardless of the synthesis conditions, the thermally stimulated discharge current spectrum maintains a strongly expressed miniband-like character throughout the entire studied temperature range, with homocharge relaxation remaining dominant. The observed differences depending on the synthesis method lie in the specific energy distribution of impurity levels, which ultimately determine the conductivity characteristics of the clathrates.

Using the theory of hopping conductivity proposed by M. Pollak and T.H. Geballe [17], which takes into account the charge carriers' hoppings between states localised in space

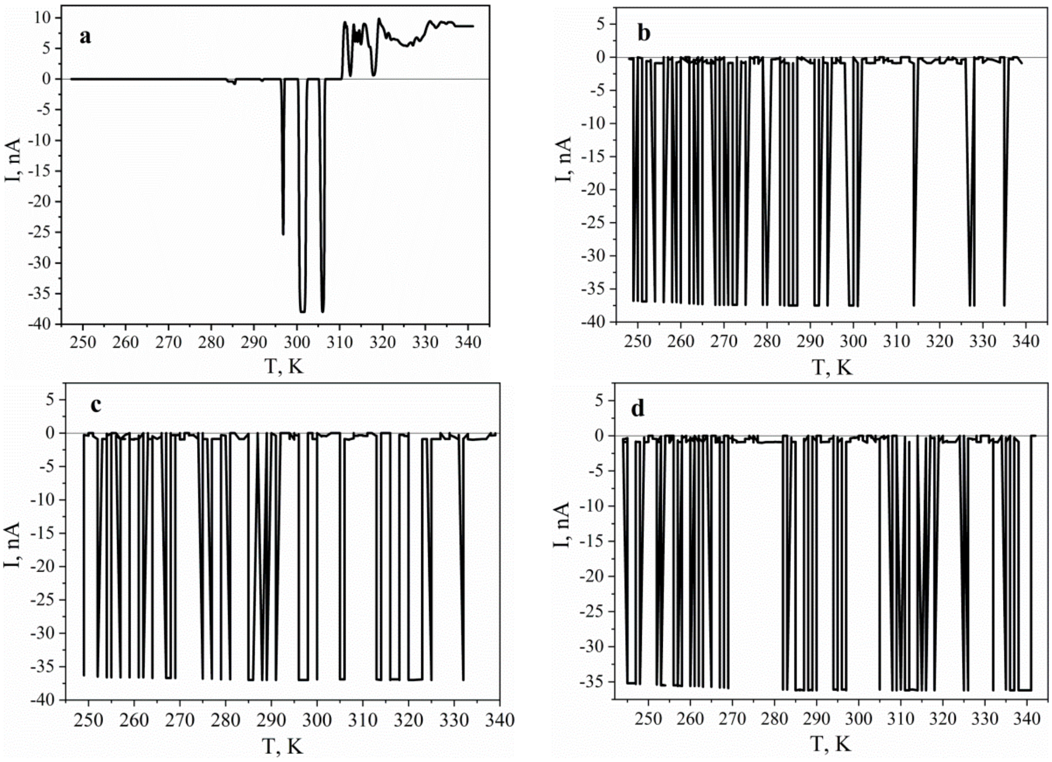

Fig. 6. Thermally stimulated discharge currents spectra for the initial unexpanded GaSe crystal (a), 5-fold expanded GaSe matrix (b), and GaSe<β-CD<FC>> clathrate synthesized under normal conditions (c) and in a constant magnetic field (d).

due to their interaction with phonons. The result is the following expression for the real part of the conductivity:

$$\sigma(\omega)=\frac{\pi}{96}e^2k_\mathrm{B}T\alpha^{-5}N_\mathrm{F}^2\omega\left[\ln\left(\frac{\nu_\Phi}{\omega}\right)\right]^4, \tag{5}$$

where e is the electron charge, $\mathrm{N_F}$ is the density of states on the Fermi level, α is the constant of the carrier localised wave function decrease, ν_Φ is the phonon frequency.

