

ISSN 1450-7404

Journal of Research in Physics

Volume 30
Number 2
2006



DEPARTMENT OF PHYSICS

Faculty of Sciences
University of Novi Sad - Novi Sad - Serbia

Journal of Research in Physics

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MIS Structures on InP Material Passivated by Anodic Oxidation. Characterization by Photoluminescence

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Received: October 29, 2004

Abstract

Condensed polyphosphates close to $\text{In}(\text{PO}_3)_3$ structure can be obtained by electrochemical oxidation. These oxides have good dielectric properties and a flexible structure allowing passivation of the fragile surface of indium phosphide. These qualities when added to the low roughness of the interface of 2 to 3 nm taken on this type of treatment may suggest applications in microelectronics technology. Thin layers of 10 to 15 nm of polyphosphates were used to passivate the interface InP/insulator. Photoluminescence spectra were recorded at low temperature, at the various stages of process of the MIS-InP structure realization. Cartographies of photoluminescence at ambient temperature made it possible to characterize the surface state after each technological stage. The results obtained, being in agreement with electrical measurements that have been carried out in former work, show the beneficial role of condensed phosphates on the properties of the MIS-InP structure. The fragile surface of InP seems to resist better to the alumina deposited by thermal evaporation. The degradation of the interface under the effect of repeated annealing is insignificant up to the temperatures of 350°C. The structure is also stable in time. The density of interface states is relatively low and its minimum is estimated to $10^{11} \text{ eV}^{-1}\text{cm}^{-2}$ using the Terman method. The integrated photoluminescence signal, at ambient temperature, measured at the end of the technological process, standardized against the PL measured on naked InP, is of the order of 30%, compared with 5% for a nonpassivated surface. Radiative major defects detected by spectral photoluminescence with the energy between 0.95 eV and 1.15 eV, assigned to the complexes impurities of phosphorus vacancies, are reduced considerably by the presence of anodic oxide.

Key words: Photoluminescence, MIS-InP, anodic oxide.

1. Introduction

In spite of the promising properties of indium phosphide, the problems which slow down the expansion of MISFET-InP are still far to being solved. The passivation of the

surface of the III-V compound is necessary, and various chemical treatments have been tried [1-4]. The electrochemical approach used in several previous works [5-7] allows a better control of the treatment and a broad range of oxidation parameters that affect the properties of the obtained oxide. However, some recent works have shown the potential passivating properties of anodic oxide for the interface of the MIS-InP structures [8-9]. The characterization of the interface of the MIS structures is generally based on measurements of high-frequency capacitance (Terman method) or in quasi-static mode (Berglund method). These methods require the use of good-quality dielectric material deposited by relatively soft methods to preserve the fragile surface of InP [10]. Hence, it is interesting to develop new methods of characterization of the interface to overcome these constraints. Photoluminescence (PL) is a simple method, fast, contactless, nondestructive and sensitive to the presence of interface defects [1, 10, 11]. Being a direct gap semiconductor, InP has a very high photoluminescence signal, even at room temperature. A broad range of utilization can be made possible for this characterization technique, namely: spectral PL at low temperature, PL cartography, integrated PL at ambient temperature and PL under electric polarization [10-13]. Although the setting for this characterization method can be made simple and very flexible, the interpretation of the measurement results is still a very delicate problem. The differences in the intensity of PL observed are generally assigned to the interface or surfaces defects and/or to the electric potential of the surface.

The objective of this work was to follow the changes of the spectral PL and the changes in its cartography measured at various technological formation stages of MIS on InP structures subjected to electrochemical treatment.

2. Experimental details

Two standard (100) oriented InP samples, doped N with 10^{16} cm^{-3} were considered. After cleaning with hot trichloroethylene and rinsing with methanol, two samples were pickled with HF 40% for one minute. Immediately after scouring the native oxide, a reference PL spectrum as well as a cartography of PL were recorded for one of the two samples. The other sample was subjected to electrochemical treatment, using a solution of AGW composed of 3% diluted orthophosphoric acid ($pH = 2$) mixed with glycol propylene in the ratio 1:2. Anodic oxidation of indium phosphide is carried out under white light illumination. The first oxidation phase was galvanostatic, whereby the current density was kept constant at 0.2 mA/cm^2 until the terminal voltage of the oxidation cell reached 20 V. Then a potentiostatic mode was employed for a softer termination of the treatment. The nature and physicochemical properties of the obtained oxides were studied in detail in previous works [14], the double-layered structure being a characteristic of this type of oxide. The outer indium-rich, strongly hydrated thin layer shows poor dielectric properties. At the interface, one finds a thicker layer of condensed phosphates of better quality, similar to $\text{In}(\text{PO}_3)_3$. The outer layer was dissolved using 0.01% diluted HF for 2 min which allowed to keep the phosphorus-rich layer at a thickness of 15 nm. The sample was then annealed at 250°C under nitrogen during 20 min, to eliminate any residual water traces. The following technological step consists of depositing the insulator (100 nm of alumina) on the two samples. The deposition was carried out by thermal evaporation with the electron gun within secondary vacuum environment and oxygen partial pressure. The annealing at 300°C under oxygen during 30 min made it possible to compensate for the deficit in oxygen, which is generally observed in this type of deposit. The last annealing under

forming gas ($\text{H}_2\text{-N}_2$) at 350°C for two hours was performed to cure certain interface defects and improve the quality of the structure. To finish the fabrication of the MIS-InP structure some semi-transparent aluminium contacts can be deposited for PL measurements under electrical polarization. Measurements of spectral PL and PL cartography were carried out after each technological step and annealing. A comparative study involving various measurements allows one to derive conclusions about the influence of the treatment used on the quality of the given structure.

3. Results and discussion

Photoluminescence spectra

The reference spectrum recorded for naked substrate is a typical one for an N-doped InP sample [15-17]. It contains three typical peaks, as shown in Figure 1:

- The highest peak P_1 , located at 1.41 eV, shows the luminescence close to the gap, which is due to bound excitons related to the surface impurities.
- The broad peak P_2 , located at 1.37 eV, is assigned to the band-acceptor or donor-acceptor transitions.
- The broader band P_3 , having the energy in the interval between 0.95 eV and 1.15 eV, also known as "Band C", is generally ascribed to the impurities (Fe, Cu, Mn, Co, Zn), forming complex defects with the phosphorus vacancies.

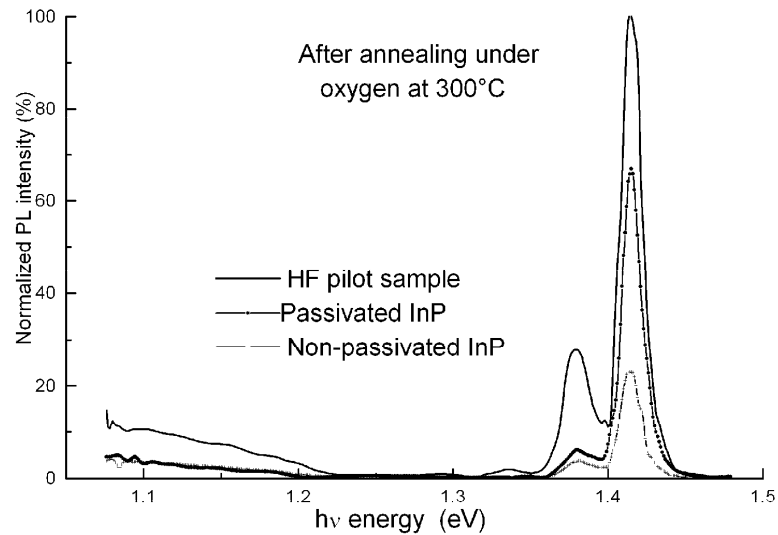


Figure 1. PL spectra measured at 77 K.

The spectrum recorded after anodic oxidation and dry annealing is of a shape comparable to the preceding one, with a considerable reduction of the intensities of all the peaks (Table 1). However an increase in the P_1/P_2 ratio is observed. This behavior can be ascribed to a strong curving of the energy bands close to the surface [18], due to negative

charges existing in the condensed anodic phosphates $\text{In}(\text{PO}_x)_y$. Indeed, y is generally higher than 3, corresponding to the stoichiometry [14]. In addition to this, measurements of $C(V)$ (capacity-voltage) characteristics of thicker anodic oxides (around 80 nm) has shown an apparent shift towards positive voltages, which indicates a situation of depletion at rest. However, this observation does not completely exclude the presence of defects in the InP-oxide interface involving nonradiative recombinations.

After depositing the insulator on the two samples, we could clearly notice (see Table 1) the difference between a surface protected by the anodic oxide and a naked InP surface. The PL grows considerably for the electrochemically treated sample, whereas it strongly falls down for the untreated sample. It is clear that the deposition of alumina by evaporation using the electron gun considerably degrades the fragile surface of InP. The increase of luminescence for the treated sample can only be explained by a change in the potential of surface due to a global positive charge in the deposited alumina. This positive charge is due to the deficiency in oxygen generally reported for this type of deposit. Annealing under oxygen is generally needed to improve the quality of thus deposited alumina [9].

After annealing under oxygen at 300°C during 30 min, the alumina loses its positive charges, while approaching the stoichiometry which, once reached, modifies the curving of the energy band at the interface. The intensity of peak P_1 (Figure 1) decreases but remains relatively high (66% of the reference P_1) compared with that of the pilot sample (20%). For the sample treated, the ratio P_1/P_3 is comparable with that of the reference spectrum (Table 1), suggesting that the surface was preserved well during the deposition process.

Thermal annealing is generally used in the technological process to cure the interface defects caused by the insulator deposit. An annealing at 350°C under forming gas ($\text{H}_2\text{-N}_2$) during two hours is recommended [9]. The PL spectra recorded for the two samples having undergone the same annealing are presented in Figure 2.

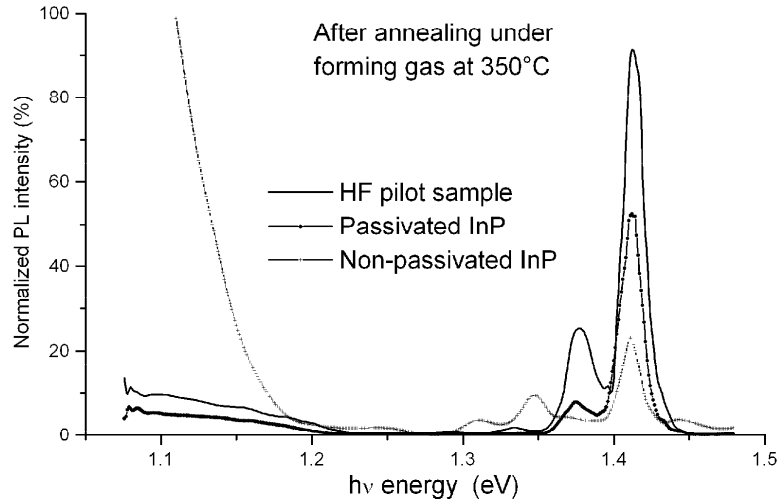


Figure 2. PL spectra (77 K) recorded after annealing at 350°C.

We can clearly see the beneficial effect of electrochemical treatment on the surface of indium phosphide. The ratio P_1/P_3 is of the order of 6 for the protected surface (its value

for the reference sample lies between 7 and 8) and only 0.1 for non-protected samples (Table 1). The increase of the peak P_3 after annealing at high temperatures is generally ascribed to the phosphorus vacancies and/or complex defects combining impurities and vacancies [15-17]. To explain the beneficial role of anodic oxide one can evoke the following two arguments:

- The condensed polyphosphates which are rich in phosphorus constitute a diffusion barrier and prevent the decomposition of InP under the influence of temperature.
- The protected surface during deposition is less damaged, and hence it is becoming less vulnerable to the effect of repeated annealing.

Table 1. Results of spectral PL.

	1 st Treatment		Alumina Deposition		1 st Annealing O ₂ - 30 min		2 st Annealing (H ₂ -N ₂) - 2 h	
	Sample HF	Anodic Oxidation	Sample HF	Anodic Oxidation	Sample HF	Anodic Oxidation	Sample HF	Anodic Oxidation
P ₁ (%)	100	31	22.4	168	20.5	65.9	25.8	57.4
P ₂ (%)	28	4.6	3.5	23.5	3.4	5.7	4.4	4.2
P ₃ (%)	13	4.8	3.8	4.5	34.2	7.5	274.7	9.1
P ₁ /P ₂	3.6	6.7	6.4	7.1	6.0	11.6	5.9	13.7
P ₁ /P ₃	7.7	6.5	5.9	37.3	0.6	8.8	0.1	6.3

At the end of our study we performed the scouring of the deposited alumina on the two samples. The treated surface was relatively preserved, whereas the untreated InP surface was characterized by a colored white-silver, which indicates the presence of the indium metal on the surface, and thus an irreversible decomposition of indium phosphide at high temperatures.

Photoluminescence cartography

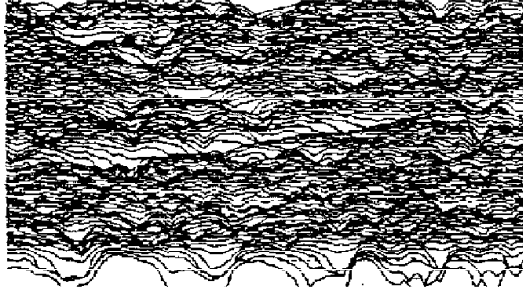
Figure 3 shows some PL cartographies taken on 1 mm × 1 mm surfaces located in the targeted regions on the surface of the two samples. Table 2 shows the average values of the integrated PL measured at 300 K for the two samples after each technological step. The PL is standardized and compared with the reference signal recorded for the naked InP.

Table 2. Integrated PL measured at 300 K after each technological step.

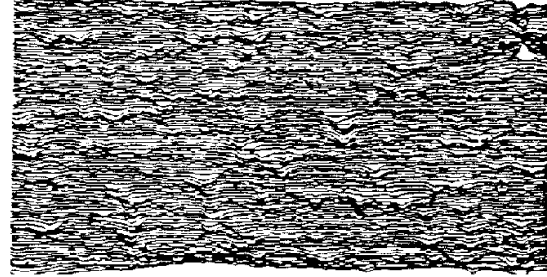
Sample	Initial Treatment	Deposition of Al ₂ O ₃ & Annealing O ₂	Annealing H ₂ -N ₂
Standard HF	100 %	5 to 10 %	< 5 %
InP/anodic oxide	10 to 20 %	30 to 40 %	25 to 30 %

It is generally admitted that a high PL signal is an indication of a good quality of the interface [15]. This fact confirms once again the beneficial role of the electrochemical treatment on the InP/alumina interface. For the protected sample, about 30% of the PL signal is preserved, whereas for the non-protected surface, the PL signal falls down to 10% after alumina deposition and to less than 5% after two thermal annealings. The

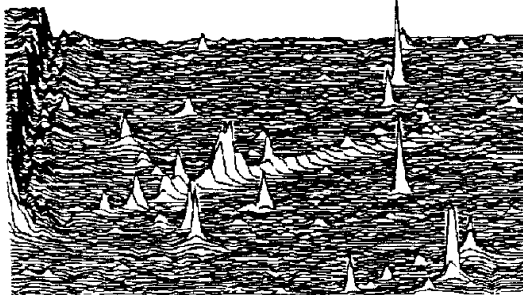
surface of the treated sample is more homogeneous because the anodic oxidation shifts the interface towards the bulk of the substrate, and thus eliminates many surface defects.



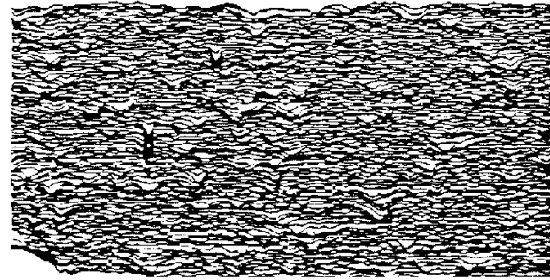
Pilot sample pickled with HF 40% for one minute. PL = 100%



InP anodically oxidized and annealed under nitrogen during 30 min at 200°C. PL = 10 to 20%



Naked InP after deposition of alumina - annealed under oxygen at 300°C during 30 min. PL = 5 to 10%



Passivated InP after deposition of alumina and annealing under oxygen at 300°C during 30 min. PL = 30 to 40%

Figure 3. PL cartographies measured at 300 K.

