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PHYSICAL PARAMETERS OF THE SYNTHESIZED COMPLEX COMPOUND OF COBALT (II) WITH N, N'-BIS(SALICYLIDENE)SEMICARBAZIDE

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Синтезовано новий матеріал стронцій тетрааквади[N,N'-біс(саліциліден)семикарбазидатокобальтат(II)] дигідрат (I) такого складу: $Sr[CoL'(H_2O)_2]_2 \cdot 2H_2O$, де H_3L = N,N'-біс(саліциліден)семикарбазид.

Молярна маса виділеної та зневодненої комплексної сполуки $Sr[Co(C_{15}H_{14}N_3O_5)]_2$ дорівнює 838,07 г/моль, а кількість валентних електронів в одній молекулі – 256. Для проведення експериментальних досліджень використовували циліндричний зразок масою 0,09 г та об'ємом $17,67 \cdot 10^{-9}$ м^3.

Проведено експериментальні вимірювання та теоретичні розрахунки основних фізичних параметрів даного синтезованого матеріалу. Розраховано густину речовини $\rho = 5,093\ 10^3$ кг / м^3 , масу однієї молекули $m_0 = 139,167\ 10^{-26}$ кг , кількість молекул в об'ємі досліджуваного циліндричного зразка $N_{мол} = 6,467\ 10^{19}$ молек. , кількість валентних електронів $N = 8,38\ 10^7$, ширину забороненої зони $\Delta E = 0,78$ еВ . Доведено, що даний матеріал є напівпровідником. Отримано залежності питомої провідності, густини струму, опору, сталої Холла та концентрації носіїв заряду від температури. В діапазоні температур від 273 К до 493 К: питомий опір матеріалу зменшується від $7,69 \cdot 10^{11}$ Ом·м до $2,88 \cdot 10^5$ Ом·м; концентрація носіїв заряду зростає з $3,25 \cdot 10^{14}$ м$^{-3}$ при 273 К до $8,66 \cdot 10^{20}$ м$^{-3}$ при 493 К; питома провідність досліджуваної структури зростає від $1,3 \cdot 10^{-12}$ (Ом·м)$^{-1}$ до $3,46 \cdot 10^{-6}$ (Ом·м)$^{-1}$; густина струму зростає від $2,6 \cdot 10^{-8}$ А/м до 6, $9 \cdot 10^{-2}$ А/м; квантова константа Холла зменшується від $2,26 \cdot 10^4$ м^3·Кл$^{-1}$до $8,49 \cdot 10^{-3}$м^3·Кл$^{-1}$. Отримано залежності напруженості електричного поля, всередині пластини розмірами 0,5×0,5×0,15 мм, від індукції магнітного поля: напруженість збільшується від $5,8 \cdot 10^{-3}$ В/м до 0,58· В/м та напруги Холла: Холлівська напруга зростає від $2,94 \cdot 10^{-6}$ до $2,94 \cdot 10^{-4}$В.

Key words: induction, temperature, magnetic field, concentration, semiconductor, heterometallic complex compounds.

Theoretical and experimental studies

The purpose of the study is to develop a new sensor based on the synthesized heterometallic complex of strontium tetraaquad[N, N'-bis(salicylidene)semicarbazidatocobaltate (II)] dihydrate.

It is known from [1 - 6] that the heterometallic complex compounds in solid compressed state have a wide range of electrically-conductive properties, which depend on features of a central atom, a heteroatom and chelating and bridging ligands and vary widely from dielectric to low impedance. In practical applications, the compounds can be used as semiconductor material for the thermistor manufacture.

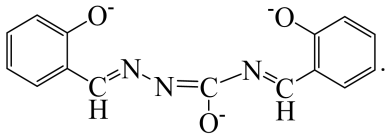
In order to found out new heterometallic complex compounds with semiconductor properties, a method of synthesing the heterometallic complex of strontium tetraaquad [N,N'-bis(salicylidene)semicarbazidatocobaltate(II)] dihydrate (I) with a composition of $Sr[CoL'(H_2O)_2]_2 \cdot 2H_2O$, where H_3L = N,N'-bis(salicylidene)semicarbazide was developed.