According to the theory of hopping conductivity on alternating current, the average hopping time τ of the carrier with phonon absorption or emission is determined by the expression:

$$\tau^{-1}=\nu_\Phi\exp(-2\alpha R), \tag{6}$$

where R is the hopping distance.

Experimentally, τ^{-1} is the average frequency at which the law $\omega^{0.8}$ is fulfilled. The average hopping distance R can be calculated by the formula after determining the value of τ^{-1} experimentally.

The scatter of trapped levels near the Fermi level J can be estimated by knowing the values of $\mathrm{N_F}$ and R from the relation

$$\frac{4}{3}\pi R^3N_\mathrm{F}\frac{1}{2}J=1. \tag{7}$$

This, in turn, makes it possible to estimate the real density of deep traps $\mathrm{N_t}$ using the formula

$$N_\mathrm{t}=N_\mathrm{F}J. \tag{8}$$

The corresponding values obtained according to the presented calculations are given in Table 1. As can be seen, 5-fold expansion of the GaSe matrix leads to more than a twofold increase in the density of states at the Fermi level N_F, and a similar, but inverse, twofold decrease in the spread of trap levels J. The hopping distance R and the density of deep traps N_t remain unchanged. The introduction of the supramolecular complex β-CD<FC> into the interlayer space of the 5-fold expanded GaSe matrix results in a 1.82-fold increase in N_F and a 1.76-fold decrease in J. The hopping distance R slightly decreases, while the deep trap

Table 1. **Band spectrum parameters for the investigated samples measured at the normal conditions**

Structure	$N_\mathrm{F}\cdot10^{44}$, $\mathrm{J^{-1}m^{-1}}$	$R\cdot10^{-8}$, m	$J\cdot10^{-22}$, J	$N_\mathrm{t}\cdot10^{22}$, $\mathrm{m^{-3}}$
GaSe	0.34	2.55	8.42	2.89
5-fold expanded GaSe matrix	0.82	2.55	3.50	2.89
GaSe<β-CD<FC>> clathrate synthesized under normal conditions	1.50	2.52	1.99	3.00
GaSe<β-CD<FC>> clathrate synthesized in a constant magnetic field	0.75	2.80	2.89	2.17

density N_{t} increases somewhat. The formation of the GaSe<β-CD<FC>> deep trap density N_{t} increases somewhat. The formation of the GaSe<β-CD<FC>> clathrate in a constant magnetic field, compared to the 5-fold expanded GaSe matrix, leads to opposite effects: N_{F} decreases by about 10%, J decreases by 18%, N_{t} decreases by 25%, and R increases by 10%. Overall, there is a fairly good correlation between the aforementioned current transport mechanisms, the measured thermally stimulated discharge current spectra, and the theoretically calculated parameters of the impurity energy spectrum.

The next step was to investigate the influence of the guest component and the conditions of its formation on the magnitude of the magnetoresistive effect of the GaSe<β-CD<FC>> clathrate (Fig. 7). The magnetoresistive effect was calculated as the ratio of resistance in a constant magnetic field to resistance in its absence ($\delta_H=\rho_H/\rho_0$). As can be seen from Fig. 7, the synthesis conditions have a dramatic effect on the magnetoresistive effect, which differs in sign and magnitude. Thus, in the low-frequency range, a 5-fold increase in magnetosensitivity is observed for the GaSe<β-CD<FC>> clathrate synthesized in a constant magnetic field, while for the clathrate synthesized under normal conditions, a decrease of more than two times is observed. This indicates an increase in magnetosensitivity under conditions of clathrate synthesis in a constant magnetic field due to the ordering of the guest component.

Next, the influence of the guest component and its formation conditions on the magnitude of the photoresistive effect of the GaSe<β-CD<FC>> clathrate was investigated (Fig. 8). The photoresistive effect was calculated as the ratio of the resistance under illumination to the resistance in the dark ($\delta_L = \rho_L/\rho_D$). As seen in Fig. 8, the clathrate synthesis conditions result in an opposite frequency dependence of the photoresistive effect. In the low-frequency range, a twofold increase in photosensitivity is observed for the GaSe<β-CD<FC>> clathrate synthesized in a constant magnetic field, while a decrease is observed for the clathrate synthesized under normal conditions. This indicates enhanced photosensitivity when the clathrate is synthesized in a constant magnetic field, due to the formation of a specific impurity energy spectrum structure.