4. Conclusion

The results obtained by measuring PL and PL cartography confirm the beneficial role of the condensed polyphosphates $\text{In}(\text{PO}_x)_y$ on the interface quality of MIS-InP structures. Electrochemical oxidation yields a shift of the interface towards the bulk, and thus eliminates many surface defects. This highly improves the homogeneity and the quality of the samples. The anodic oxide protects the fragile InP substrate during the alumina deposition. The phosphorus-rich condensed phosphates, obtained by electrochemical deposition, build a diffusion barrier and limit the creation of phosphorus vacancies, as well as of complex defects related to them and formed during repeated annealing. We expect that the PL measurements under electrical polarization will allow the determination of surface states density. In addition, some other chemical treatments will be considered in the future using the same techniques.

Acknowledgments

We would like to thank the research groups of Prof. J. Joseph and Prof. S. K. Krawczyk

of ECLyon for their assistance in accomplishing this work.

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Experimental Test of Exponential Decay of ^{198}Au

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Received: January 13, 2005

Abstract

The experimental test of the exponential decay of ^{198}Au has been performed applying the Ge semiconductor spectrometer. The decay of ^{198}Au nuclei was followed by the precise measurement of the decay constant over the time interval of 1.3 half-life in the time period from 0.02 to 25 half-lives after the irradiation. No deviations from the exponential law have been detected within the limits of the experimental error. The measured value of the ^{198}Au half-life was in good agreement with the previously measured value.

Key words: Half-life, ^{198}Au , non-exponential decay

1. Introduction

Considering general problems of the decay theory of the quasi-stationary states, Khalfin [1] demonstrated that the decay rate of the quasi-stationary state does not strictly obey the exponential law for all $\Gamma t/\hbar$, where $2\Gamma/\hbar$ is the reciprocal value of the quasi-stationary state half-life, t is time and $2\pi\hbar$ is the Planck constant. The evidence for a non-exponential decay of the quasi-stationary state was produced on the basis of the general quantum-mechanical presumptions and its validity was general one and showed no dependence on the applied decay model of the quasi-stationary state. The decay rate deviations from the exponential law were expected when $t \rightarrow 0$ and for long times. The first derivative of the survival probability of the quasi-stationary state is equal to zero for $t = 0$ [2], and therefore decay rate tends to zero when $t \rightarrow 0$. Applying Paley-Wiener's theorem, Khalfin demonstrated that the decay rate was slowing-down for long times. Between these two time intervals, the decay of the quasi-stationary state obeys the exponential law with a high accuracy [1]. The experimental testing of the exponential decay have been performed by Rutherford - 27 half-lives of ^{222}Rn [3], Butt and Wilson - 40 half-lives of ^{222}Rn [4], Winter - 34 half-lives of ^{56}Mn [5] and Norman *et al.* - 45 half-lives of ^{56}Mn [6]. Within the limits of the experimental error, the observed nuclei decay rates did not deviate from the exponential law. The decay of elementary particles, also, strictly obey exponential law [7]. The experimental investigation of the ^{198}Au decay in the time interval from 0.02 to

25 half-lives ($T_{1/2}$) is presented in this paper.

2. Experiment

The half-life of ^{198}Au amounts to 2.69517 d [8], and its decay is followed by emission of three photons having energies larger than 100 keV : 411.8 keV (yield=95.5%), 675.89 keV (yield=1.06%) and 1087.7 keV (yield=0.23%). All three energies can be easily detected with an HPGe coaxial detector and the decay rate of ^{198}Au measured in the long time interval. The most convenient energy is 411.8 keV, due to its high yield. The gold foils of high nuclear purity (activation detectors) can be applied for that purpose. In the present experiment, the gold foils produced by Reactor Experiments, Inc., USA, were used. The nuclear purity of these foils was extremely high; the measured impurities were Zn (weight fraction $\approx 1.5 \cdot 10^{-6}$) and Ag (weight fraction $\approx 2 \cdot 10^{-6}$) [9]. In order to measure the decay rate in a long time period, two samples of gold foils were made and irradiated by different neutron fluxes. The first sample of the mass of 1 g was irradiated for 0.5 h with a flux of 10^7 n/cm²s in the reactor of the Institute for Nuclear Sciences "Vinča". The activity of this sample was sufficiently high for measurement of the decay rate from 0.02 $T_{1/2}$ to 5.86 $T_{1/2}$ with a high accuracy. The second sample of the mass of 170 mg was irradiated 0.5 h by the flux of $1.9 \cdot 10^{14}$ n/cm²s in the reactor of the Institute of Isotopes Co., Ltd, Budapest, Hungary. The activity of the sample immediately after irradiation was about 50 GBq and its decay rate was measured to 25 $T_{1/2}$.

The spectrometer used in this experiment was a HPGe coaxial detector in the lead shield of efficiency = 15% and $FWHM = 2.1$ keV (Schlumberger) and 8k digital multichannel analyzer - Canberra DSA1000. The MCA contains high voltage power supply, amplifier, ADC converter and spectrum stabilizer. Canberra program Genie 2000 was used for the spectra recording, and extraction of the necessary data from the recorded spectra.

Data acquisition by HPGe spectrometers can be insufficiently accurate due to dead time losses and pile-up of pulses. It means that the ratio net-area of the peak/live time can be an insufficiently accurate value for the precise measurement of the decay rate with a high accuracy. Parker [10] suggested the application of reference sources for the accurate measurement of the half-lives, in order to avoid errors caused by the combined influence of the dead time and pile-up of pulses. The ratio of the net-areas of two peaks, of the element the half-life of which should be determined and of the reference, is,

$$\frac{N_1(t)}{N_2(t)} = \frac{N_1(0)}{N_2(0)} e^{-(\lambda_1 - \lambda_2) t} \quad (1)$$

where $N(t)$ is the net-area of the peak at a time t , and λ is the decay constant; the index 1 denotes the radionuclide the decay constant of which is measured and 2 denotes the reference source. From the above equation, one obtains the linear function

$$\ln \left(\frac{N_1(t)}{N_2(t)} \right) = \ln \left(\frac{N_1(0)}{N_2(0)} \right) - (\lambda_1 - \lambda_2) t, \quad (2)$$

which is convenient for the determination of the decay constant λ_1 without the dead time and pulse pile-up corrections. The implicit assumption of this method is that the quantities of lost pulses are the same in both peaks. Parker [10] suggested that the energy difference

of the peaks should be as small as possible and, also, that short time constants of the amplifier should be applied in order to fulfill this assumption.

Before the measurement of decay rate of ^{198}Au over the period of 70 days, the experimental examination of the HPGe spectrometer was performed by the measurement of the net-area ratio of the peaks of energies 356 keV and 661.66 keV of ^{133}Ba and ^{137}Cs , respectively. From the solution containing a mixture of ^{133}Ba and ^{137}Cs three point sources of different activities were made and their activities covered the input counting rate range from 590 cps to 3050 cps. The net-area ratio of the both peaks was constant within the limits of the experimental error (Fig. 1). All measurements of the irradiated samples (together with the reference source) were within the input counting rate range from 650 cps to 3200 cps. This relatively narrow range was achieved by choosing the appropriate quantity of the irradiated gold and by changing the source-detector distance. The total number of measured samples was fifteen. The reference source was ^{137}Cs for the first 20 $T_{1/2}$. After 20 $T_{1/2}$, the peak of the energy of 657.8 keV of ^{110m}Ag started to disturb exact evaluation of the net-area of the reference peak (661.66 keV). Further measurements were performed using ^{54}Mn (834.8 keV) as the reference source. The sum-peak of the energy $2 \cdot 411.8 = 823.6$ keV was sufficiently distant from the reference peak and it did not disturb net-area calculation of the reference peak. The reference sources were positioned at the same detector-source distance during the experiment.

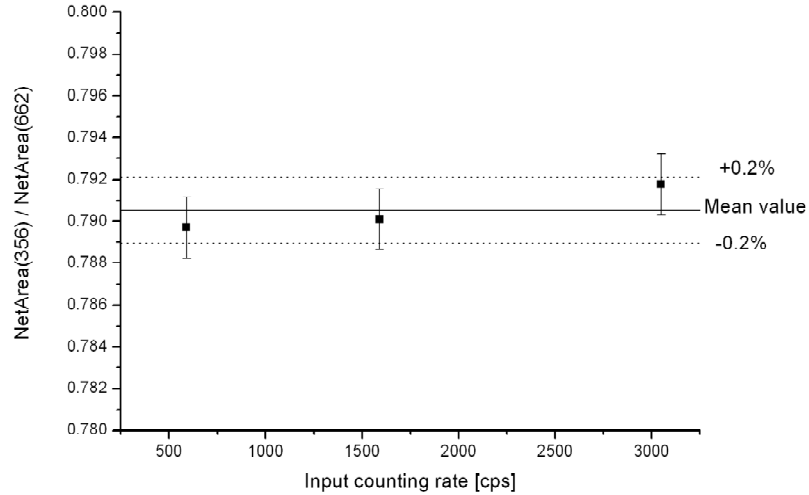


Figure 1. Ratio of the 356 keV and 662 keV net areas versus input counting rate.

The time interval of the spectrum data collection was 10000 s of real time. The 30 successively recorded spectra were used for the determination of the decay constant, so the total time interval of one series amounted 300000 s or 1.3 $T_{1/2}$. The new series of measurement started with a shorter detector-source distance, and/or with increased quantity of irradiated gold in order to keep the range of the input counting rate (Fig. 1) and achieve high accuracy.

The Canberra program Genie 2000 and its batch files were used for the extraction of the necessary data: the start time of the spectrum collection, live time, net-areas of the both peaks and errors of the net-areas determination. The internal computer time, used in the experiment, was controlled by the program Internet time (server: time.windows.com).

3. Discussion and conclusion

The logarithm of the net-areas ratio of ^{198}Au peak and reference peak is a linear function of time (Eq. 2). The slope of the straight line is equal to $-(\lambda_1 - \lambda_2)$, which can be determined with a high accuracy by the least-squares method since all points on the line are determined with high accuracy (Fig. 2). The values of the decay constant of ^{198}Au measured at different times after the irradiation of the gold foils (column 2), their errors (column 3) and reduced χ^2 (column 4) are listed in Table 1. The reduced χ^2 shows the ratio of the external error caused by the device instability and internal error determined by the statistical laws. If the value of the reduced χ^2 is close to 1, the stability of the device is satisfactory and the assumed λ v.s. t dependence is correct. The values of the decay constant of ^{198}Au measured over the period from $0.02 T_{1/2}$ to $25 T_{1/2}$ are shown in Fig. 3. The mean value of all 15 values of the decay constant is,

$$\lambda = (2.97707 \pm 0.00012) \cdot 10^{-6}.$$

The difference between the above value and the already published value [8], $\lambda = 2.97663 \cdot 10^{-6} \text{ s}^{-1}$, is +0.015%. The confidence level of the calculation of the error of λ is 95%.

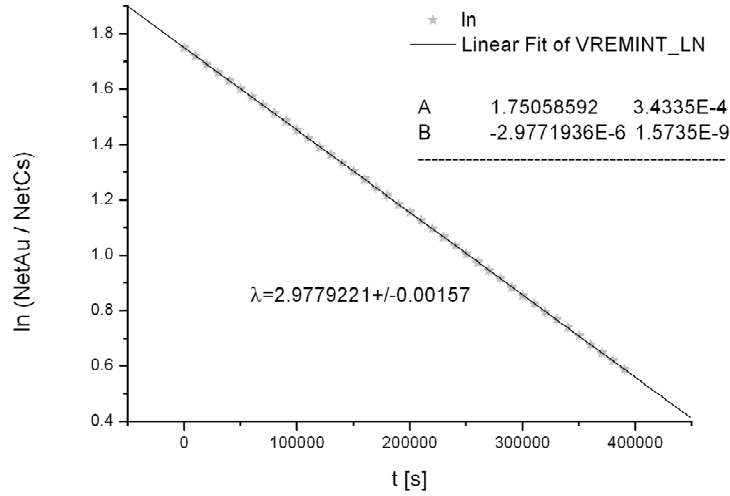
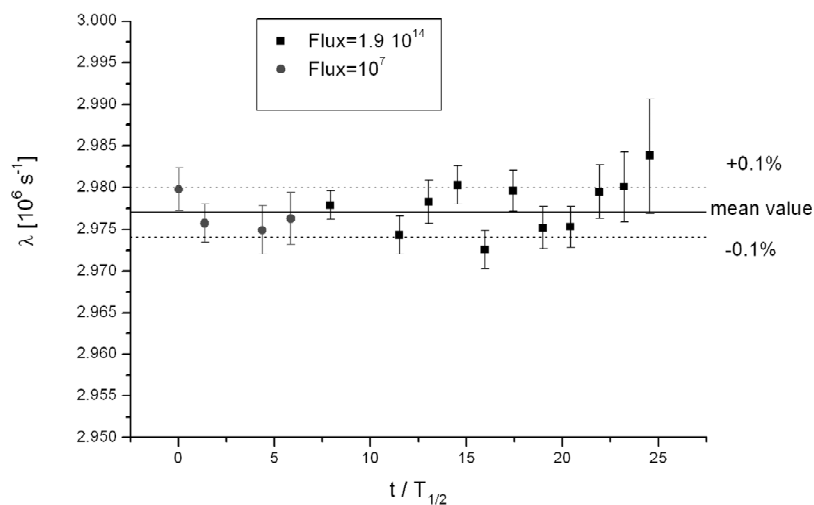


Figure 2. Typical graph of logarithm of the net area ratios versus time.

The chosen time interval for the measurement of one series was a compromise between two opposite requirements: the detection of the potentially short time decay rate deviations from the exponential law demands a measurement in short time intervals, but accurate measurement of the decay constant demands long time intervals and the eventual oscillatory deviations from the exponential law are integrated. The chosen time interval of 300000 s is sufficiently long for accurate determination of λ and, also, for noticing the potential variations of λ (which are not caused by the statistical laws) measured in the course of time. However, the variations of λ (from -0.16% to $+0.22\%$ about the mean value) were within the limits of statistical error.

Table 1. The measured values of the decay constant of ^{198}Au .

$t/T_{1/2}$	Decay constant [10^6 s^{-1}]	Standard error [10^6 s^{-1}]	χ^2 reduced	Note
0.02017	2.97981	0.00256	1.16	Flux = 10^7
1.3821	2.97572	0.00231	0.89	
4.3774	2.97949	0.00294	1.00	
5.8562	2.97626	0.00312	0.63	
7.9167	2.97791	0.00169	1.11	Flux = $1.9 \cdot 10^{14}$
11.514	2.97427	0.00228	0.93	
13.048	2.97827	0.00258	1.17	
14.552	2.98027	0.00233	0.97	
15.966	2.97252	0.00229	0.98	
17.4321	2.97962	0.00246	1.03	
18.9961	2.97518	0.00251	1.02	
20.4275	2.97529	0.00245	0.93	
21.9361	2.97949	0.00321	1.34	
23.2248	2.98006	0.00420	1.27	
24.5598	2.98382	0.00687	1.28	

**Figure 3.** Decay constants over 25 half-lives of ^{198}Au .

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Characteristics of Plasma and Plasma Jet Formed by High Current Pulses Applied to the Wall Stabilized Arc

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Received: April 25, 2005

Abstract

This paper deals with some of basic characteristics of the plasma and plasma jet formed during high current pulses applied on the wall stabilized electric arc. Plasma diagnostics for closed and for one-side open arc is performed. Using open arc, a pulsed plasma jet in free space was obtained, outside the plasma column. The plasma characteristics, which have been significantly modified, are presented here together with arc modification details as well as spatially resolved radiation intensity of the plasma jet.

Key words: Wall stabilized electric arc, plasma diagnostics, plasma jet

1. Introduction

The aim of this work was to determine electron density and temperature of wall stabilized electric arc plasma formed by high current pulses applied to the arc, and to study characteristics of a pulsed plasma jet obtained in free space, outside the plasma column.

Wall stabilized electrical arc is often used as a plasma source in various fields of spectroscopy, as well as plasma source for material processing. Since this kind of arc usually works in DC regime, power delivered is limited, so the current is typically few tens of amps. The arc working in this regime is suitable for observation of spectral lines emitted by neutral atoms. In some special cases arc current reaches 200 A (helium arcs [1]). High arc current can be realized in pulses, using power from AC network, and these currents can reach values up to 1000 A or more.

Increasing the arc current is important since higher current means higher plasma temperature, electron density and emissivity. In this paper we present the characteristics of arc plasma with $1.35 \cdot 10^{23} \text{ m}^{-3}$ electron density and 13500 K electron temperature reached during a pulse of 200 A. This implies the possibility to use wall stabilized arc as a source of ionic spectral lines, as well as for material processing in different ways.

2. Wall stabilized electric arc as a pulsed plasma source

A wall stabilized electric arc operating at atmospheric pressure was used as a plasma source [2]. The arc is described in detail by Voigt and Roberts [3].