Synthesis of strontium tetraaquad [N,N'-bis(salicylidene)semicarbazidatocobaltate(II)] dihydrate. A portion of 1.79 g (0.01 mol) semicarbazone salicylic aldehyde was dissolved in 20 ml of ethanol in a water bath (t ~ 60 ºC). Then, 2.39g (0.01 mol) of $CoCl_2 \cdot 6H_2O$ dissolved in 20 ml of ethanol and 1.22g (0.01 mol) of salicylic aldehyde were added to the solution. The obtained mixture was heated to 60 ºC, kept in a water bath for 30-40 min and stirred intensively. A water-ethanolic (1:1) solution of $Sr(OH)_2$ was gradually added to the heated mixture (t ~ 60 ºC) to pH = 9 – 10. The color of the reaction mixture was constantly changing from green (at pH = 8) to brown (at pH = 10), the final fine crystalline precipitate formating. The reaction mixture was kept in a water bath for an hour, cooled, filtered in the

Schott filter, washed thoroughly with cold ethanol, ether and dried in a desiccator with $CaCl_2$ till the mass became constant at room temperature. A fine crystalline compound of brown color was obtained with a practical yield of 2.62 g, which is 60% of calculated theoretically.

The extracted complex compound I is insoluble in water, benzene, chloroform, acetonitrile, ether, poorly soluble in aliphatic alcohols and acetone, soluble in DMF and DMSO.

Considering the data of elemental analysis and physical-chemical analsis research methods (X-ray phase analysis, IR-spectroscopy, conductometry, magnetochemistry, thermogravimetry), the composition of the heterometal coordination compound of cobalt (II) and strontium with N,N'-bis(salicylidene)semicarbazide was determined by the following chemical formula [7]:

$Sr[CoL'(H_2O)_2]_2 \cdot 2H_2O$, where $L' = C_{15}H_{10}N_3O_3$ or .

The molar mass of the exacted and dehydrated complex compound $Sr[Co(C_{15}H_{14}N_3O_5)]_2$ equals 838,07 g/mol, while the number of valence electrons in one molecule is 256.

Since the synthesized heterometallic coordination compound of cobalt (II) and strontium with N, N'-bis(salicylidene) semicarbazide contains water crystallization molecules, electrically-conductive properties were measured after having kept it in an oven at 105 ºC until the sample weight stopped changing.

Investigations of the electrically-conductive properties of compound I in the form of a compressed cylindrical sample showed that at the temperature of 20 ºC its specific resistivity was $8 \cdot 10^{12}$ Ohm·cm. Moreover, when the temperature increased from 20 ºC to 150 ºC there was a typical for semiconductor materials rectilinear dependence between the specific resistivity (ρ) and the temperature (T). The calculated values of the temperature resistance coefficient (TCO) at 60 ºC for the compound I (-10.55% K^{-1}) and the sensitivity (B) of semiconductor materials (9055 K) substantiate that it is a semiconductor of medium sensitivity in the operating temperature range 20 – 150 ºC in comparison with other similar materials [8].

Experimental studies were conducted in the temperature range from 293 K to 423 K, on their base a mathematical model was obtained, which allowed modeling in a wider range from 273 K to 493 K.

A cylindrical specimen with mass of 0.09 g and volume of $17.67 \cdot 10^{-9}$ m^3 , which was made of the dehydrated complex compound (I) by compression method, was used in experimental studies. The substance density was calculated considering these data by the formula (1):

$$\rho = m / v = 5,093 \ 10^3 kg / m^3, \quad (1)$$

where ρ is the substance density; m is the test sample mass; V is the test sample volume.

Formula (2) was applied to calculate the mass of one molecule of the compound (I):

$$m_0 = M / N_A = 139,167 \ 10^{-26} kg, \quad (2)$$

where m_0 is the mass of the compound's molecule; N_A is the Avogadro number; M is the molar mass of the compound (I).