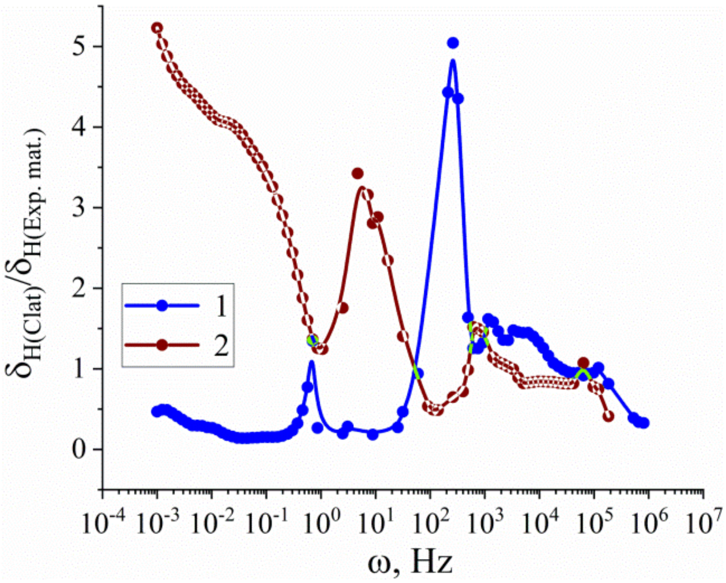

Fig. 7. Change in the magnetoresistive effect for the GaSe<β-CD<FC>> clathrate synthesized under normal conditions (1) and in a constant magnetic field (2).

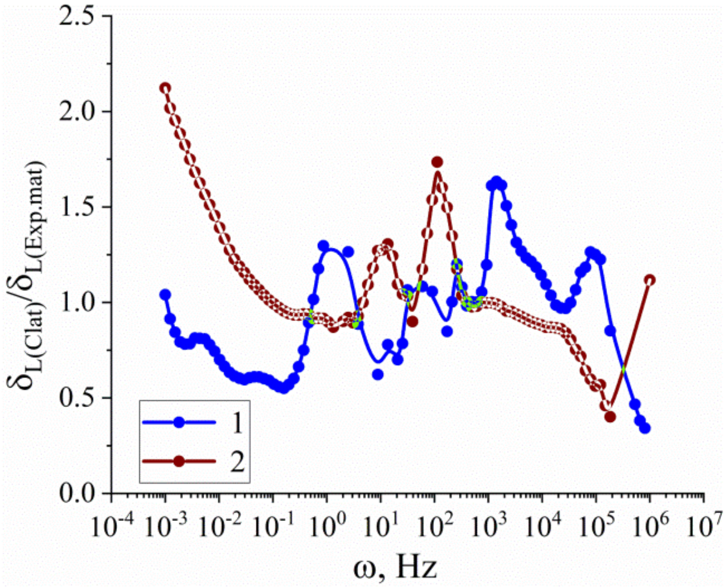

Fig. 8. Change in the photoresistive effect for GaSe<β-CD<FC>> clathrate synthesized under normal conditions (1) and in a constant magnetic field (2).

However, the most unexpected look is the I–V characteristics of the GaSe<β-CD<FC>> clathrate, regardless of the synthesis conditions, when measured under a constant magnetic field. (Fig. 9). While the I–V curves of the initial GaSe single crystal and the 5-fold expanded GaSe matrix exhibited a linear behaviour under all measurement conditions, the I–V characteristics of the GaSe<β-CD<FC>> clathrate synthesized under normal conditions and measured in a constant magnetic field demonstrate a somewhat unconventional appearance. In the presence of a magnetic field, the I–V curve takes on an oscillatory form.