The arc consists of six water-cooled discs, 7.1 mm thick, separated by 0.5 mm Teflon gaskets which serve as insulators and seal off the channel from the air. The diameter of the arc channel is 5 mm and its length is 50 mm. Arc operates in the pure argon at the atmospheric pressure and a mixture of argon and 2 % of hydrogen is introduced in the central part of the arc. The hydrogen is necessary for recording the Balmer H_β line, which is used for electron density determination. All gases exit from the two sections adjacent to the central section of the arc. This flow arrangement is necessary in order to keep hydrogen away from electrode regions, where plasma conditions are quite different from those at the central part of the arc.

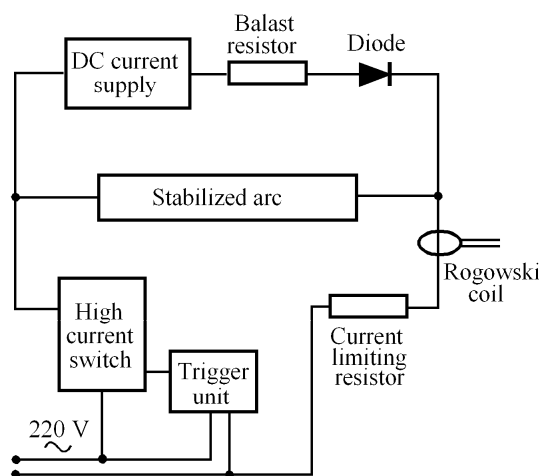


Figure 1. Block scheme of the electric circuit.

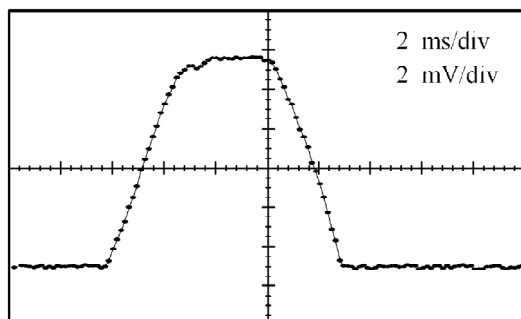


Figure 2. Pulsed current recording.

The wall stabilized arc in DC regime is supplied from a current stabilized electrical source with the current stability of 0.3 %. Maximum current is 30 A. This current provides plasma electron temperature between 10000 K and 11000 K and electron density of the order 10^{16} cm^{-3} [2, 4]. Higher values of these plasma parameters demand higher discharge currents. One way to do this economically is to apply high current pulses superimposed to the DC current. This can be done using the AC network of 220 V in combination with appropriate electronic circuit. In combination with appropriate resistor it provides current pulses lasting 8 ms, with the peak current of 170 A. Block scheme of the electric circuit is presented in Fig. 1.

The DC source is connected to the arc via diode which protects DC power supply from high current pulses. Pulsed current source is connected to the arc via resistor of 0.9Ω . Every 16th halfperiod of 50 Hz cycle is used to produce high current pulse. So, repetition rate of the high current pulses is 3.12 Hz. This repetition rate is low enough not to affect temperature of the arc walls which are water-cooled in usual manner. The pulsed current was measured by means of a Rogowski coil, and monitored by digital oscilloscope. Example of pulsed current recording is given in Fig. 2.

3. Experimental setup

Spectroscopic observations were made along the arc axis through a cathode hole. Scheme of the optical and control systems is presented in Fig. 3.

The arc is imaged 1:1 on to the entrance slit of the 1m monochromator by means of a

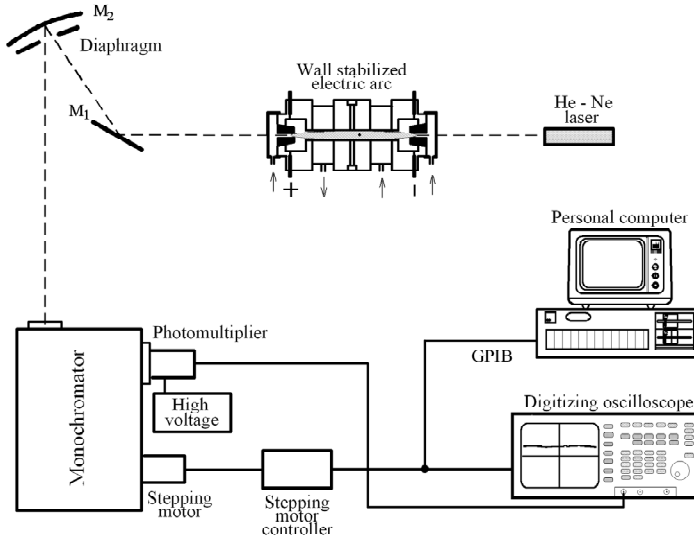


Figure 3. Schematic diagram of the optical and control systems.

computer is used for data acquisition. Using this technique the error in the spectral intensity measurements was less than 1 %.

4. Pulsed plasma diagnostics

Electron density $N_e = 1.35 \cdot 10^{23} \text{ m}^{-3}$ was determined from the halfwidth of the Balmer H_β line. This measurement was performed in conjunction with theoretical calculations [5]. Example of the experimentally obtained H_β line profile is shown in Fig. 4.

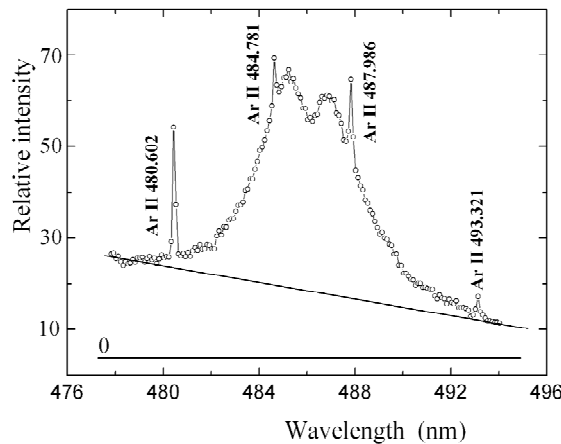


Figure 4. Experimental H_β line profile.

concave focusing mirror [2, 4]. He-Ne laser is used for the optical alignment. The monochromator is equipped with 1200 g/mm grating (0.833 nm/mm inverse linear dispersion), stepping motor with 36000 step/rev and a photomultiplier at the exit slit. The accuracy of wavelength setting was 0.0025 nm. Signals from the photomultiplier are led to the digitizing oscilloscope working in the averaging mode (32 samples over 200 ms for each sample). The stepping motor and oscilloscope are controlled by the personal computer through an HP-IB interface. The same

computer is used for data acquisition. Using this technique the error in the spectral intensity measurements was less than 1 %. From Fig. 4 it can be seen that there are several Ar II spectral lines superimposed onto the H_β line profile. These lines are very narrow and they have no influence on the H_β line halfwidth measurements. A few neutral argon lines, which are mostly placed at the red wing of the H_β line profile, are more broadened and of much smaller intensity than Ar II lines. In that sense, these Ar I lines rise the red wing of the H_β line profile and therefore a correction of the red wing is necessary. Estimated error of the measured electron density, which does not exceed 9 %, was derived from the error in the H_β line halfwidth measurements and typical uncertainty in electron density determination [6].

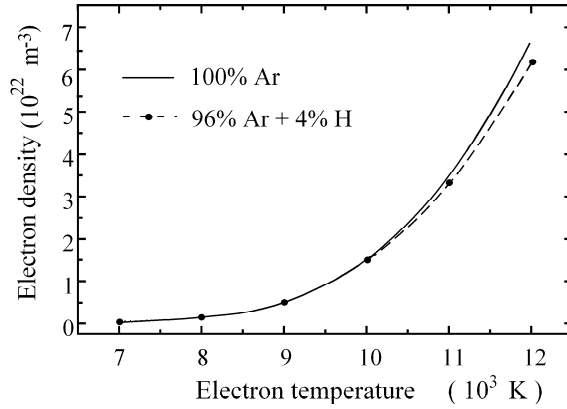


Figure 5. Electron density and temperature dependence.

Electron temperature $T_e = 13500$ K was derived from [7]. Calculations from the plasma composition data using procedure described in [8] showed that the plasma of a mixture of argon with small addition of hydrogen (less than 4 %), can be treated as a pure argon plasma (see Fig. 5). This confirms that the results from Ref. 7. can be used for temperature determination. The error in temperature determination of 3 % was estimated from the uncertainty of N_e and its influence on the T_e determination.

5. Pulsed plasma jet

Wall stabilized arcs usually have closed ends in the region of electrodes, and when high current pulses are applied, effects on plasma column are limited only to the plasma column between the arc electrodes. In the case when one or both ends are opened, the applied high current pulses superimposed to the DC current, cause the appearance of plasma jet outside the plasma column, in free air. This is illustrated in Fig. 6.

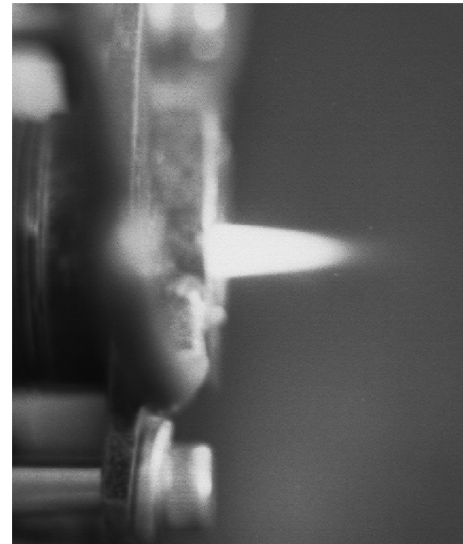
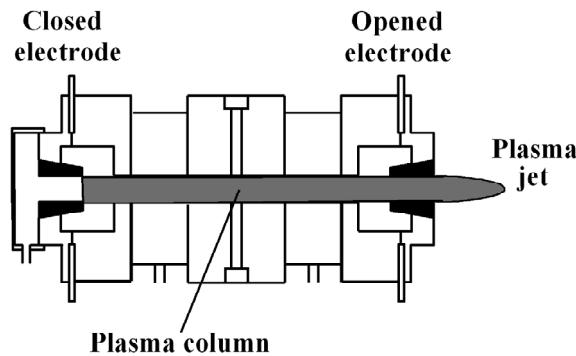


Figure 6. Illustration of plasma jet formed in free air when high current pulses are applied in addition to DC current (a) and plasma jet photography (b).

The arc normally operates in pure argon at the flow rate of 3 l/min, but when high current pulses are applied, the flow rate of argon must be considerably higher (6 l/min), so the plasma jet is formed practically in argon, but outside of the arc plasma column.

The plasma jet was photographed, and a 1:1 image is shown in Fig. 6b. The brightest part of this jet is the part closest to the arc electrode and at the axis of the discharge. Measurements of the average dimensions of the jet from photographed image gave the

length of 20 mm, and maximal radius of 2.5 mm.

6. Optical assembly for pulsed plasma jet observation

In order to record optical emission from plasma jet, the optical system shown in Fig. 7 was assembled. It enables recording of spatially resolved integral intensity of the plasma jet radiation. The X-Y moving system provides recordings of integral optical emission at different positions. Optical signals are led to the digitizing oscilloscope through the optical fibre and photomultiplier. The rest of the apparatus is the same as shown in Fig. 3.

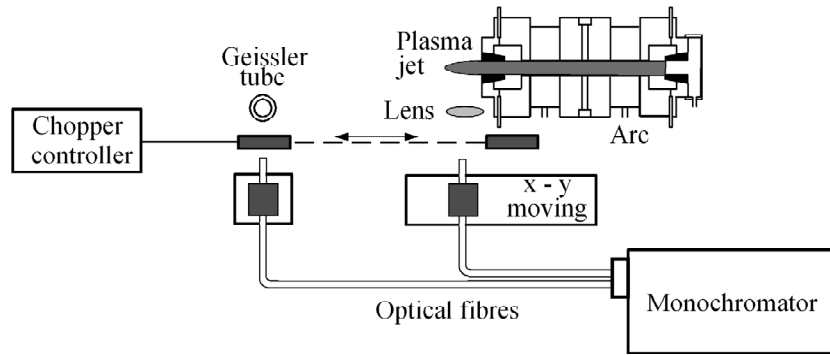


Figure 7. Optical system.

An example of time resolved recorded optical signal is given in Fig. 8.

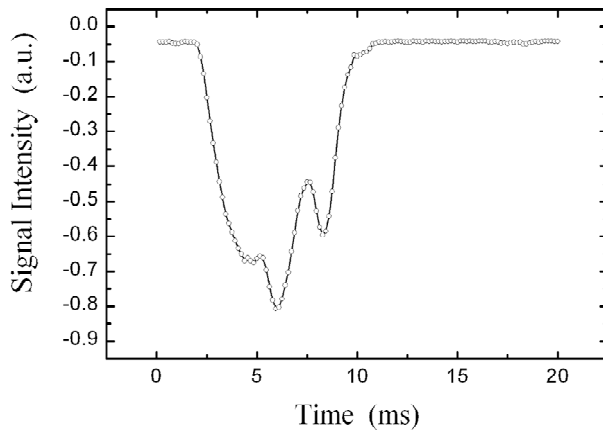


Figure 8. Time resolved optical signal.

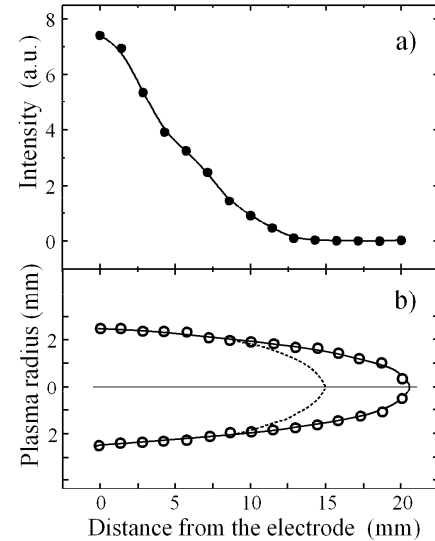


Figure 9. Results of the optical measurements.

Using the optical signal, jet dimension measurements were also performed. These measurements gave results of 20 mm for the length and 2.4 mm for the maximal radius. This is presented in Fig. 9. The cut-off distance for radiation is approximately 15 mm, although beyond this distance radiation is still visible.

Finally, in Fig. 10, spatially resolved radiation intensity of the plasma jet is presented. It can be seen that the brightest part of the jet extends up to 15 mm from the electrode.

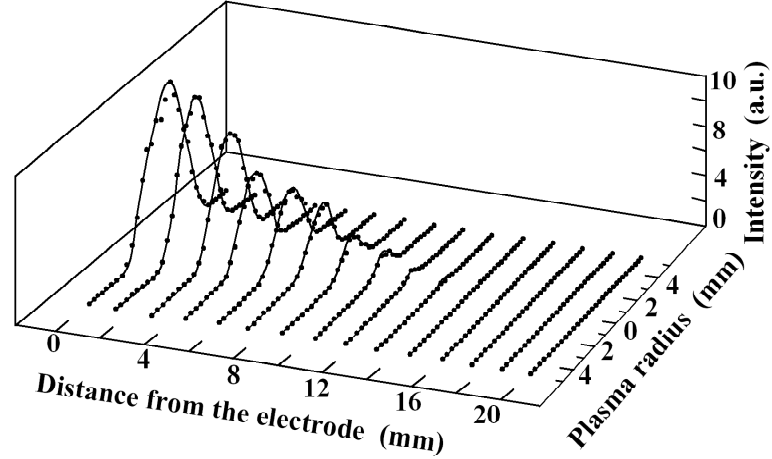


Figure 10. Spatially resolved radiation intensity of the plasma jet.

7. Pulsed plasma temperature determination

The temperatures at different moments of the plasma jet decay were determined from the measured dependence of Ar I 415.86 nm line shift on the temperature [4, 7].

A low pressure argon Geissler tube is used as a reference source of unshifted argon spectral line. For the shift measurements, the light from both plasma jet and reference source is directed onto the entrance slit of the monochromator by optical fibers (see Fig. 7). In this way, by using a chopper, the light from the reference source or from plasma jet can be detected alternatively by the photomultiplier placed at the exit slit of the monochromator. Both signals are recorded at each wavelength step along the investigated wavelength interval.

An example of recorded Ar I 415.86 nm spectral line from the plasma jet and reference source is shown in Fig. 11. This profile corresponds to the time of maximal emissivity and it was recorded at the position on the jet axis close to the exit hole of the arc.

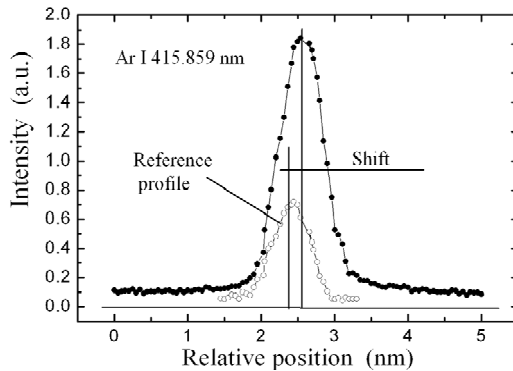


Figure 11. Example of the recorded profiles from plasma jet and reference source.