The total number of molecules in the cylindrical test sample filled with the compound (I) was found from formula (3).

$$N_{mol} = m / m_0 = 6,467 \ 10^{19} molec., \quad (3)$$

where N_{mol} is the total number of molecules; m_0 is the mass of one molecule of the compound (I); m is the mass of the test sample.

The number of valence electrons was determined by dividing the charge passing through the test cylinder per time unit by the electron charge (4):

$$N = \frac{q_\Sigma}{q_e} = 8,38 \ 10^7. \quad (4)$$

The charge carrier concentration in the structure with sizes of 0.5×0.5×0.15 mm was calculated at the temperature of 373 K:

$$n = N / V = 2,3568\ 10^{18} m^{-3}\ . \quad (5)$$

The conducted studies of electrically-conductive properties for the synthesized, dehydrated and compressed strontium tetraaquad[N,N'-bis(salicylidene)semicarbazidatocobaltate (II)] dihydrate in the temperature range of 293-423 K showed that its specific resistivity fell sharply from $8 \cdot 10^{10}$ Ohm·m to $6 \cdot 10^{6}$ Ohm·m with temperature rising, which was typical for semiconductor materials.

Experimental measurements enabled to calculate the specific conductivity of the material for these temperatures. For $T_1 = 293$ K we got $\sigma_1 = 12{,}5 \cdot 10^{-12}$ $(\text{Ohm} \cdot \text{m})^{-1}$, and for $T_2 = 423$ K we got $\sigma_2 = 16{,}6 \cdot 10^{-8}$ $(\text{Ohm} \cdot \text{m})^{-1}$. These experimental studies enabled to find out the width of the bandgap:

$$\Delta E = \frac{k \ln \frac{\sigma_1}{\sigma_2}}{\frac{1}{T_2} - \frac{1}{T_1}} = 1,249\ 10^{-19}\ J = 0,78\ eB\ , \quad (6)$$

where T is the absolute temperature; σ is the specific conductivity of the material; k is the Boltzmann constant.

The calculations proved that the material was a semiconductor [9].

Dependence of the specific conductivity on temperature was calculated considering the bandgap of the material and experimental data [10]. The graph of the logarithmic dependence of the conductivity on temperature is shown in Fig. 2.

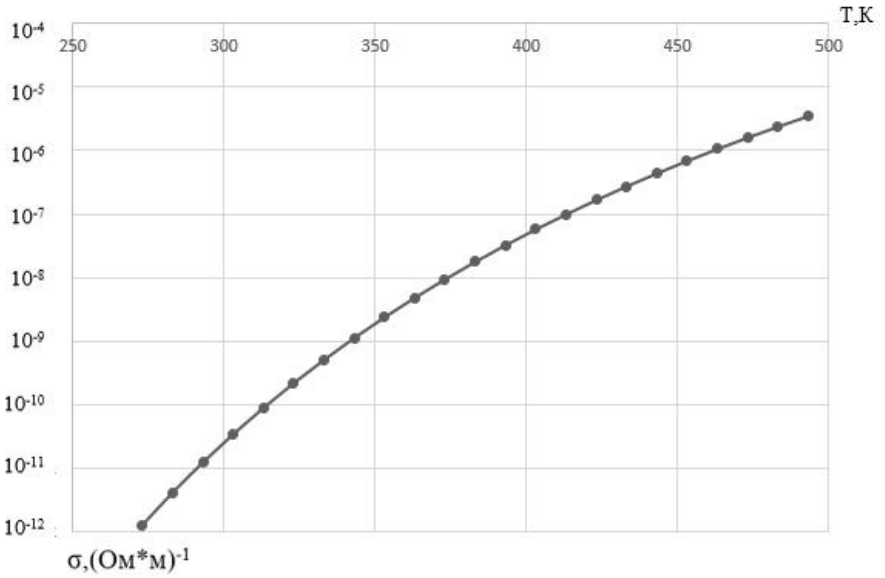


Fig. 2. Logarithmic dependence of the material specific conductivity on temperature

Fig.2 demonstrates that the structure's specific conductivity increases from $1.3 \cdot 10^{-12}$ $(\text{Ohm} \cdot \text{m})^{-1}$ to $3.46 \cdot 10^{-6}$ $(\text{Ohm} \cdot \text{m})^{-1}$, with temperature increasing from 273 K to 493 K.