This behaviour may be related to the following. Based on the architecture of the synthesized clathrate GaSe<β-CD<FC>> and the above research results, it is likely to assume that the formed nano-dispersed magnetic particles are an ensemble of quantum dots localised in the corresponding hierarchical structure. This means that the determining processes in charge transfer will be the tunnelling of current carriers and their limitation by a localised charge, like the Coulomb blockade [18]. Non-core current carriers will be localised in quantum wells, creating an energy barrier for the main ones. It is for such cases

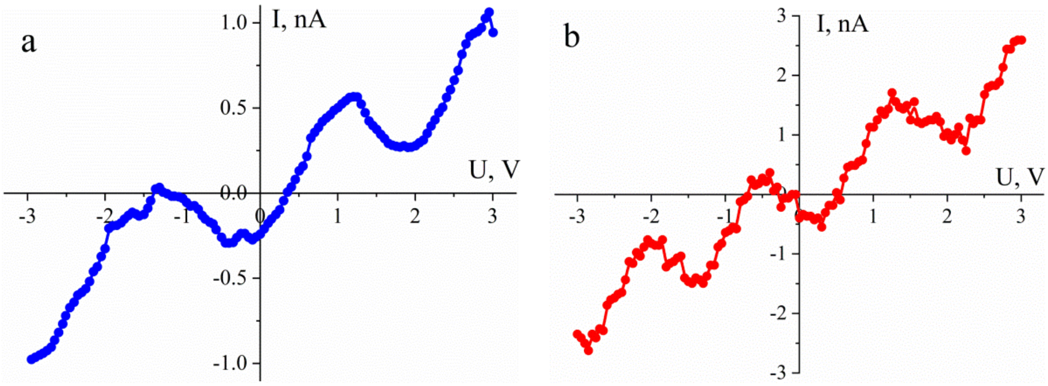

Fig. 9. I–V characteristics of GaSe<β-CD<FC>> clathrate synthesized under normal conditions (a) and in a constant magnetic field (b).

that the extraordinary behaviour of the dynamic volt-ampere characteristic is characteristic. The reason is that the “charging” and “discharging” of the 1D-barrier-0D nanocapacitor occur at different speeds: charging due to the inertial process of movement of delocalized media, and discharge due to their emission into the layer of traps with a lifetime τ. The competition of the processes of charging and discharging of these nanocapacitors in combination with the effect of the accumulation of a significant nonequilibrium charge determines the nature of the behaviour of the volt-ampere characteristic. It is clear that such effects will be the more significant, the greater the τ.

The qualitatively nonmonotonic nature of the volt-ampere characteristic can be understood based on a simple quantum mechanical model. Let us consider a one-dimensional crystal characterised by a band spectrum. The introduction of a molecule (atom or, in our case, a nanocluster) is accompanied by additional potential of the molecule. Depending on the specific content of the molecule, the potential can be both a barrier against the background of the crystal potential and a well.

Consider the case when the intercalated supramolecular complex generates additional localised potential (albeit rectangular) in the form of wells. In an ideal structure, where the geometric and energy characteristics of such wells are strictly maintained and the wells are positioned at fixed distances from each other, they are separated by the chain potential, which acts as a barrier between them. Electronic states in the wells are discrete. The voltage applied to such a structure can lead to the appearance of current by the mechanisms of jumping conductivity and/or resonant tunnelling. The attached magnetic field changes the position of the discrete levels. Each time such levels intersect with a fixed level, there is an abrupt change in carrier concentration, which is repeated with each subsequent intersection. The frequency of jumps is determined by the degree of discreteness of electronic states. Using the conclusions of the infinite deep well problem, namely

$$E_n = \frac{\pi^2\hbar^2}{2ma^2}n^2 \Rightarrow \frac{0.37}{a^2}, \tag{9}$$

(here the width of the well is expressed in nm), the observed frequency of jumps *I*(*U*) should be expected for narrow wells and/or high excited states.