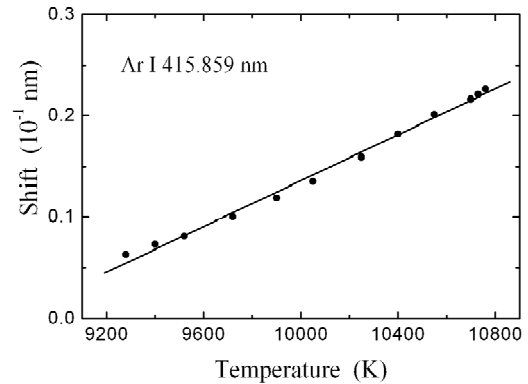


Figure 12. Dependence of Ar I 415.86 nm line shift on the temperature.

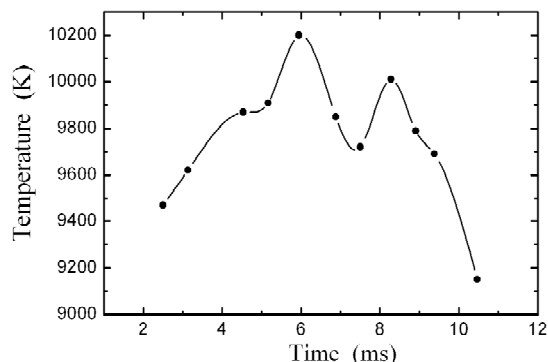


Figure 13. Time dependence of the plasma jet temperature.

Combining the results of measured shifts with the graph in Fig. 12, the temperatures of plasma jet for various moments of plasma decay were obtained. This is presented in Fig. 13. The values on the horizontal axis correspond to the time measured from the beginning of the plasma jet formation. As can be seen from Fig. 13, the maxima of the temperature are at 6 ms and 8.3 ms after plasma jet formation. This corresponds to the maxima of the plasma emissivity (see Fig. 8). At 6 ms plasma temperature reaches 10200 K, while in the later times it falls to 9000 K.

8. Conclusion

If an arc works in DC regime, with 30 A current, electron density is typically $3 \cdot 10^{22} \text{ m}^{-3}$ and electron temperature is 10700 K.

This experiment shows that the superimposed pulsed current can significantly increase electron density and also electron temperature. In this way the spectral lines of ions become more intensive (see Fig. 4), which makes it possible to examine ionic lines.

Changing the resistor in the electronic circuit the pulse current can attain much higher values, which produces further electron density and temperature increase.

Here, only basic characteristics of the plasma jet were described. These results are the preliminary ones. Further work will be concentrated on detailed characterisation of plasma jet, since it can be used for material processing in different ways.

Since plasma jet is formed in the free space under atmospheric pressure and practically in pure argon atmosphere, it can be used for high temperature material processing.

Acknowledgments

This work was supported by the Ministry of Science and Environmental Protection, Republic of Serbia, under contract No. 141024.

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Magnetic Properties of Quasi Two-dimensional Antiferromagnet Rb_2MnCl_4

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Received: September 15, 2005

Abstract

Two-dimensional Heisenberg antiferromagnet Rb_2MnCl_4 with an XXZ spin anisotropy is studied using the method of double-time-temperature Green's functions (GF) with arbitrary spin S (in particular case $S = 5/2$) within Tyablikov's decoupling approximation. The Neel temperature T_N is calculated employing the Callen method for an arbitrary spin value. Within the given approximation, the expression for the sublattice magnetization is derived in the whole temperature range. The calculated transition temperature agrees rather well with the measured values for the quasi two-dimensional antiferromagnet Rb_2MnCl_4 in a zero magnetic field.

Key words: Two-dimensional Heisenberg antiferromagnet, spin anisotropy, Green's function, Callen technique

1. Introduction

The last several decades have seen a permanently increasing interest in the magnetic properties of low-dimensional antiferromagnets [1-10], in particular the structure with square-planar layers of the type K_2MnF_4 , Rb_2MnF_4 , etc. [11-13]. Magnetic ions Mn^{2+} (or Fe and Ni, for example) of these systems are distributed within the layers and antiferromagnetically ordered, creating a complex tetragonal lattice. Dominant interaction between the magnetic ions within the plane (layer) acts between the nearest neighbours, while the interactions between the next neighbours and between the neighbouring layers is significantly weaker. Due to anisotropic structure of these compounds, these systems, sometimes called layered magnetic systems, possess rather interesting properties. The physics of layered magnetic systems is now one well-developed branch of magnetism [14]. The mentioned family of compounds is a good example of two-dimensional¹ (2D) antiferromagnetic ordering.

¹Here and further on, we assume that in a two-dimensional system, spins are distributed within the planes, which are the part of a real three-dimensional structure.

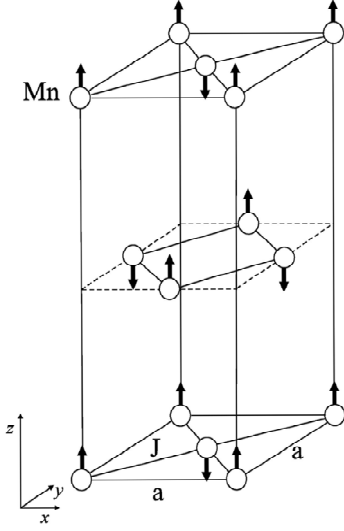


Figure 1. Magnetic unit cell of Rb_2MnCl_4 .

In this paper, we present an analysis of the temperature dependence of the sublattice magnetization and calculation of the transition temperature T_N in the chalcide Rb_2MnCl_4 . Experimental results for this compound [2, 11] indicate that the dominant exchange interaction in this material is the interaction between the neighbours within the layers and that interactions with further neighbours within the layers and between the layers are rather small and can be neglected. This can be understood by looking at the magnetic structure (Fig. 1) of this compound. It is certain that the compounds with Mn components responsible for the antiferromagnetism can be described by the standard Heisenberg Hamiltonian. However, it is also well known that in 1D or 2D isotropic Heisenberg ferromagnets and antiferromagnets at finite temperatures there can not exist long-range magnetic order (Mermin and Wagner theorem [15]). Long-range order in our compound is caused by a small but finite anisotropy.

The previous theoretical studies [1-3] solved this problem within the Heisenberg model with dipole-dipole interaction and an external field, mostly by performing the bosonization. The agreement between the theory and experiment is not too well. Our approach is based on the Heisenberg model for spin $S = 5/2$ with the spin anisotropy of XXZ type. Applying Green's function (GF) method within Tyablikov's approximation, we achieve a rather good agreement with the experimental value [2, 11].

2. The System Hamiltonian and Green's Function Method

Our theoretical analyses are based on the quasi 2D Heisenberg antiferromagnetic exchange model with nearest neighbour interaction within the layers. The studied lattice consists of two sublattices a (spin "up") and b (spin "down"). In the presence of an external field, the antiferromagnetic Hamiltonian is written as follows:

$$\hat{H} = J \sum_{\vec{\varrho}, \vec{\lambda}} \left\{ \frac{1}{2} \left[\hat{S}_{\vec{\varrho}}^+(a) \hat{S}_{\vec{\varrho}+\vec{\lambda}}^+(b) + \hat{S}_{\vec{\varrho}}^-(a) \hat{S}_{\vec{\varrho}+\vec{\lambda}}^-(b) \right] - \eta \hat{S}_{\vec{\varrho}}^z(a) \hat{S}_{\vec{\varrho}+\vec{\lambda}}^z(b) \right\} - g\mu_B \mathcal{H} \sum_{\vec{\varrho}} \left[\hat{S}_{\vec{\varrho}}^z(a) - \hat{S}_{\vec{\varrho}}^z(b) \right] \quad (1)$$

where J is the intralayer antiferromagnetic exchange interaction; g and μ_B are Lande's g-factor and Bohr's magneton, respectively; $\mathcal{H}$ is a z-component external field, while η is the spin anisotropy. The vector $\vec{\varrho}$ is a two-dimensional vector determining the position of the magnetic ions within the plane, and the direction of spins can be either a ("up") or b ("down"). In order to simplify the calculations, we performed the rotation of quantization axis in b -sublattice by 180° . Our choice of the particular form of anisotropy is based on the fact that the similar layered magnetic structures occurring in high T_c -parent compound can be well described by this type of anisotropy [16, 17].

Our primary aim is to determine the spectrum of the elementary excitations. The knowledge of the spectrum will allow us to calculate the sublattice magnetizations and further on the transition temperature for the compound Rb_2MnCl_4 . For that purpose, we shall use spin GF method and introduce the following Green's functions:

$$G_1^a(\vec{\rho}, \vec{\rho}') = \langle \langle \hat{S}_{\vec{\rho}}^+(a) | \hat{B}_{\vec{\rho}'} \rangle \rangle, \quad \Gamma_1^b(\vec{\rho}, \vec{\rho}') = \langle \langle \hat{S}_{\vec{\rho}}^-(b) | \hat{B}_{\vec{\rho}'} \rangle \rangle, \quad (2)$$

and corresponding system GF for the corresponding adjoint operators $\hat{S}_{\vec{\rho}}^-(a)$ and $\hat{S}_{\vec{\rho}}^+(b)$:

$$G_2^a(\vec{\rho}, \vec{\rho}') = \langle \langle \hat{S}_{\vec{\rho}}^-(a) | \hat{B}_{\vec{\rho}'} \rangle \rangle, \quad \Gamma_2^b(\vec{\rho}, \vec{\rho}') = \langle \langle \hat{S}_{\vec{\rho}}^+(b) | \hat{B}_{\vec{\rho}'} \rangle \rangle \quad (3)$$

where $\hat{B}_{\vec{\rho}'}$ is at present an arbitrary operator to be chosen in a suitable manner later. The system of equations (2) reads:

$$\begin{aligned} E G_1^a(\vec{\rho}, \vec{\rho}') &= \frac{i}{2\pi} \langle [\hat{S}_{\vec{\rho}}^+(a), \hat{B}] \rangle + J \sum_{\vec{\lambda}} \left[\langle \langle \hat{S}_{\vec{\rho}}^z(a) \hat{S}_{\vec{\rho}+\vec{\lambda}}^-(b) | \hat{B}_{\vec{\rho}'} \rangle \rangle + \eta \langle \langle \hat{S}_{\vec{\rho}+\vec{\lambda}}^z(b) \hat{S}_{\vec{\rho}}^+(a) | \hat{B}_{\vec{\rho}'} \rangle \rangle \right] + \\ &\quad + g\mu_B \mathcal{H} G_1^a(\vec{\rho}, \vec{\rho}') \end{aligned} \quad (4)$$

$$\begin{aligned} E \Gamma_1^b(\vec{\rho}, \vec{\rho}') &= \frac{i}{2\pi} \langle [\hat{S}^-(b), \hat{B}] \rangle - J \sum_{\vec{\lambda}} \left[\langle \langle \hat{S}_{\vec{\rho}}^z(b) \hat{S}_{\vec{\rho}+\vec{\lambda}}^+(a) | \hat{B}_{\vec{\rho}'} \rangle \rangle + \eta \langle \langle \hat{S}_{\vec{\rho}+\vec{\lambda}}^z(a) \hat{S}_{\vec{\rho}}^-(b) | \hat{B}_{\vec{\rho}'} \rangle \rangle \right] + \\ &\quad + g\mu_B \mathcal{H} \Gamma_1^b(\vec{\rho}, \vec{\rho}') \end{aligned} \quad (5)$$

The higher order GFs appearing in equations (4) and (5) will be decoupled in the spirit of Tyablikov's approximation scheme [18]

$$\langle \langle \hat{S}_{\vec{\rho}}^z \hat{S}_{\vec{\rho}'}^{\pm} | \hat{B}_{\vec{\rho}'} \rangle \rangle \longrightarrow \langle \hat{S}_{\vec{\rho}}^z \rangle \langle \langle \hat{S}_{\vec{\rho}'}^{\pm} | \hat{B}_{\vec{\rho}'} \rangle \rangle \quad (6)$$

Next step is the transition to reciprocal lattice by the following Fourier transformation:

$$\hat{S}_{\vec{\rho}}^{\pm} = \frac{1}{\sqrt{N_2}} \sum_{\vec{k}_{\parallel}} \hat{S}_{\vec{k}_{\parallel}}^{\pm} e^{i\vec{k}_{\parallel} \cdot \vec{\rho}} \quad (7)$$

where N_2 is the number of unit cells within the layer. We obtain the system of equations for the Fourier components:

$$\begin{aligned} (E - \varepsilon_1) G_1^a(\vec{k}_{\parallel}) - \langle \hat{S}^z(a) \rangle J(\vec{k}_{\parallel}) \Gamma_1^b(\vec{k}_{\parallel}) &= \frac{i}{2\pi} 2 \langle \hat{S}^z(a) \rangle \\ \langle \hat{S}^z(b) \rangle J(\vec{k}_{\parallel}) G_1^a(\vec{k}_{\parallel}) + (E + \varepsilon_2) \Gamma_1^b(\vec{k}_{\parallel}) &= 0 \end{aligned} \quad (8)$$

where $J(\vec{k}_{\parallel}) = z_1 J \gamma_1(\vec{k}_{\parallel})$, z_1 is the number of in-plane nearest neighbours,

$$\varepsilon_1 = z_1 J \eta \langle \hat{S}^z(b) \rangle + g\mu_B \mathcal{H}, \quad \varepsilon_2 = z_1 J \eta \langle \hat{S}^z(a) \rangle - g\mu_B \mathcal{H} \quad (9)$$

while $\gamma_1(\vec{k}_{\parallel})$ is a geometrical factor given by

$$\gamma_1(\vec{k}_{\parallel}) = \frac{1}{z_1} \sum_{\vec{\lambda}} e^{i\vec{k}_{\parallel} \cdot \vec{\lambda}} = \cos \frac{ak_x}{2} \cos \frac{ak_y}{2} \quad (10)$$

Here $\vec{\lambda}$ is the nearest-neighbour displacement within one of the layers, and a is the dimension of the 2D magnetic unit cell (in our case $a = 5.05 \cdot 10^{-10}$ m). In Eq. (8) we choose

$\hat{B}$ to be $\hat{S}^-(a)$. One can easily obtain the adjoint system of equations for GFs (3), so it will not be explicitly quoted. The determinant of the system of Eqs. (8) determines the energies of the elementary excitations in the spin system:

$$E_{1/2}(\vec{k}_{\parallel}) = \frac{1}{2} \left(\varepsilon_1 - \varepsilon_2 \pm \sqrt{(\varepsilon_1 + \varepsilon_2)^2 - 4\langle \hat{S}^z(a) \rangle \langle \hat{S}^z(b) \rangle J(\vec{k}_{\parallel})} \right) \quad (11)$$

Due to translational invariance, for a given compound, in the particular case of vanishing external field ($\mathcal{H} = 0$), the sublattice magnetizations are equal, i.e. $\langle \hat{S}_{\vec{\rho}}^z(a) \rangle = \langle \hat{S}_{\vec{\rho}}^z(b) \rangle = \langle \hat{S}^z \rangle$ for each site $\vec{\rho}$, then $\varepsilon_1 = \varepsilon_2 = \varepsilon$ and the energies are

$$E_{1/2}(\vec{k}_{\parallel}) = \pm \sqrt{\varepsilon^2 - (\langle \hat{S}^z \rangle J(\vec{k}_{\parallel}))^2} \quad (12)$$

Using these equations one can calculate the sublattice magnetization (for $\mathcal{H} = 0$) and determine the Neel temperature.