Fig.3 demonstrates the material's specific resistivity changing with the temperature.

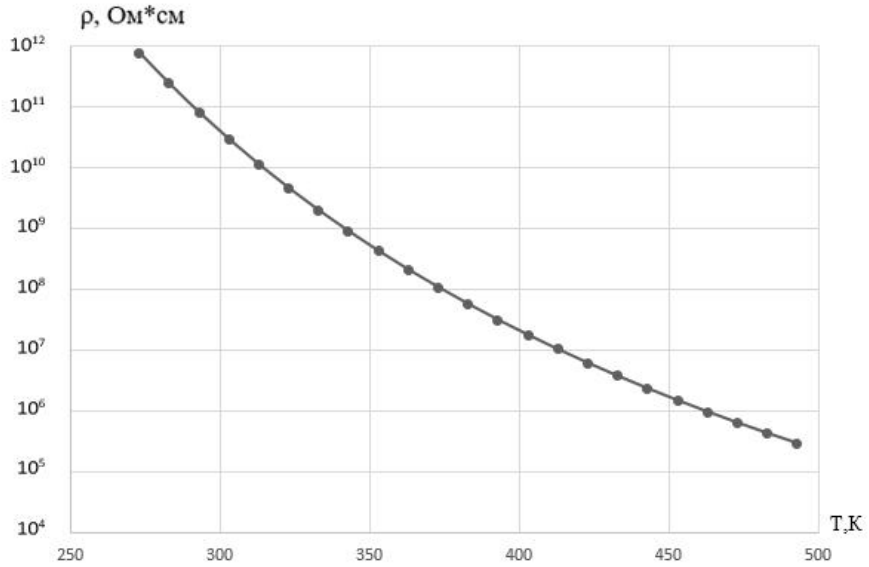


Fig. 3. Logarithmic dependence of the specific resistivity on temperature

The graph illustrates that the specific resistivity falls from $7.69 \cdot 10^{11}$ Ohm·m to $2.88 \cdot 10^{5}$ Ohm·m.

Fig. 4 illustrates the dependence of resistance on temperature for the semiconductor with sisez 0.5×0.5×0.15 mm.