The blurred nature of the maxima observed in Fig.9 may be the result of imperfections in the structure described above, differences in the values of geometric and energy characteristics of the system, as well as the temperature factor. In the case of the presence of a magnetic field, there is a Zeeman effect, which in turn non-trivially changes the electronic states of the system, and therefore the dependence of *I*(*U*).

CONCLUSION

As a result of the study, supramolecular clathrate structures were formed based on a 5-fold expanded GaSe matrix with an intercalated β-CD<FC> complex, featuring a hierarchical architecture of the subhost<host<guest>> type. Intercalation was performed under two technological conditions: under normal conditions and in the presence of a constant magnetic field. Based on the analysis of electrophysical measurements, the following conclusions were drawn:

1. Intercalation of the β-CD<FC> complex into the expanded GaSe structure leads to a substantial modification of the electrical conductivity, in particular an increase in resistance in the low-frequency range, an enhancement of the non-monotonic behaviour of the frequency dependence ReZ(ω), and the formation of additional trap levels associated with the emergence of quantum wells in the structure.
2. The synthesis conditions of the clathrate have a decisive effect on the electronic nature of the guest component: under normal conditions, the supramolecular complex β-CD<FC> exhibits acceptor-type conductivity, while intercalation in a constant magnetic

field induces donor properties. This is supported by the analysis of the frequency behavior of ReZ(ω) and the changes in the density of states near the Fermi level.

3. Analysis of the impurity energy spectrum parameters revealed that the introduction of the β-CD<FC> complex under normal conditions increases the density of states at the Fermi level and reduces the dispersion of trap levels near it. In contrast, the influence of the magnetic field leads to a nearly 10% decrease in the Fermi-level density of states N_F and a 10% increase in the hopping radius R.
4. The thermally stimulated discharge spectra indicate that the unexpanded GaSe crystal is characterised by a quasi-continuous distribution with heterocharge relaxation, whereas in the 5-fold expanded GaSe and the GaSe<β-CD<FC>> clathrates (regardless of synthesis conditions), the spectra exhibit a mini-zone structure with homocharge relaxation, suggesting the formation of trap centers localized within narrow bands in the bandgap.
5. The magnetoresistive and photoresistive effects of the GaSe<β-CD<FC>> clathrate are strongly dependent on the synthesis conditions. In particular, synthesis under a magnetic field results in a fivefold increase in magnetosensitivity and a twofold enhancement in photosensitivity, attributed to the ordering of the guest component and the specific configuration of impurity states.
6. The current-voltage characteristics (I-V curves) measured in a magnetic field for GaSe<β-CD<FC>> clathrates synthesized by both methods exhibit oscillatory behaviour, which may result from charge carrier tunnelling through quantum wells, Coulomb blockade, and the dynamic accumulation of nonequilibrium charge within the hierarchical subhost<host<guest>> architecture.

The results demonstrate the potential for targeted control over the electrical, magnetic, and optical properties of clathrate structures by tuning the intercalation conditions and guest component composition. This opens promising avenues for the development of sensor elements, photosensitive and magnetosensitive devices, and components for functional nanoelectronics.

COMPLIANCE WITH ETHICAL STANDARDS

The authors declare that the research was conducted in the absence of any potential conflict of interest.

AUTHOR CONTRIBUTIONS

Conceptualization, [F.I.]; methodology, [V.M.]; validation, [O.K., O.B.]; formal analysis, [N.P., O.B.]; investigation, [V.M]; resources, [R.S.]; data curation, [O.K.]; writing – original draft preparation, [F.I.]; writing – review and editing, [V.M.]; visualization, [F.I., V.M.]; project administration, [F.I.].

All authors have read and agreed to the published version of the manuscript.