3. Spontaneous Sublattice Magnetization

For $\mathcal{H} = 0$, the two sublattice magnetizations are equal, $\langle \hat{S}_{\vec{\rho}}^z(a) \rangle = \langle \hat{S}_{\vec{\rho}}^z(b) \rangle = \langle \hat{S}^z \rangle$. In this case, it is easy to use the system (8) to calculate the necessary Green's function, as

$$\langle \langle \hat{S}^+(a) | \hat{S}^-(a) \rangle \rangle_{\vec{k}_{\parallel}, \omega} = \frac{i}{2\pi} \frac{\langle \hat{S}^z \rangle}{E_1(\vec{k}_{\parallel})} \left(\frac{E_1(\vec{k}_{\parallel}) + \varepsilon}{E - E_1(\vec{k}_{\parallel})} + \frac{E_1(\vec{k}_{\parallel}) - \varepsilon}{E + E_1(\vec{k}_{\parallel})} \right) \quad (13)$$

Now, using the spectral theorem, one can find the corresponding correlation function

$$\langle \hat{S}^-(a) \hat{S}^+(a) \rangle = 2\langle \hat{S}^z \rangle \cdot P_S^a(T) \quad (14)$$

where

$$P_S^a(T) = \frac{1}{N_2} \sum_{\vec{k}_{\parallel}} \left(\frac{\varepsilon}{E_1(\vec{k}_{\parallel})} \frac{1}{e^{E_1(\vec{k}_{\parallel})/k_B T} - 1} + \frac{\varepsilon}{2E_1(\vec{k}_{\parallel})} - \frac{1}{2} \right) \quad (15)$$

Let us notice that the right-hand side of Eq. (14) depends only on $\langle \hat{S}^z \rangle$. Finally, using Callen's technique [19], we obtain the magnetization of each sublattice as

$$\langle \hat{S}^z \rangle = \frac{(S + P_S^a(T))(1 + P_S^a(T))^{2S+1} + (1 + S + P_S^a(T))(P_S^a(T))^{2S+1}}{(1 + P_S^a(T))^{2S+1} - (P_S^a(T))^{2S+1}} \quad (16)$$

By joint solution of the system of Eqs. (15) and (16) we obtain the magnetization of each sublattice in terms of the temperature and parameter of spin anisotropy. At $T = 0$ K, the sublattice magnetization is given by

$$\langle \hat{S}^z \rangle_0 = \frac{(S + P_0)(1 + P_0)^{2S+1} + (1 + S + P_0)P_0^{2S+1}}{(1 + P_0)^{2S+1} - P_0^{2S+1}} \quad (17)$$

where

$$P_0 = P_S^a(0) = \frac{1}{N_2} \sum_{\vec{k}_{\parallel}} \left(\frac{\varepsilon}{2E_1(\vec{k}_{\parallel})} - \frac{1}{2} \right) \quad (18)$$

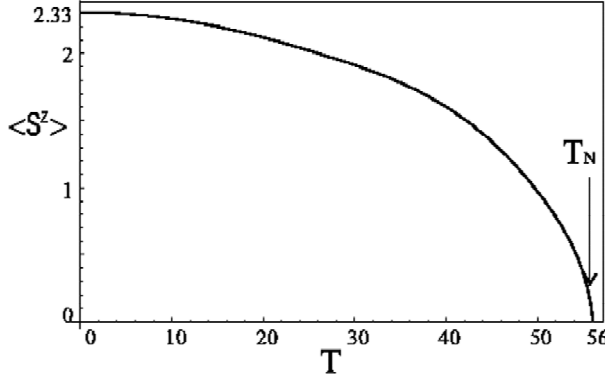


Figure 2. Sublattice magnetization as a function of the temperature. Parameters used: $J/k_B = 11.2$ K, $\eta = 1 + 5 \cdot 10^{-3}$.

In our numerical analysis of Eqs. (15)-(16) for particular case of Rb_2MnCl_4 , we take $S = 5/2$, $J/k_B = 11.2$ K and spin anisotropy $\eta = 1 + 5 \cdot 10^{-3}$. In this way we retain the same parameters characterising the Heisenberg interaction as in previous studies [1, 2], yet varying only the type of the anisotropy. This allows a correct comparison. We obtain the results presented in Figure 2. One can see from Figure 2 that the magnetization at $T = 0$ K is smaller than 2.5, and according to (17) is equals $\langle \hat{S}^z \rangle_0 = 2.33$, which is a consequence of the so-called spin quantum

fluctuations, which are strongest at absolute zero.

Now we turn to the evaluation of the Neel temperature T_N , i.e. to considering the limit $\langle \hat{S}^z \rangle_0 \rightarrow 0$. When temperature approaches the Neel temperature, the spontaneous sublattice magnetization $\langle \hat{S}^z \rangle_0$ is almost zero and spin-wave energy $E(\vec{k}_{\parallel})$ becomes a small quantity. Expanding $P_S^{\alpha}(T)$ in powers of $E(\vec{k}_{\parallel})$ we have

$$P_S^{\alpha}(T \approx T_N) \simeq \frac{k_B T_N}{\langle \hat{S}^z \rangle} \frac{1}{N_2} \sum_{\vec{k}_{\parallel}} \frac{\varepsilon}{E_1^2(\vec{k}_{\parallel})} \quad (19)$$

In this case Eq. (16) for the sublattice magnetization becomes

$$\langle \hat{S}^z \rangle \simeq \frac{S(S+1)}{3} \frac{1}{P_S^{\alpha}(T \approx T_N)} \quad (20)$$

Combining Eqs. (19) and (20) we obtain an explicit expression for the transition temperature:

$$k_B T_N = \frac{S(S+1)}{3} \frac{z_1 J}{C_2} \quad (21)$$

where

$$C_2 = \frac{1}{N_2} \sum_{\vec{k}_{\parallel}} \frac{\eta}{\eta^2 - \gamma_1^2(\vec{k}_{\parallel})} \quad (22)$$

For purely isotropic antiferromagnets, the coefficient C_2 diverges in 2D, excluding long-range order at finite temperature. It is important to stress that Tyablikov's decoupling leads to the results that comply with the Mermin-Wagner theorem [15]. In the presence of spin anisotropy there is an energy gap, and T_N becomes finite.

Now we apply our theory to real quasi two-dimensional antiferromagnets, like the tetragonal antiferromagnetic compound Rb_2MnCl_4 , as well as the chalcides from the same family. We calculate numerically the Neel temperature for Rb_2MnCl_4 . The calculation is based on the previously mentioned set of parameters: intralayer exchange interaction $J/k_B = 11.2$ K and spin anisotropy $\eta = 1 + 5 \cdot 10^{-3}$ and spin $S = 5/2$. We finally obtain

the transition temperature $T_N = 55.76$ K, while the experimental value is, according to [2, 11], $T_N = 56$ K.

Numerical calculations of the transition temperature, based on our approach, agree well with measured values for T_N [2, 11] for the particular compound. One should compare this result with the one by Pich and Schwabl [1-3]. They obtained the value for $T_N = 48$ K, a difference of order of an 10 %. We estimate that this discrepancy is a consequence of the different choice of anisotropy. Our choice of anisotropy and its numerical value of the order 10^{-3} was confirmed by recent very precise experiment [20].

4. Conclusion

We have applied the technique of double-time-temperature Green's function to the quasi two-dimensional antiferromagnet with arbitrary spin S . Our results were applied to the particular compound Rb_2MnCl_4 with the spin $S = 5/2$, where we chose a different type of anisotropy. We derived the analytical expressions for the energies of elementary excitations, sublattice magnetization and Neel temperature in terms of intralayer exchange interaction and spin anisotropy. Our numerical results showed a better agreement with measured values of T_N than the results of other authors. It is our opinion that in chalcides, there exists a spin anisotropy allowing us to perform this kind of theoretical analysis.

Acknowledgments

This work was supported by the Serbian Ministry of Science and Environmental Protection: Grant No. 1895.

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Review article

Complex Non-crystalline Chalcogenides: Technology of Preparation and Spectral Characteristics

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Received: November 20, 2005

Abstract

In the first part of the paper we summarize the results of our research in the technology of obtaining complex four- and five-component non-crystalline glasses. We present diagrams of the processes for the preparation of chalcogenide samples of the type

$\text{Cu}_x(\text{AsSe}_{1.4}\text{I}_{0.2})_{100-x}$, $\text{Cu}_x[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{100-x}$, $\text{Cu}_x\text{As}_y\text{Se}_z\text{I}_w$, $\text{Ge}_x\text{As}_y\text{S}_z\text{I}_w$,
 $(\text{GeS}_2)_x(\text{AsSI})_{100-x}$, $(\text{GeS}_2)_x(\text{AsSBr})_{100-x}$, $\text{Ge}_{20}\text{As}_{14}(\text{Se}_{0.5}\text{S}_{0.5})_{66-x}\text{I}_x$,
 $\text{Ge}_{20}\text{As}_{14}\text{Se}_x\text{S}_{52-x}\text{I}_{14}$, $\text{Ge}_x\text{As}_{34-x}\text{Se}_{26}\text{S}_{26}\text{I}_{14}$, $\text{Fe}_x[(\text{Sb}_2\text{S}_3)_{0.75}(\text{SbI}_3)_{0.25}]_{100-x}$,
 $\text{As}_{47-x}\text{Sb}_x\text{S}_{48}\text{I}_{15}$, $(\text{As}_2\text{Se}_3)_x(\text{SbSI})_{100-x}$, $(\text{As}_2\text{S}_3)_x(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_{1-x}$.

In the second part of the paper we report results of studying general spectral properties of these complex amorphous materials. High transparency was established in the wide spectral range for all of the glasses.

Key words: Chalcogenide glass, spectral characteristics, optical energy gap

1. Introduction

Multicomponent chalcogenide glasses are widely used in the field of semiconductor technologies. The great interest in these materials is due to their simple preparation technology either in bulk form or thin films, chemical and radiation resistance, relatively good thermal and mechanical properties, low optical losses, transparency and photosensitivity in IR and VIS spectral regions, as well as the possibility of wide variation of properties with the composition [1-6]. These properties give the possibility of their practical application for pulse generation of acoustic and optical radiation. Thin films deposited from the chalcogenide glasses are applicable in opto- and micro-electronics for different purposes electrical switches, data recording, protective, passivity and optical coatings [7, 8]. These glasses generally exhibit p-type electrical conduction due to the pinning of the *Fermi* level, arising from the trapping of charge carriers at localized gap states [9-11].

Four- and five-component systems offer special possibilities because one can substantially change the properties of the system simply by changing the ratio of their components. This is primarily related to the spectral interval of photosensitivity and characteristics of

the recording - erasing processes [12]. It should be pointed out that a relatively complex technology of obtaining multicomponent glasses and thin films on their bases have been the reason why the processes of optical recording in these systems have received relatively little attention.

It has been observed that the possibility of preparation of the homogeneous glassy chalcogenides with transition elements in their structure is limited to relatively low metal concentrations. With increase in metal concentration, their thermal and mechanical properties remain practically unchanged, whereas electrical conductivity shows an abrupt transition from the semiconducting to metal type [13, 14].

In this work we present results of the many-years long research dealing with complex chalcogenide systems. We pointed out some specific features of the technological processes of preparation of different types of four- and five-component glasses. The emphasis was placed on the analysis of spectral characteristics of bulk samples.

2. Technology of preparation of four-component amorphous materials

As a rule, the nature and composition of the components of the given system determine the structural units forming the glass lattice.

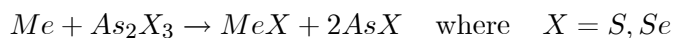
With increase in the number of components the glass formation capability increases too, since this enhances the possibility of forming various structural units.

It has been shown that the materials with amorphous structure can be successfully prepared by introducing transition elements into some of the quasi-binary eutectic compositions.

Chalcogenide glasses with copper

Taking into account that arsenic forms stable and unstable binary systems with sulfur, selenium, and iodine, and the fact that copper forms a number of compounds with chalcogenide elements (Cu_2S , Cu_2Se , CuSe , CuSe_2 , Cu_3Se_2), and with arsenic (Cu_2As , Cu_3As , Cu_6As_2 , Cu_3As_2 and Cu_5As_2) [6], as well as that there exist the three-component compounds CuAsS_2 , CuAsSe_2 , Cu_3AsSe_3 , Cu_3AsS_4 , Cu_3AsSe_4 , it might be expected that a procedure for obtaining complex glasses of the system Cu-As-S(Se)-I could be effective.

The range of amorphous phase formation in the three-component system Cu-As-S [15] is significantly smaller than with the Cu-As-Se system, which means that significantly lower amounts of copper can be introduced into the composition of arsenic sulfide than into the arsenic selenide system. It has been shown that the chemical reaction of a metal with the chalcogenide glasses can be described by the following equation:



It has been found that different tendencies of amorphous arsenic sulfide and arsenic selenide to interact with metals can be related to the enhanced vitrification capacity of AsSe and to the almost complete absence of this property with AsS.

The area of the amorphous phase in the system As-S-Se is extremely large [16]. The energies of the bonds As-S and As-Se are insignificantly different, so that the probabilities of arsenic binding with sulfur and selenium are almost the same. However, no tertiary compounds have been identified in this system. It was found that along the cuts As_2S_3 - As_2Se_3 and AsS-AsSe continuous series of solid solutions can be formed [17], so that making the system more complex by introducing copper, offers the possibility for obtaining new materials with programmed properties.

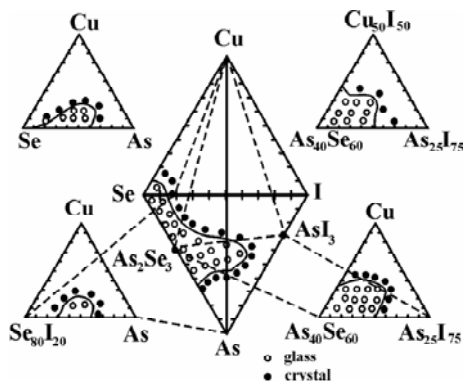


Figure 1. The glass-forming region in the system Cu-As-Se-I.

The highest tendency to amorphous phase formation in the system Cu-As-Se have the melts in which arsenic and selenium are present in an approximately equal ratio. In the system Cu-Se-I, the probability of glass formation is low [19], which is in agreement with the small area in the corresponding plane in Fig. 1. The glasses that are still obtained in this combination have a structure analogous to that of elemental selenium. These glasses are, however, unstable and they are characterized by a high tendency to crystallization and decomposition, accompanied by the evolution of elemental iodine.

In the course of many years of research it has been established that the materials of the same microstructure and physico-chemical properties are obtained when starting from the elementary components and the binary compounds As_2X_3 , Cu_2X and AsI_3 . Hence, all the experiments described here involve, as a rule, the glasses synthesized starting from the corresponding high-purity elementary components.

The synthesis was conducted according to a special program, in cylindrical quartz ampoules evacuated to a pressure of the order of magnitude of 10^{-3} Pa. The ampoule length was usually about 15 cm, its diameter 15 mm, and the wall thickness 2 mm, in order to be able to withstand the relatively high pressures in the ampoule during the synthesis.

The synthesis was carried out in semiautomatic horizontal tube furnaces Carbolite, Model CTF 12/65, with a temperature controller Eurotherm 91-3, according to the empirically defined regimes shown in Fig. 2. Cooling at a rate of $800^\circ\text{C}/\text{min}$ resulted in amorphous samples [20, 21].

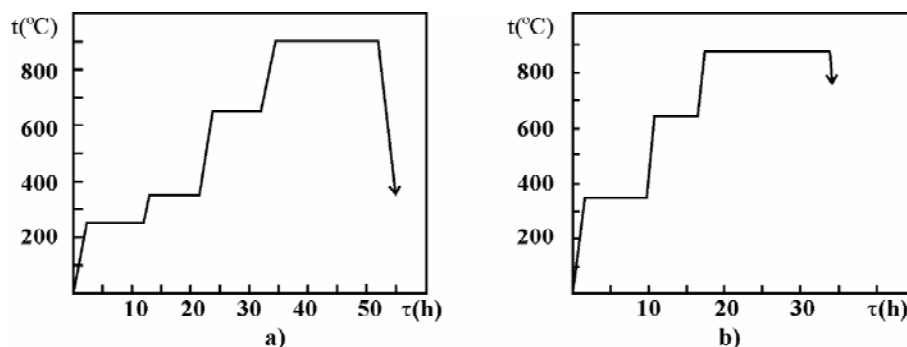


Figure 2. Diagram of the process for obtaining glasses in the system Cu-As-S-Se (a) and Cu-As-Se-I (b).

Such synthesis regime with a cascade increase of temperature made it possible to reduce the pressure due to the vapors of iodine and arsenic, interacting with each other, as well as with sulfur, selenium and copper. This prevented the ampoule from destruction during the synthesis. To facilitate sample homogenization, the melt was kept at the highest temperature for a prolonged time (17-20 hours).

As a result of successful syntheses the corresponding amorphous materials in the form of oval rods, with no visible fissures or defects, were obtained in appropriate yields. Amorphous character of samples was checked by x-ray diffraction and polarization microscopy.

High-quality chalcogenide semiconductor samples of the type $\text{Cu}_x[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{100-x}$ ($x = 0, 0.5, 1, 3$ at % Cu) and $\text{Cu}_x(\text{AsSe}_{1.4}\text{I}_{0.2})_{100-x}$, ($x = 0, 1, 5, 10, 15, 20$ and 25 at % Cu), as well as the glasses of the general formula $\text{Cu}_x\text{As}_y\text{Se}_z\text{I}_w$ were obtained. It appeared that copper content in the first sample has to be below 5 %, in order to avoid partial crystallization of the material, whereas with other selected series this content could amount even to 25 %. Such a result was a consequence of the presence of sulfur in the system.