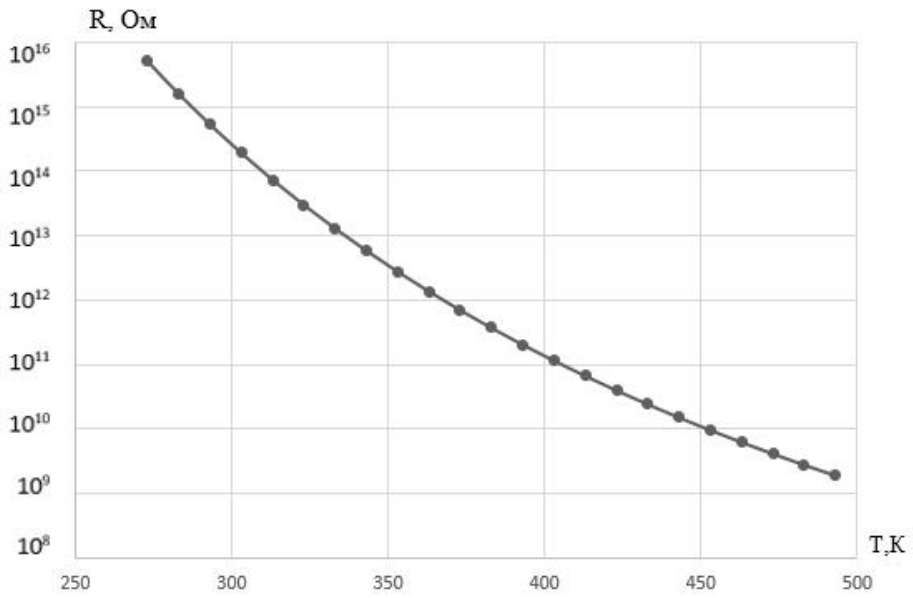


Fig. 4. Logarithmic dependence of the material resistance on temperature

The figure shows that the material's resistance falls from $5.127 \cdot 10^{15}$ Ohm at the temperature of 273 K to $1.92 \cdot 10^{9}$ Ohm at the temperature of 493 K.

Fig. 5 demonstrates the dependence of the current on temperature.

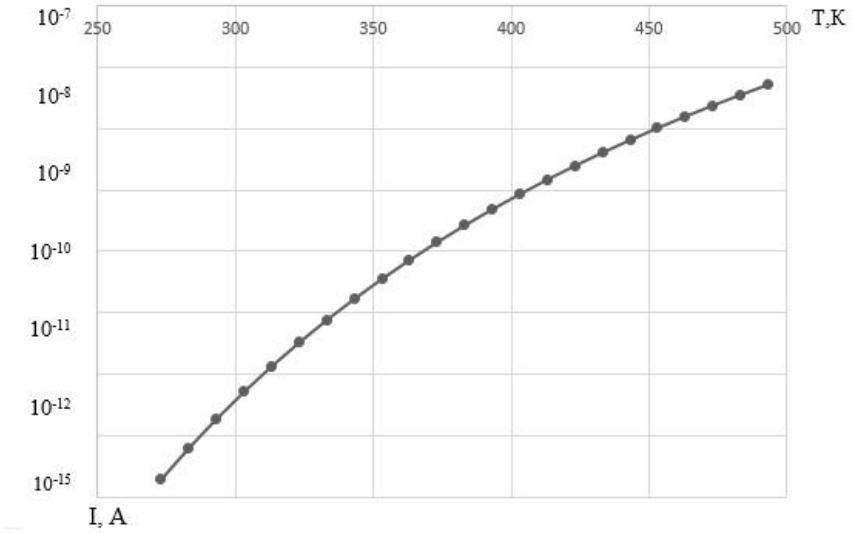


Fig. 5. Logarithmic dependence of the current on temperature

The graph shows that the current through the cylinder varies from $1.95 \cdot 10^{-15}$ A to $5.19 \cdot 10^{-9}$ A at the supply voltage of 10 V.

Fig. 6 illustrates the logarithmic dependence of current density on temperature at the supply voltage of 10 V.