REFERENCES

[1] Ramamurthy, V., & Mondal, B. (2015). Supramolecular photochemistry concepts highlighted with select examples. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 23*, 68–102. https://doi.org/10.1016/j.jphotochemrev.2015.04.002

[2] Amabilino, D. B., Smith, D. K., & Steed, J. W. (2017). Supramolecular materials. *Chemical Society Reviews, 46*, 2404–2420. https://doi.org/10.1039/C7CS00163K

[3] Hashim, P., Bergueiro, J., Meijer, E., & Aida, T. (2020). Supramolecular polymerization: A conceptual expansion for innovative materials. *Progress in Polymer Science, 105*, 101250. https://doi.org/10.1016/j.progpolymsci.2020.101250

[4] Hung, N. T., Nugraha, A. R. T., & Saito, R. (2017). Two-dimensional InSe as a potential thermoelectric material. *Applied Physics Letters, 111*, 092107. https://doi.org/10.1063/1.4999321

[5] Geim, A. K., & Grigorieva, I. V. (2013). Van der Waals heterostructures. *Nature, 499*, 419–425. https://doi.org/10.1038/nature12385

[6] Maksymych, V., Klapchuk, M., Borysiuk, A., Kulyk, Y., Stadnyk, V., Bordun, I., Kohut, Z., & Ivashchyshyn, F. (2023). Hierarchical heterostructure built on the basis of SiO_2 dielectric matrix and supramolecular complex β-cyclodextrin–ferrocene: Fabrication, physical properties and applications. *Materials Research Bulletin*, 164, 112220. https://doi.org/10.1016/j.materresbull.2023.112220

[7] Liu, G., Yang, J., & Xu, X. (2021). β-Cyclodextrin-calcium complex intercalated hydrotalcites as efficient catalyst for transesterification of glycerol. *Catalysts, 11*(11), 1307. https://doi.org/10.3390/catal11111307

[8] Yang, H., Chen, H., Chen, Z., Li, Y., Yao, L., Wang, G., Deng, Q., & Fu, P. (2023). Inductive effect of MXene membrane influenced by β-cyclodextrin intercalation. *Canadian Journal of Chemical Engineering, 101*(4), 1985–1992. https://doi.org/10.1002/cjce.24573

[9] Huang, T., Su, Z., Dai, Y., & Zhou, L. (2021). Enhancement of the heterogeneous adsorption and incorporation of uranium(VI) caused by the intercalation of β-cyclodextrin into the green rust. *Environmental Pollution, 290*, 118000. https://doi.org/10.1016/j.envpol.2021.118000

[10] Nair, A., Zhao, X., Glushenkov, A. M., et al. (2024). Metallocene intercalation in 2D materials: Recent advances and opportunities. *Journal of Materials Chemistry A, 12*, 1629–1650. https://doi.org/10.1039/D3TA07097B

[11] Gao, Y., Hu, G., Zhang, W., Ma, D., & Bao, X. (2011). π-π interaction intercalation of layered carbon materials with metallocene. *Dalton Transactions, 40*(17), 4521–4526. https://doi.org/10.1039/C0DT01392G

[12] Bal, B., Ganguli, S., & Bhattacharya, M. (1985). Intercalation of ferrocene in $CdPS_3$. *Physica B+C, 133*(1), 72–75. https://doi.org/10.1016/0378-4363(85)90026-9

[13] Harada, A., & Takahashi, S. (1984). Preparation and properties of cyclodextrin–ferrocene inclusion complexes. *Journal of the Chemical Society, Chemical Communications*, (10), 645–646. https://doi.org/10.1039/C39840000645

[14] Dupliak, I., Ivashchyshyn, F., Całus, D., Seredyuk, B., Chabecki, P., Maksymych, V., & Li, F. (2020). Influence of optical radiation and magnetic field on the properties of InSe<$NaNO_2$> clathrate. *Ukrainian Journal of Physics Optics, 21*(3), 115–122. https://doi.org/10.3116/16091833/21/3/115/2020

[15] Maksymych, V., Całus, D., Shvets, R., Chabecki, P., Pokladok, N., & Ivashchyshyn, F. (2022). GaSe<β-CD<I_2>> architecture supramolecular clathrate: Properties and application. *Journal of Nano- and Electronic Physics, 14*(1), 01002. https://doi.org/10.21272/JNEP.14(1).01002

[16] Barsoukov, E., & Macdonald, J. R. (2005). *Impedance spectroscopy: Theory, experiment and applications* (2nd ed.). Wiley.