It is known that the physico-chemical properties, phase composition, and structure of thin films depend on the technology used for their preparation, and especially on the temperature of the substrate on which they are deposited. Thin-film samples were prepared by thermal evaporation in vacuum of powdered previously synthesized complex glasses.

In order to obtain films from the synthesized glasses from the system Cu-As-Se-I that are homogeneous and exhibit high optical characteristics, their preparation was conducted using a specially-constructed evaporator. Its use enabled to carry out discrete evaporation at optimally high temperatures (430 – 600°C), whereas the composition of the prepared films, within tolerable limits, was close to the molten glasses.

Condensation was carried out on the substrates made of the glass of the known index of refraction, kept at room temperature ("cold" substrates).

Film thickness in the course of evaporation was controlled by optical method on the basis of the interference of reflected laser beam.

Chalcogenide glasses with germanium

The choice of the methodology to synthesize glasses from the system Ge-As-S-I and Ge-As-Se-I was influenced by the characteristics of the elementary components forming the binary and tertiary compounds that could be expected as a result of interaction of these components, as well as by the magnitude of the area of amorphous state in the phase diagram. The area of non-crystalline phase that can be realized in the quaternary system involving sulfur is presented in Fig. 3 [22], and for the system with selenium in Fig. 4.

As can be seen from Figs. 3 and 4, the amorphousness area in the tetrahedron Ge-As-S(Se)-I occupies its relatively large portion and comes out to the lateral planes of the three-component systems As-S(Se)-I, Ge-As-S(Se) and Ge-S(Se)-I. The low tendency to crystallization of the glasses in these systems is primarily a consequence of the possibility of formation of a larger number of compounds of different structures such as GeX_2 , As_2X_3 , AsXI ($\text{X} = \text{S}, \text{Se}$) with relatively low melting temperatures.

The diagram of the synthesis process with the cascade regime of heating and melt cooling by annealing [22-24] was employed to obtain also these four-component glasses. Such a mode of heating allowed the interactions of the components at a minimal temperature needed for their occurrence to proceed to an extent sufficient to eliminate the build-up of the pressure in the ampoule.

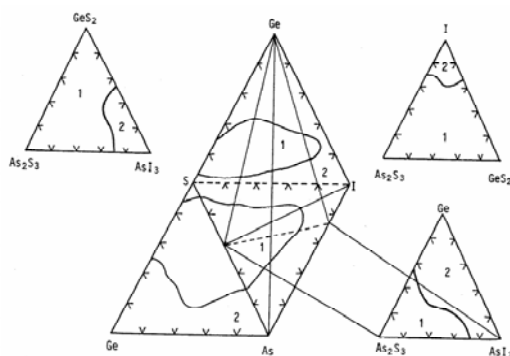


Figure 3. The glass-forming region in the system Ge-As-S-I: 1 - glass, 2 - crystal.

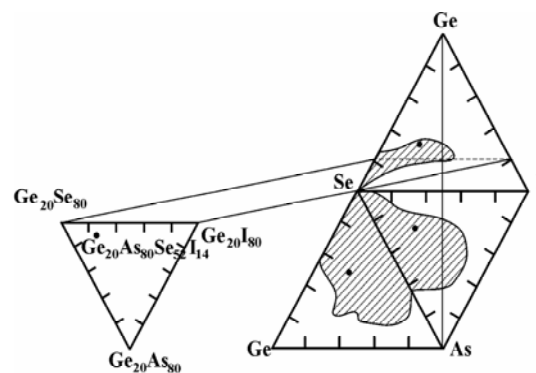


Figure 4. The glass-forming region in the system Ge-As-Se-I.

The relatively high temperatures of the synthesis ($870 - 930^{\circ}\text{C}$) were needed to prevent liquefaction in the melts with higher sulfur contents. In order to achieve its homogenization, the melt was kept at the maximal temperature for 25-30 hours, and then cooled at a rate of 600°C/h . In some cases, samples were kept for additional 10-15 hours at a temperature that was $20 - 30^{\circ}\text{C}$ lower than the softening temperature, T_g .

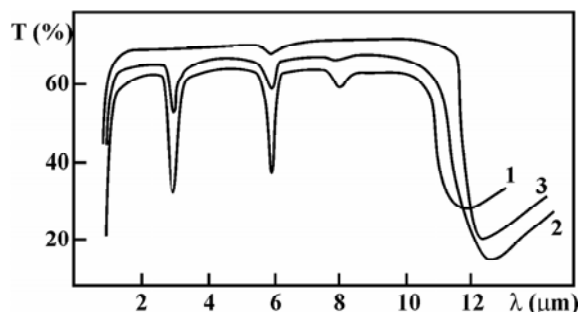


Figure 5. IR spectra of $\text{Ge}_6\text{As}_{30}\text{S}_{60}\text{I}_4$ bulk glass obtained by different procedures.

with significantly less pronounced absorption maxima whose origin is due to the presence of the impurities (curve 2). Almost complete elimination of the absorption bands (curve 3) is a characteristic of the glass prepared from the prepurified components (by prior sublimation) in the Pyrex glass ampoules that were kept in the argon atmosphere. After the filling and evacuating to a pressure of $6.67 \cdot 10^{-3} \text{ Pa}$, the ampoules were placed into quartz ampoules that were then finally sealed. Only after such preparation could start the synthesis according to the established synthesis procedure.

The composition of the glass $\text{Ge}_{20}\text{As}_{14}\text{S}_{52}\text{I}_{14}$ belongs to the range of amorphous state and this lies in the plane of the triangle $\text{Ge}_{20}\text{As}_{80}\text{I}_{80}$ - $\text{Ge}_{20}\text{S}_{80}$ and $\text{Ge}_{20}\text{I}_{80}$. The projections of this point onto the lateral sides of the tetrahedron fall into the amorphous state region of the corresponding three-component systems, which indicates that this composition is far from the boundary surface in the direction of the crystalline state.

In the system Ge-As-Se-I, there is also a stable amorphous compound of the type $\text{Ge}_{20}\text{As}_{14}\text{Se}_{52}\text{I}_{14}$. In view of the existence of both limiting compositions it could be ex-

The significance of the technology of preparation for the optical characteristics of the obtained chalcogenides can be judged from the IR spectra given in Fig. 5. The lower curve (1) is the spectrum of the sample obtained by standard procedure. Additional treatment of the ampoule at $800 - 850^{\circ}\text{C}$ in the argon atmosphere for 10 hours eliminates the presence of oxygen in the quartz, so that the samples contain less impurities. The transmission curve is by its shape almost identical to curve (1), but

pected that any combination of sulfur and selenium in the system $\text{Ge}_{20}\text{As}_{14}\text{S}_x\text{Se}_{52-x}\text{I}_{14}$ would give a stable amorphous material. The process of cascade heating and cooling in the air, gave the glasses of this type for $x = 0, 4, 6, 8, 10, 12, 18, 26, 34, 40, 42, 44, 46, 48, 50, 52$.

Melting temperatures of the starting components of this five-component system are markedly different, and heating during the synthesis was carried out in several stages [24–26]. Heating of the starting components in the evacuated ampoules yields first to melting and evaporation of iodine and sulfur. This, however, produces a high pressure of iodine and sulfur vapors, and the purpose of the first temperature plateau at 250°C is to enable reaction of these two elements, which reduces the pressure. Analogously, at the plateau of 650°C , molecules of As_2S_3 and As_2Se_3 are formed, and at 800°C the molecules GeS_2 and GeSe_2 .

With the aim of attaining its homogenization, the melt was kept at the maximum temperature for about 15 hours, and amorphous state was obtained by cooling it at a rate of about 800°C/h .

An analogous synthesis procedure yielded the samples $\text{Ge}_x\text{As}_{34-x}\text{Se}_{26}\text{S}_{26}\text{I}_{14}$, for $x = 2, 6, 10, 14, 20$ [27].

The temperature conditions presented in Fig. 6 were used to synthesize samples of the type $\text{Ge}_{20}\text{As}_{14}(\text{Se}_{0.5}\text{S}_{0.5})_{66-x}\text{I}_x$. The procedure yielded the glasses for $x = 2, 4, 6, 8, 10, 12, 14$ and 18 [28]. The methods of x-ray diffraction and polarization microscopy confirmed the amorphous character of the obtained samples [25, 29].

Electron microscopic studies of the films whose thickness was from 55 to 60 nm, showed the presence of two-phase grainy microstructure. The grains are uniformly distributed in the bulk of the glass. At the same time, electron microscopy enabled also identification of some "irregular" amorphous forms of the size from 50 to 150 nm, as well as typical chain defects of the size $3 - 5 \mu\text{m}$, appearing as a consequence of the presence of imperfection centers [30].

Chalcogenide glasses with iron and antimony

The Sb-S-I phase diagram [16] is of an "island" character (Figure 7). The fact that the presence of transition elements contribute to relatively easy crystallization of sulfur-containing glasses suggested that doping with iron (while preserving amorphous structure) can be carried out only at its relatively small contents.

The temperature regime employed in the synthesis of the samples from the system Fe-Sb-S-I is presented in Fig. 8 [31]. The starting elements were of the purity 99.99 % (Fe, Sb) and 99.999 % (S, I). The method of cascade heating, isothermal heating at selected tempe-

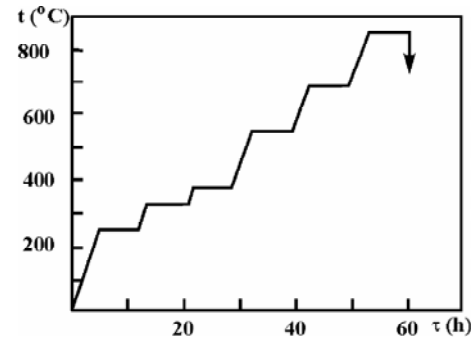


Figure 6. Diagram of process for obtaining glasses $\text{Ge}_{20}\text{As}_{14}\text{S}_x\text{Se}_{52-x}\text{I}_{14}$.

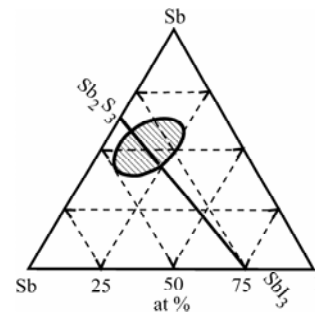


Figure 7. The glass-forming region in the system Sb-S-I.

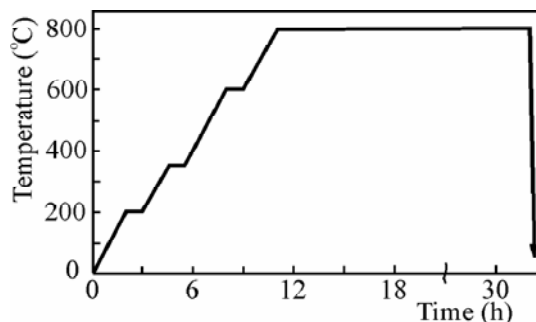


Figure 8. Diagram of the process for obtaining glasses in the system Fe-Sb-S-I.

the matrix of the eutectic quasibinary cut $(\text{Sb}_2\text{S}_3)_{0.75}-(\text{SbI}_3)_{0.25}$ is less than 5 at %; in the materials with higher iron contents crystalline centers could be detected immediately after the synthesis [31, 32].

Using an analogous procedure of cascade heating and abrupt cooling of the melt in the air, it was possible to obtain amorphous bulk four-component samples from the series $\text{As}_{47-x}\text{Sb}_x\text{S}_{48}\text{I}_{15}$ [33]. Their amorphous character was established by x-ray diffraction and polarization microscopy.

These two series of chalcogenides represent especially prospective materials since their additional thermal treatment can initiate generation of the crystalline centers SbSI that have ferroelectric properties. Of course, the concentration of these centers depends on the composition, but also on the sintering process. These special glass-ceramics materials are known in the literature as *sitals* (the term derives from the names of the main components of the classical glass-ceramics Si-Ti-Al, and usually applies to the majority of glass-ceramics materials, irrespective of their composition).

Optimization of the process of heating in the synthesis of glasses from the system Fe-Sb-S-I was carried out with the aim of forming the carriers of ferroelectric characteristics [32].

The synthesis of the complex glasses from the system As-Sb-S-Se-I along the selected cut $(\text{As}_2\text{Se}_3)_x(\text{SbSI})_{100-x}$ ($x = 20, 30, 50, 70, 80$) was carried out starting from the high-purity elementary components, employing the regime illustrated in Fig. 9 [34].

Five-component glasses with three chalcogen elements

The synthesis of complex glasses of the type $(\text{As}_2\text{S}_3)_x(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_{100-x}$ ($x =$

ratues and melt annealing yielded samples with amorphous internal structure. In the course of such a process, the components react, so that at the maximal temperature the liquid and gaseous phases exist in a sort of dynamic equilibrium under high pressure. After the homogenization of the material for several hours, the melt was cooled in the air to the temperature below the liquidus point (initial cooling rate was about 100°C/s).

It appeared that maximal concentration of iron that can be introduced into

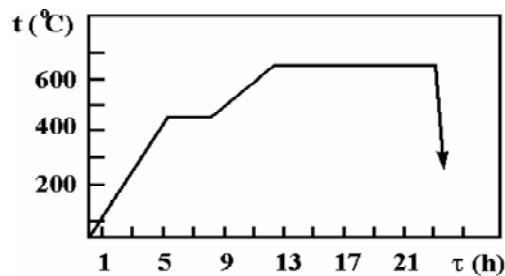


Figure 9. Diagram of the process for obtaining $(\text{As}_2\text{Se}_3)_x(\text{SbSI})_{100-x}$.

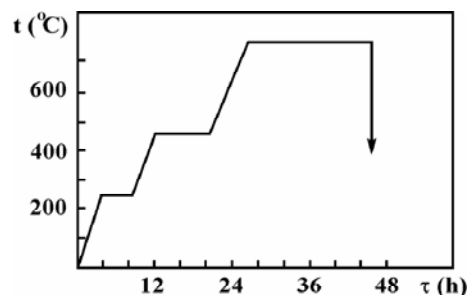


Figure 10. Diagram of the process for obtaining $(\text{As}_2\text{Se}_3)_x(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_{100-x}$ glasses.

65, 70, 75, 80, 85, 90, 95) was also carried out starting from high-purity elements and employing the regime illustrated in Fig. 10 [35].

The amorphous character of the obtained samples was confirmed by the methods of x-ray diffraction and polarization microscopy.

3. Spectral characteristics

Experimental

Transmission spectra in the range of 400 – 1600 nm were recorded using an SPM-2 system (Zeiss-Jena) with the monochromator and quartz optics. The light source was a bulb with tungsten filament; an EMI 9684 B photomultiplier served as detector, and the current signal was measured using a universal instrument Philips PM-2436/06. Measurement samples were prepared by mechanical polishing with silicon carbide powder of different grade (from 260 μm to 28 μm), to obtain highly-polished plates of different thickness. Final polishing was carried out with the powder of grain size of 0.3 μm .

Reflection spectra in the IR range from 2.5 to 10 μm were taken (KBr pellet) on a Perkin Elmer Infracord spectrometer.

Transmission and reflection IR spectra in the interval of wave numbers from 400 to 33 cm^{-1} were recorded at room temperature using a Hitachi FIS-3 and UR-10 spectrometer. Samples were prepared by pressing powdered glass into hot polyethylene.

Raman spectra were recorded at room temperature using the double-beam DSF-24 spectrometer (Russia) with the He-Ne laser as excitation source, at a 90-degree configuration of laser excitations.

Results and Discussion

The transmission spectra of some glassy materials from the system Ge-As-S-I shown in Fig. 11 give evidence of the high transparency of these materials in a wide spectral range. The long-wavelength absorption edge in the range of about 13.3 μm suggests the involvement of the 3ν frequency mode, characteristic of the structural unit $\text{AsS}_{3/2}$ of the pyramid type. The bands at 2.8 and 6.3 μm are due to the absorbed water, present as sample impurity, which can be avoided by employing strictly controlled synthesis conditions [23].