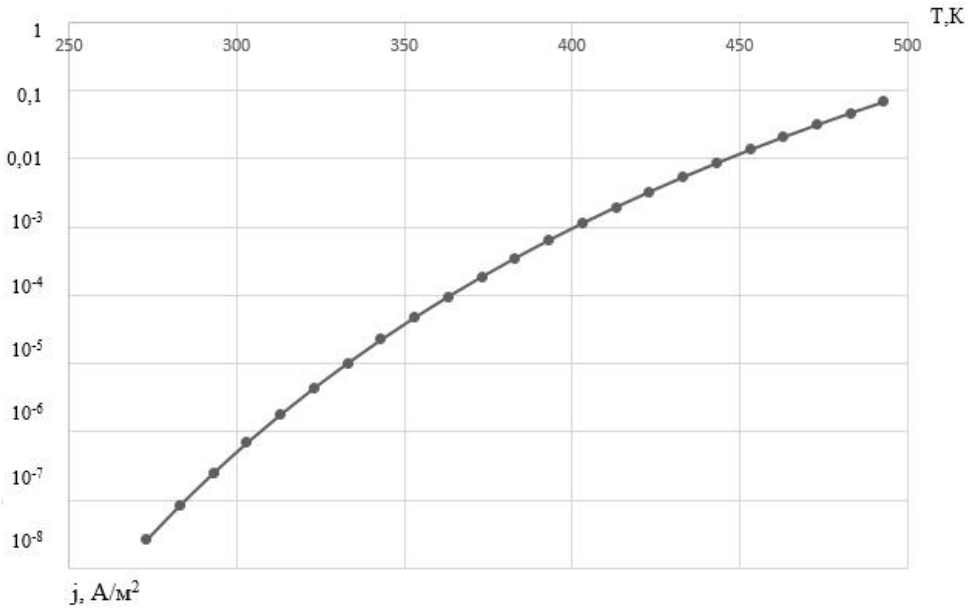


Fig. 6. Logarithmic dependence of the current density on temperature

The graph illustrates that the current density rises by 6 orders of magnitude from $2.6 \cdot 10^{-8}$ A/m to $6.9 \cdot 10^{-2}$ A/m in the temperature range from 273 K to 493 K.

Calculating the bandgap and the dependence of the semiconductor's charge carrier concentration on temperature provides a graph of the charge carrier concentration dependence on temperature, presented in logarithmic form in Fig. 7.

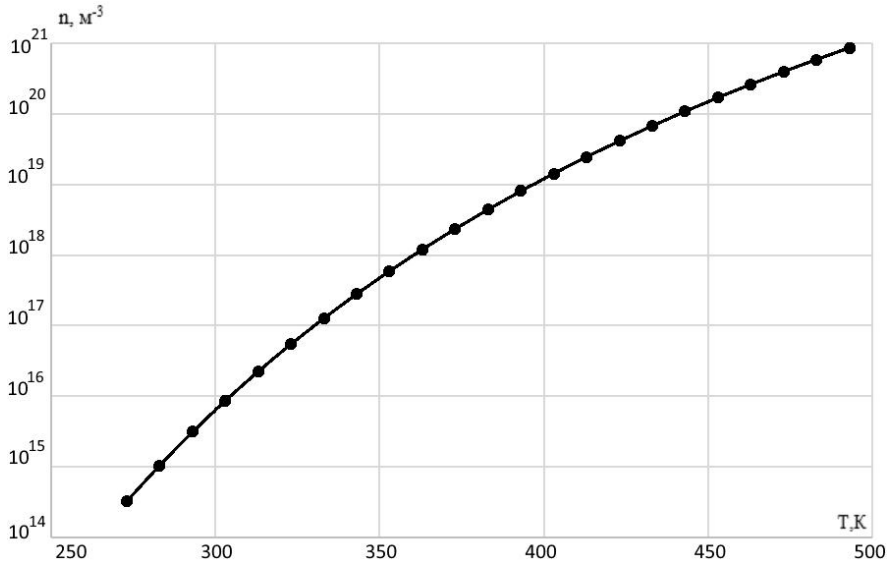


Fig. 7. Logarithmic dependence of the charge carrier concentration on temperature

Fig. 7 shows the charge carrier concentration rising from $3.25 \cdot 10^{14}$ m^{-3} to $8.66 \cdot 10^{20}$ m^{-3} in the temperature range from 273 K to 493 K.

Calculation of the Hall coefficient at 373 K provided the following results:

$$R_H = 1/nq = 2,66\, m^3 \ \ C^{-1}, \tag{7}$$

where q is the electron charge; n is the charge carrier concentration.

The quantum Hall coefficient was calculated by formula (8):

$$R_{q\,H} = -3\pi / 8nq = 3,12\, m^3 \ \ C^{-1}. \tag{8}$$

Having combined the equation of the charge carrier concentration dependence on temperature and formula (8), we get the Hall coefficient dependence on temperature (9):

$$R_{q\,H} = -\frac{3\pi}{8qn_0}\, e^{\frac{\Delta E}{kT}}. \tag{9}$$

A logarithmic dependence of the quantum Hall coefficient on temperature was obtained by applying this formula:

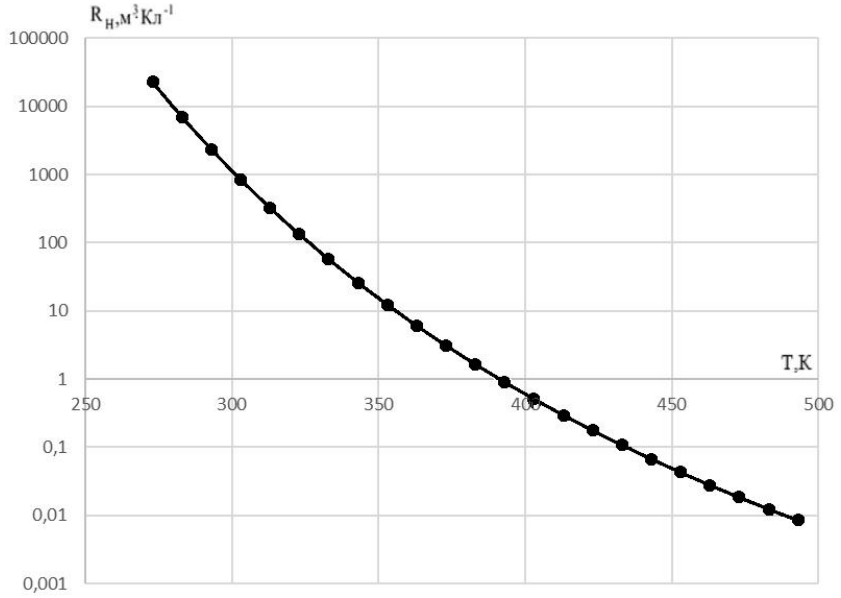


Fig. 8. Logarithmic dependence of the quantum Hall coefficient on temperature

The graph in fig. 8 shows the value of the quantum Hall coefficient for this complex compound falling from $2.26 \cdot 10^4$ $m^3 \cdot C^{-1}$ to $8.49 \cdot 10^{-3} m^3 \cdot C^{-1}$ with temperature rising from 273 to 493 K.

The mobility of charge carriers for a quantum case is:

$$\mu_n = R_{q\,H}\ \ \sigma\ =\ 2{,}94\ 10^{-8} m^3\ \ (B\ \ c)^{-1}. \qquad (10)$$

Substitution of the dependence of the specific conductivity and the Hall coefficient on temperature into (10) proved that the mobility of charge carriers did not depend on temperature.

Figure 9 shows calculation of the Hall voltage dependences for the electric field in the semiconductor with sizes 0.5×0.5×0.15 mm under action of the magnetic field in the semiconductor.

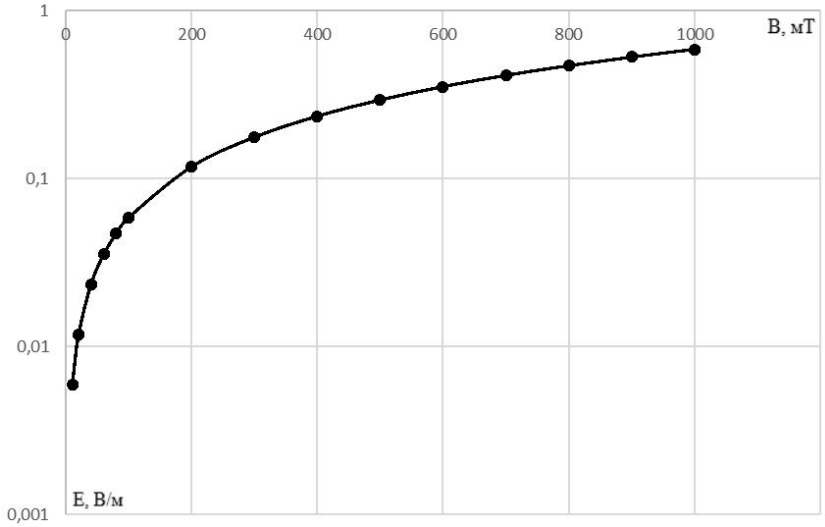


Fig. 9 Logarithmic dependence of the electric field strength in the semiconductor on the magnetic field induction

Fig. 9 illustrates the voltage rising from $5.8 \cdot 10^{-3}$ to 0.58 V/m in the range from 10 to 1000 mT.