[17] Pollak, M., & Geballe, T. H. (1961). Low-frequency conductivity due to hopping processes in silicon. *Physical Review, 122*(6), 1743–1753. https://doi.org/10.1103/PhysRev.122.1743

[18] Gyakushi, T., Asai, Y., Tsurumaki-Fukuchi, A., Arita, M., & Takahashi, Y. (2020). Periodic Coulomb blockade oscillations observed in single-layered Fe nanodot array. *Thin Solid Films*, *704*, 138012. https://doi.org/10.1016/j.tsf.2020.138012

МАГНІТО- ТА ФОТОКЕРОВАНІ СУПРАМОЛЕКУЛЯРНІ КЛАТРАТИ НА ОСНОВІ СЕЛЕНІДУ ГАЛІЮ

Віталій Максимич[1]*, Олексій Корчев[2], Надія Покладок[2],
Роман Швець[2], Олег Бордун[1], Федір Іващишин[3]
[1] Факультет електроніки та комп’ютерних технологій,
Львівський національний університет імені Івана Франка,
вул. Драгоманова, 50, 79005, м. Львів, Україна
[2] Інститут прикладної математики та фундаментальних наук,
Національний університет «Львівська політехніка»,
вул. Степана Бандери, 12, 79013, м. Львів, Україна
[3]Електротехнічний факультет,
Ченстоховський політехнічний університет,
вул. Я.Г.Домбровського, 69, 42-201, м. Ченстохова, Польща

АНОТАЦІЯ

Вступ. Розвиток сучасної наноелектроніки та сенсорних технологій потребує створення нових функціональних матеріалів з керованими електричними, оптичними та магнітними властивостями. Одним із перспективних підходів є формування супрамолекулярних клатратів на основі шаруватих напівпровідників групи A^3B^6. У цій роботі представлено результати електрофізичного аналізу клатратних систем на основі GaSe з інтеркальованим комплексом β-циклодекстрин<фероцен> (β-CD<FC>), синтезованих за нормальних умов та в постійному магнітному полі.

Матеріали та методи. Як матриця-господар використовувався монокристал GaSe. Інтеркаляцію гостьового комплексу β-CD<FC> проводили у двох режимах: за нормальних умов і в постійному магнітному полі напруженістю 220 кА/м. Електрофізичні властивості досліджували методом імпедансної спектроскопії в діапазоні 10^{-3}–10^{6} Гц та методом термостимульованого розряду.

Результати. Інтеркаляція β-CD<FC> у розширену структуру GaSe призводить до зростання опору в низькочастотному діапазоні та немонотонної поведінки ReZ(ω). Для зразків, синтезованих у магнітному полі, спостерігається зменшення ReZ(ω), що вказує на перехід гостьового компонента від акцепторного до донорного типу. Спектри термостимульованого розряду демонструють перехід від квазінеперервної до мінізонної структури рівнів з переважанням релаксації гомозаряду в клатратах. У зразках, синтезованих у магнітному полі, спостерігається п’ятикратне зростання магніторезистивного ефекту та збільшення фоточутливості вдвічі.

Висновки. Проведене дослідження продемонструвало, що інтеркаляція супрамолекулярного комплексу β-CD<FC> у розширену матрицю GaSe дозволяє цілеспрямовано модифікувати домішкову структуру і тим самим змінювати електропровідність та сенсорні властивості клатрату. Встановлено, що умови синтезу, зокрема дія постійного магнітного поля, суттєво впливають на електронну природу гостьового компонента, тип носіїв заряду, параметри пасткових рівнів і прояв квантових ефектів при перенесенні зарядів.

Ключові слова: Інтеркаляція, імпедансна спектроскопія, магніторезистивний ефект, фоторезистивний ефект, супрамолекулярний комплекс, ієрархічна архітектура.

Received / Одержано	Revised / Доопрацьовано	Accepted / Прийнято	Published / Опубліковано
09 May, 2025	30 May, 2025	05 June, 2025	26 June, 2025