The far-infrared and Raman spectra of the glasses of the type $(\text{AsSI})_x(\text{GeS}_2)_{100-x}$ are shown in Fig. 12, and Fig. 13, respectively [22]. The IR spectra of the samples containing less than 40 % of GeS_2 are characterized only by the bands at 210 cm^{-1} and 310 – 360 cm^{-1} , indicating the vibrations of the structural units $\text{AsS}_{2/2}\text{I}$. Only at the contents of germanium sulfide above 50 % there appeared a band at about 370 cm^{-1} that is characteristic of the tetrahedral bond in GeS_2 . It is also possible to notice a shift of the

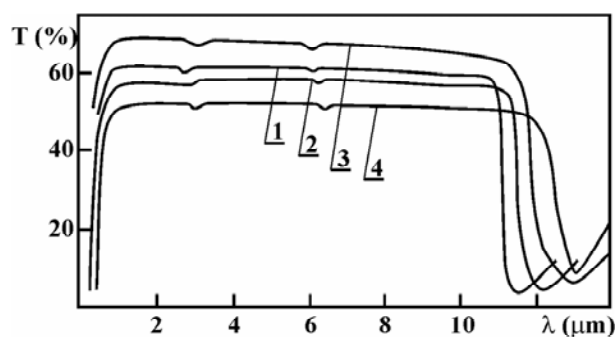


Figure 11. Transmission spectra of the glasses of the $(\text{GeS}_2)_x(\text{AsSI})_{100-x}$ system: (1) $x = 90$, $d = 3.6$ mm; (2) $x = 70$, $d = 3.8$ mm; (3) $x = 50$, $d = 2.8$ mm; (4) $x = 30$, $d = 4.4$ mm (d - thickness of the sample) .

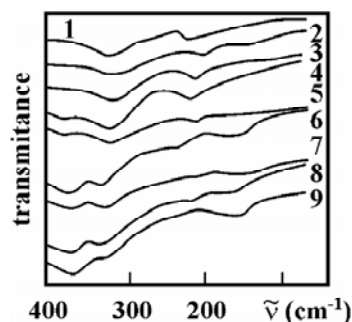


Figure 12. Far-infrared spectra of the glasses of the type $(\text{AsSI})_x(\text{GeS}_2)_{100-x}$: (1) $x = 90$; (2) $x = 80$; (3) $x = 70$; (4) $x = 60$; (5) $x = 50$; (6) $x = 40$; (7) $x = 30$; (8) $x = 20$; (9) $x = 10$.

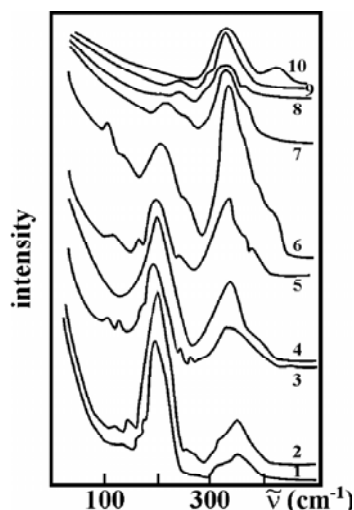


Figure 13. Raman spectra of the glasses of the type $(\text{AsSI})_x(\text{GeS}_2)_{100-x}$: (1) $x = 100$; (2) $x = 80$; (3) $x = 70$; (4) $x = 60$; (5) $x = 50$; (6) $x = 40$; (7) $x = 30$; (8) $x = 20$; (9) $x = 10$; (10) $x = 0$.

high-frequency band of arsenic iodide to lower wavelengths, accompanying the change in the ratio of the relevant molecules in the quasibinary combination. It appeared that only the spectra of the four-component glasses enriched with germanium (20 – 30 %) contain both the high- and low-frequency bands that are characteristic of GeS_2 ($340 - 380 \text{ cm}^{-1}$, $140 - 180 \text{ cm}^{-1}$).

Analogous conclusions can be drawn on the basis of the analysis of the presented Raman spectra.

The above discussion indicates that the dominant structural unit in these four-component glasses is $\text{AsS}_{2/2}\text{I}$ when the AsSI ratio is exceeding 50 mol %.

In Figure 14 are presented Raman spectra of the four-component system of the type $(\text{GeS}_2)_x(\text{AsSBr})_{100-x}$ [36]. It is possible to identify structural units of the same type as with the glasses $(\text{GeS}_2)_x(\text{AsSI})_{100-x}$, whereby bromine is introduced instead of iodine. There is a strong and well-defined band in the frequency range of $250 - 280 \text{ cm}^{-1}$, as well as a broad band in the range of $320 - 420 \text{ cm}^{-1}$. The former band is due to the oscillation of the As-Br bonds formed in the compound AsSBr , and the latter is characteristic of the oscillations of the As-S and Ge-S bonds.

The increase of the AsSBr content in the glass is accompanied by a shift of the low-frequency band from 287 cm^{-1} (for $x = 80$) to 255 cm^{-1} (for $x = 0$), and of the maximum of the low-frequency band from 342 cm^{-1} (for pure GeS_2) to 356 cm^{-1} (for AsSBr). At the same time, the intensity of the band in the range of $255 - 290 \text{ cm}^{-1}$ becomes enhanced.

In contrast to the analogous glasses with iodine, it is obvious that in the glasses of the type $(\text{GeS}_2)_x(\text{AsSBr})_{100-x}$ the characteristic band of germanium sulfide appears already at a content of 20 % GeS_2 . This offers the basis for the conclusion that a dominant structural unit in the glasses of the system Ge-As-S-Br is $\text{AsS}_{2/2}\text{Br}$ in the case when the molar ratio of this compound exceeds 80 %. The lattice of the glass containing less than 50 % AsSBr is basically formed of tetrahedral units GeS_2 , with statistically distributed structural units $\text{AsS}_{2/2}\text{Br}$, partly dissociated into $\text{AsS}_{3/2}$ and AsBr_3 [36].

The analysis of spectral characteristics of the structurally unordered materials of the type $\text{Cu}_x[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{100-x}$, $x < 3$ at %, in the infrared and visible part of spectra showed that these glasses are characterized by a high transparency in a wide spectral range [37].

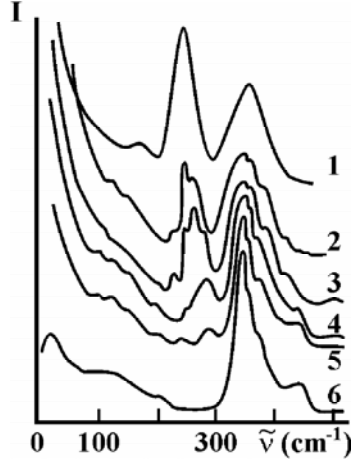


Figure 14. Raman spectra of the glasses of type $(\text{GeS}_2)_x(\text{AsSBr})_{100-x}$: (1) $x = 0$; (2) $x = 20$; (3) $x = 40$; (4) $x = 60$; (5) $x = 80$; (6) $x = 100$.

the range of higher energies as a consequence of increase in the temperature of the synthesis and the rate of melt cooling.

On the other hand, it is known that the structural disorderliness of the chalcogenide glasses and sample temperature determine the position and slope of the edge of optical absorption. If the relation for the Urbach rule [7] is written in the form

$$\ln \alpha \cong \Gamma(T)[h\nu - E_g^{opt}] \quad (1)$$

then, taking into account the weak temperature dependence

$$\Gamma(T) = \Gamma_0 + \Gamma_1(T) \quad \text{and}$$

$$E_g^{opt}(T) = E_0 + E_1(T) \quad (2)$$

and retaining only the linear terms, we obtain

$$\ln \alpha \approx \Gamma_0(h\nu - E_0) - \Gamma_0 E_1(T) + \Gamma_1(T)[h\nu - E_g^{opt}] = D_{str} + D_{fon}(T) \quad (3)$$

where $D_{str} = \Gamma_0(h\nu - E_0)$ and $D_{fon}(T) = -\Gamma_0 E_1(T) + \Gamma_1(T)[h\nu - E_g^{opt}]$

It can be noticed that the structural component responsible for the Urbach absorption edge (D_{str}) is independent of temperature. It is important to emphasize that the second term in the phonon component ($D_{fon}(T)$) is responsible for the slope of the absorption edge.

Experiments showed that the increase in the temperature of the synthesis at a constant cooling rate, or the constant temperature of the synthesis at a faster cooling, caused a shift and decrease of the fundamental absorption edge. If the measurements are carried

In Fig. 15 are presented the infrared transmission spectra for the sample containing no copper, i.e. $\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3$, and for the sample $\text{Cu}_3[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{97}$. The detected absorption maxima are due to the presence of the absorbed water in KBr, which is practically unavoidable in the applied experimental methodology. The maximum at about 3450 cm^{-1} indicates the presence of the H-O-H bond, and the one at about 1600 cm^{-1} is due to the presence of the OH-group.

It should be pointed out that for this energy range such transparency spectrum is quite expectable, bearing in mind that the vibration energies corresponding to the potential bonds between the components are in the far-infrared range.

The edge of the fundamental absorption with the majority of chalcogenide glasses is shifted to

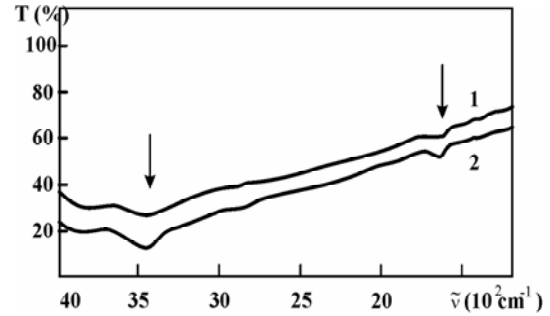


Figure 15. IR transmission spectra (KBr pellet) of the $\text{Cu}_x[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{100-x}$ glasses: (1) $x = 0$; (2) $x = 3$ at % Cu.

out at the same temperature ($D_{fon} = const$) it can be thought that the nature of the structural unit is responsible for the potentially detected changes in the absorption edge. The decrease of the slope of the exponential part of the fundamental absorption edge is determined by the increased degree of disorderliness.

With many chalcogenide materials it is possible to detect the temperature dependence of the coefficient of optical absorption. The studies concerning the fundamental absorption edge, carried out for the glasses of the type $(GeS_2)_x(AsSBr)_{100-x}$ in a relatively narrow spectral interval showed that with decrease in the temperature the absorption edge is shifted towards higher energies [36]. As can be seen from Fig. 16, in the temperature range from 5 to 77 K, the position of the absorption edge changes more slowly than in the range above 77 K. This can be explained in terms of the electron-phonon interaction. The linear dependence above 77 K indicates that for the systems constant in the temperature interval from 77 to 300 K holds the relation of the type

$$\Gamma(T) = \Gamma(77) + aT, \quad (4)$$

where $\Gamma(T)$ - slope of the Urbach absorption edge of the amorphous material, and a - constant.

In Fig. 17 is presented the temperature dependence of the optical bandgap for these chalcogenides. As can be seen, in the interval from 77 to 300 K, this dependence can be described by the linear function:

$$E_g(T) = E_g(77) + \beta T, \quad (5)$$

where $\beta = dE_g/dT$.

The decrease of the coefficient β (Table 1) is most probably a consequence of a decrease of the contribution to thermal expansion of the glass in the transition from a chain structure (characteristic of AsSBr) to the solid network based on the tetrahedral structural units $GeS_{4/2}$ (forming the binary compound GeS_2). A consequence of this transition is a nonlinear dependence of E_g and n on x , which is especially pronounced in the range $40 \leq x \leq 60$. In accordance with this, as well as on the basis of the results obtained from Raman and IR spectra, it can be concluded that the glasses in the system Ge-As-S-Br are prone to liquefaction.

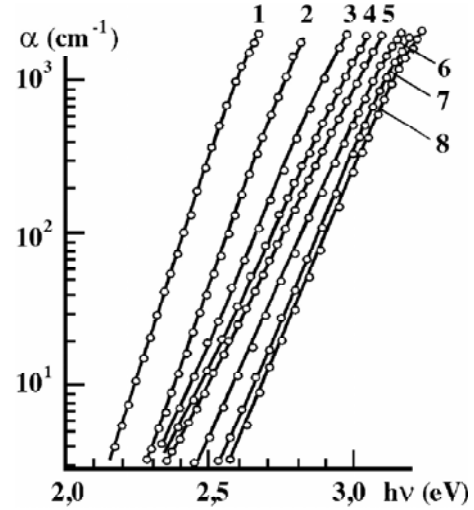


Figure 16. Absorption coefficients for $(GeS_2)_x(AsSBr)_{100-x}$ glasses at different temperatures: (1) $x = 20$; (2) $x = 40$; (3) $x = 60$; (4) $x = 80$; (5) $x = 100$; curves 1-5, $T = 300$ K; curve 6, $T = 200$ K; curve 7, $T = 77$ K; curve 8, $T = 5$ K.

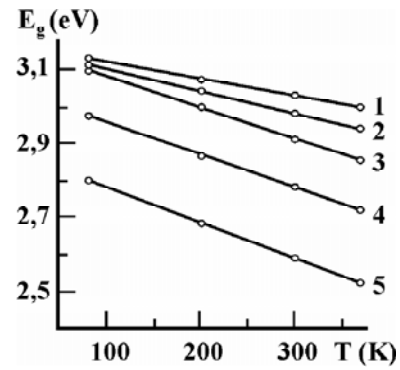


Figure 17. Temperature dependence of the optical bandgap for $(GeS_2)_x(AsSBr)_{100-x}$ glasses: (1) $x = 100$; (2) $x = 80$; (3) $x = 60$; (4) $x = 40$; (5) $x = 20$.

Table 1. Characteristic physical parameters for the glasses of the type $(\text{GeS}_2)_x(\text{AsSBr})_{100-x}$: E_g - optical bandgap, β - coefficient, n - refractive index, T_g - softening temperature .

x , mol %	E_g [eV] ($\alpha = 10^3 \text{ cm}^{-1}$, $T = 300 \text{ K}$)	$\beta \cdot 10^4$ [eV/K]	n ($\lambda = 5 \mu\text{m}$)	T_g [K]
100	3.03	4.6	2.016	753
90	2.98	6.2	2.027	601
60	2.91	8.4	2.041	513
40	2.78	8.8	2.074	434
20	2.60	9.5	2.120	376

The behavior of the absorption maxima in the range of the short-wavelength fundamental absorption edge of bulk samples of the type $\text{Cu}_x(\text{AsSe}_{1.4}\text{I}_{0.2})_{100-x}$, for $x = 0, 1, 5, 10, 15, 20$ and 25 at % copper, was determined by the method of sample thickness reduction.

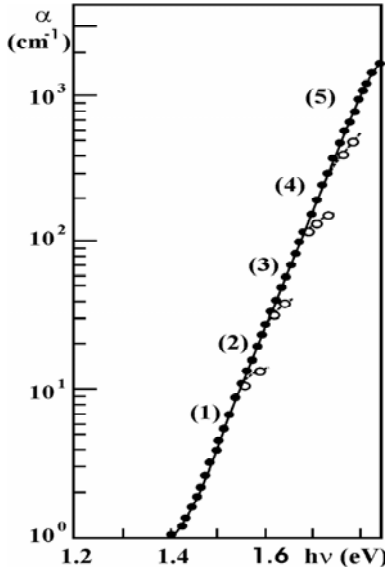


Figure 18. Frequency dependence of the absorption coefficient for $\text{AsSe}_{1.4}\text{I}_{0.2}$ (thickness of the sample for part (1) is $d = 0.2 \text{ cm}$; (2) - $d = 0.07 \text{ cm}$; (3) - $d = 0.022 \text{ cm}$; (4) - $d = 0.0073 \text{ cm}$; (5) - $d = 0.0024 \text{ cm}$).

In Fig. 18 is shown the frequency dependence of the absorption coefficient for the sample whose composition corresponds to the eutectic.

The analysis of the spectra recorded in the visible spectral range showed that increase in copper content in the material reduced the range and level of its transparency. Even small contents of copper exhibited a significant effect on the transmission properties. The results showed that the presence of only 0.5 at % of copper reduced the transparency level by about 20 %.

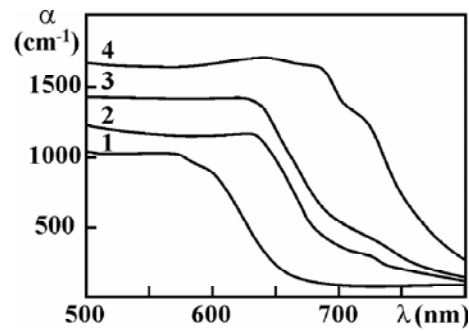


Figure 19. Frequency dependence of the absorption coefficient for bulk glasses of the $\text{Cu}_x[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{100-x}$ system: (1) $x = 0$, $d = 0.12 \text{ mm}$; (2) $x = 0.5$, $d = 0.1 \text{ mm}$; (3) $x = 1.0$, $d = 0.11 \text{ mm}$; (4) $x = 3.0$, $d = 0.1 \text{ mm}$.

Fig. 19 illustrates the behavior of the absorption coefficient of the glasses from the system Cu-As-S-Se. The short-wavelength edge (λ_g) was determined by extrapolation of the linear portion of the dispersion curves $\alpha = f(\lambda)$ to the region of the Urbach edge. The values of absorption edge of 661.7 nm, 687 nm, 707.7 nm and 776.8 nm for the samples with $x = 0, 0.5, 1$ and 3 at % Cu, respectively, served as the basis for calculating the

corresponding values of optical bandgap.