The logarithmic dependence of the Hall voltage on the magnetic field induction for the studied compound is presented in Fig. 10.

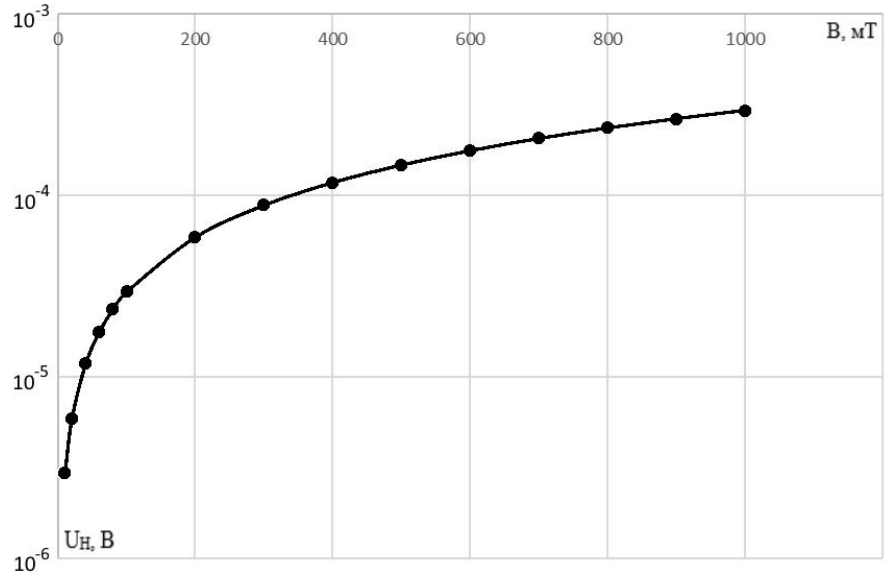


Fig. 10. Logarithmic dependence of the Hall voltage on the magnetic field induction

The graph illustrates the Hall voltage rising from $2.94 \cdot 10^{-6}$ to $2.94 \cdot 10^{-5}$ V in the range from 10 to 100 mT; from $2.94 \cdot 10^{-5}$ V to $1.17 \cdot 10^{-4}$ V in the range from 100 to 400 mT, and from $1.17 \cdot 10^{-4}$ to $2.94 \cdot 10^{-4}$ V in the range from 400 mT to 1000 mT.

Conclusions

A new sensitive element based on the synthesized heterometallic complex compound of strontium tetraaquad[N,N'-bis(salicylidene)semicarbazidatocobaltate (II)] dihydrate has been developed. The method of synthesizing this material is given and the influence of temperature and magnetic field on physical properties of this semiconductor is investigated.

The investigation of electrically-conductive properties for the synthesized material in compressed form at the temperature range of 273-493 K has demonstrated that its bandgap was 0,78 eB and its specific resistivity fell sharply from $7.69 \cdot 10^{11}$ Ohm·m to $2{,}88 \cdot 10^{5}$·Ohm·m with temperature rising, which was typical for semiconductor materials. The chemical compound starts to decompose from 523 K, the charge carrier concentration rises from $3.25 \cdot 10^{14}$ m^{-3} at 273 K to $8.66 \cdot 10^{20}$ m^{-3} at 493 K, while the Hall coefficient falls from $2.26 \cdot 10^{4}$ $m^{3} \cdot C^{-1}$ to $8.49 \cdot 10^{-3}$ m^{3} C^{-1} with temperature rising from 273 K to 493 K, the Hall voltage varies from $2.94 \cdot 10^{-6}$ to $2.94 \cdot 10^{-4}$V in the magnetic field range from 0 to 1000 mT.

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