Graphical presentation of the dependence of the bandgap E_g on copper content in the glass is given in Fig. 20. It can be noticed that in the investigated range of elemental concentrations an increase in copper content results in a linear decrease of the energy bandgap. The modeled analytical expression for this dependence is of the form

$$E_g = 1.874 - 0.089 \cdot x \text{ (eV)} \quad (6)$$

where x - copper content in the material.

The obtained values for optical bandgap (from 1.596(20) to 1.874(28) eV) indicate that we deal with semiconducting materials [37].

Investigations of the four component glasses from series $\text{Fe}_x[(\text{Sb}_2\text{S}_3)_{0.75}(\text{SbI}_3)_{0.25}]_{100-x}$ [31] showed that they have a wide range of transparency from about 650 nm to 20 μm (Fig. 21).

With increase in Fe content, the absorption edge shifts to higher wavelengths, whereas the sample transparency shows a decrease. The IR spectra show a relatively high transparency in the whole investigated range. The registered absorption maxima (at 1600 and 3450 cm^{-1}) belong to the already mentioned optical activity related to the substrate (KBr).

The relatively small values of the coefficients of optical absorption were in this case a limiting factor in selecting the appropriate method to assess E_g (Stukes method or graphical extrapolation of the dependence $\sqrt{\alpha h\nu} = f(h\nu)$). To solve the problem of correct assessment of the ener-

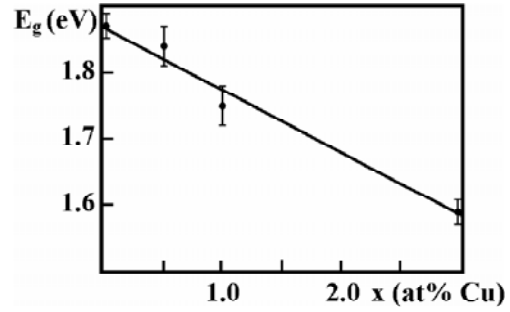


Figure 20. Dependence of the energy gap on concentration of copper for $\text{Cu}_x[\text{As}_2(\text{S}_{0.5}\text{Se}_{0.5})_3]_{100-x}$ glasses.

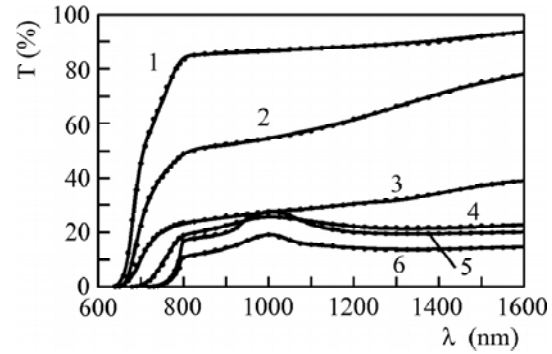


Figure 21. Transmission spectra of bulk samples of the $\text{Fe}_x[(\text{Sb}_2\text{S}_3)_{0.75}(\text{SbI}_3)_{0.25}]_{100-x}$ type (1) $x = 0$; (2) $x = 0.01$; (3) $x = 0.1$; (4) $x = 0.5$; (5) $x = 0.8$; (6) $x = 1$ at % Fe. (thickness of the samples - 0.10; 0.15; 0.13; 0.11; 0.13 and 0.11 mm, respectively).

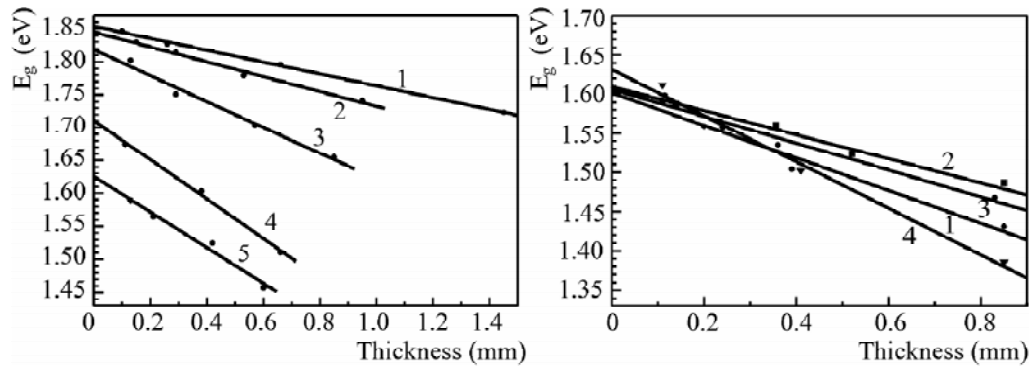


Figure 22. Dependence of extrapolation values of the optical bandgap and sample thickness for $\text{Fe}_x[(\text{Sb}_2\text{S}_3)_{0.75}(\text{SbI}_3)_{0.25}]_{100-x}$ glasses: (1) $x = 0$; (2) $x = 0.01$; (3) $x = 0.1$; (4) $x = 0.5$; (5) $x = 0.8$ at %.

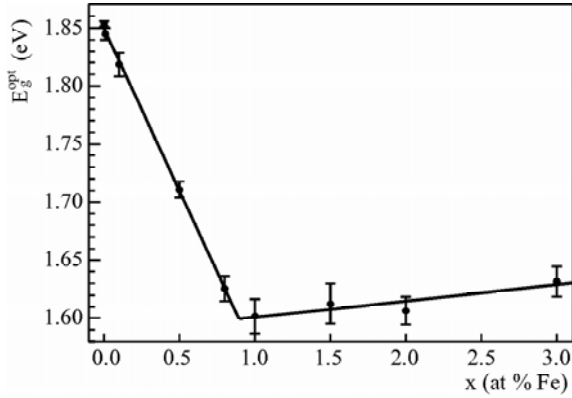


Figure 23. Dependence of energy gap on concentration of iron for the $\text{Fe}_x[(\text{Sb}_2\text{S}_3)_{0.75}(\text{SbI}_3)_{0.25}]_{100-x}$ glasses.

A linear decrease of the value of optical bandgap with the chalcogenides of the type $\text{Fe}_x[(\text{Sb}_2\text{S}_3)_{0.75}(\text{SbI}_3)_{0.25}]_{100-x}$, for the iron concentrations below 1 at % (from 1.853(2) eV for the glasses containing no Fe to 1.625(11) eV for the sample with 0.8 at % Fe), shows that the Fe atoms are incorporated into the matrix of these materials and influence their energy pattern. Similar effect has also been observed in the investigation of electrical conductivity of the samples [38]. To the concentration of 1 at % Fe the glasses behave as semiconductors: iron is present in the high-spin Fe^{2+} state in an octahedral surroundings, with the chalcogen atom in the first coordination sphere.

With increase in the Fe concentration above 1 at % the optical bandgap becomes practically independent on the Fe content. Such a result suggests the occurrence of some specific changes in the structure of the material with higher iron contents, influencing the energy pattern. Besides, the amount of Fe above 1 at % is present in the form of finely dispersed isolated centers that exhibit weak interaction with the glass matrix.

Hence, the optical bandgap can be described by the two analytical functions:

$$E_{\text{opt}}(\text{eV}) = 1.850(2) - 0.280(4) \cdot x \quad 0 < x < 1 \text{ at \% Fe} \quad (7)$$

$$E_{\text{opt}}(\text{eV}) = 1.587(5) + 0.014(2) \cdot x \quad 1 < x < 3 \text{ at \% Fe} \quad (8)$$

The glasses $\text{Ge}_{20}\text{As}_{14}\text{S}_x\text{Se}_{52-x}\text{I}_{14}$ exhibit high transparency in the visible and infrared spectral range, and this is illustrated in Fig. 24 for the sample $\text{Ge}_{20}\text{As}_{14}\text{Se}_{40}\text{S}_{12}\text{I}_{14}$ [25].

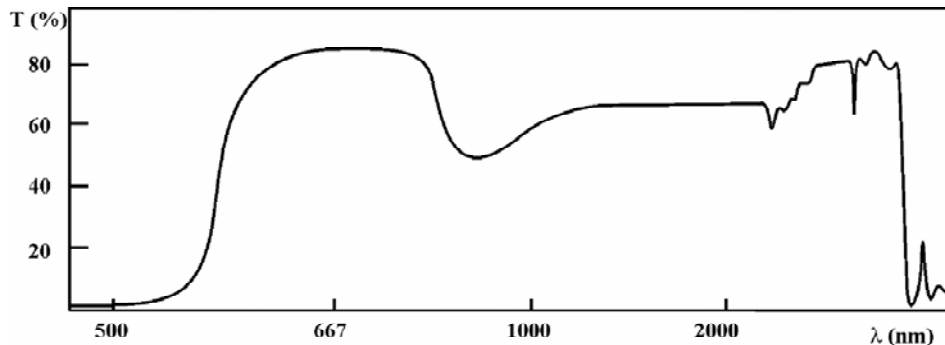


Figure 24. Transmission spectra of glassy $\text{Ge}_{20}\text{As}_{14}\text{Se}_{40}\text{S}_{12}\text{I}_{14}$.

gy bandgap we employed a specific approach based on the correlation between the energies obtained as extrapolation values of the absorption edge and sample thickness. It appeared that this correlation could be characterized by a linear function (Fig. 22). The extrapolation of this function to a zero thickness gives the value of optical bandgap of the glass.

Fig. 23 illustrates the dependence of the energy gap on iron concentration in the glasses. It is evident that the value of optical bandgap changes significantly with increase in iron content.

A high transparency (about 70 %) is observed in a wide range, from the edge of the visible range to the far-infrared range at about 850 cm^{-1} . Here, the strong absorption is due to the characteristic oscillations of the As-S and As-I bonds, marking the beginning of multiphonon absorption characteristic of the chalcogenide glasses containing As, S, and Se [39]. This is especially evident in the transmission spectrum recorded in the far-infrared range, presented in Fig. 25 and in the Raman spectrum shown in Fig. 26.

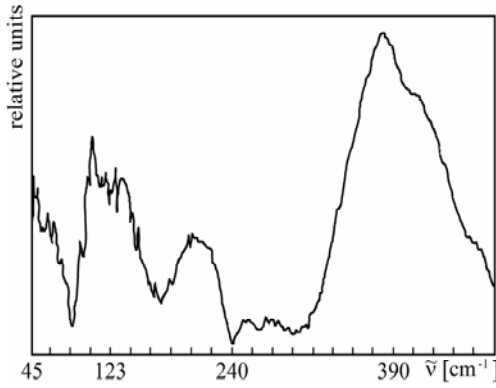


Figure 25. Far-infrared spectra of glassy $\text{Ge}_{20}\text{As}_{14}\text{Se}_{12}\text{S}_{40}\text{I}_{14}$.

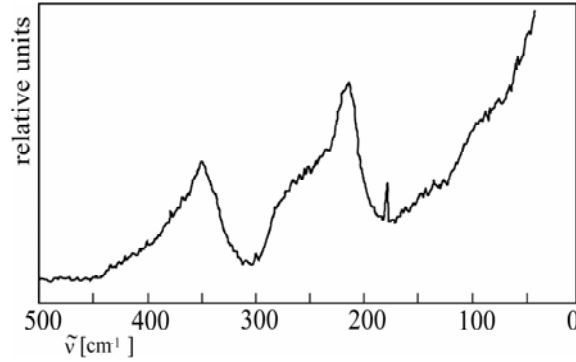


Figure 26. Raman spectra of glassy $\text{Ge}_{20}\text{As}_{14}\text{Se}_{12}\text{S}_{40}\text{I}_{14}$.

A typical transmission spectrum for the glass of the type $\text{Ge}_{20}\text{As}_{14}(\text{Se}_{0.5}\text{S}_{0.5})_{66-x}\text{I}_x$ is shown in Fig. 27.

The experimentally established behavior of the absorption coefficients served as the basis for determining optical bandgap of the glasses from the system $\text{Ge}_{20}\text{As}_{14}(\text{Se}_x\text{S}_{1-x})_{52}\text{I}_{14}$, for $x = 0, 2, 4, 6, 8, 10, 12, 18, 26, 34, 40, 42, 44, 46, 48, 50, 52$ [25, 26].

In Fig. 28 is presented the dependence of the energy bandgap on the sulfur/selenium content in the glasses. The corresponding analytical form of the functional dependence between the energy bandgap E_g and the parameter x is:

$$E_g(\text{eV}) = 2.39 - 0.008 \cdot x \quad (9)$$

The corresponding maximal change of the energy bandgap is in the range from 1.97 to 2.39 eV [25].

Detailed studies of the absorption spectrum in the range of fundamental absorption made it possible to determine the changes of optical bandgap with temperature [42]. The linear dependence can be

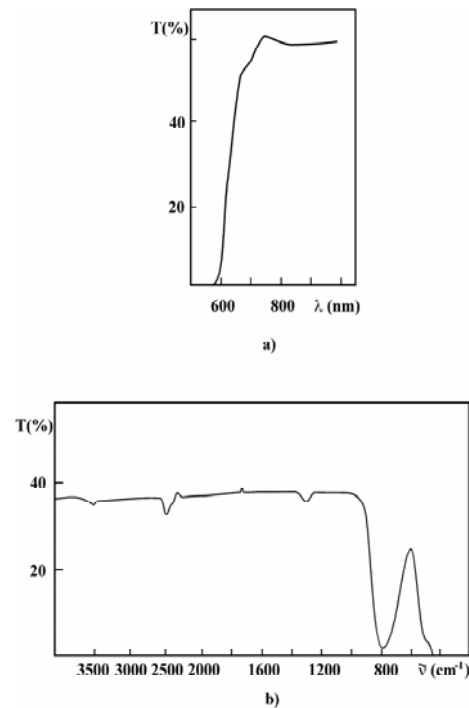


Figure 27. Transmission spectra of glassy $\text{Ge}_{20}\text{As}_{14}\text{Se}_{30}\text{S}_{30}\text{I}_6$ in the intervals of 600 – 1100 nm (a) and 4000 – 200 cm^{-1} (b).

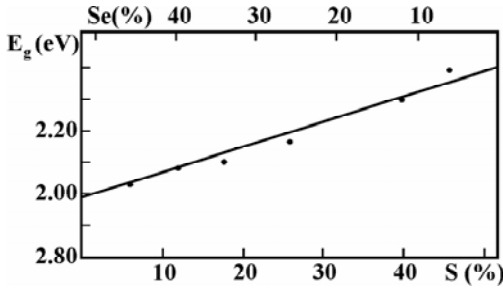


Figure 28. Dependence of energy gap on concentration of sulfur/selenium in the system $\text{Ge}_{20}\text{As}_{14}\text{S}_x\text{Se}_{52-x}\text{I}_{14}$.

described by the function:

$$E_g = E_g(77) + \beta \cdot T \quad (10)$$

where $E_g(77)$ is the value of the optical bandgap at 77 K, and $\beta = dE_g/dT$. The changes in the quantity β as a function of sulfur/selenium concentration are presented in Fig. 29.

It can be seen that this quantity has a minimum approximately at the equilibrium concentration of these two elements.

The determination of refractive index made it possible to carry out the appropriate corrections of the absorption coefficient using the calculated reflection values. The behavior of the absorption coefficient for the samples in the system $\text{Ge}_{20}\text{As}_{14}\text{S}_x\text{Se}_{52-x}\text{I}_{14}$ upon such treatment is illustrated in Fig. 30 [29, 42].

It appeared that the reflection corrections for these materials are within the limits of the experimental error.

In Fig. 31 are shown the excitation luminescence spectra (ES) and photoluminescence spectra (PS) for the five-component $\text{Ge}_{20}\text{As}_{14}\text{S}_x\text{Se}_{52-x}\text{I}_{14}$ glasses. The analysis of the dependence of the energy maximum on selenium concentration shows that these energies are approximately equal to the one half

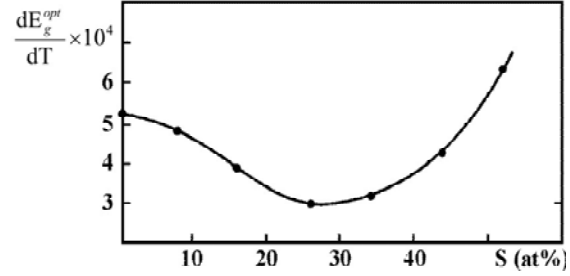


Figure 29. Temperature dependence of the optical bandgap as a function of sulfur content in the system $\text{Ge}_{20}\text{As}_{14}\text{S}_x\text{Se}_{52-x}\text{I}_{14}$.

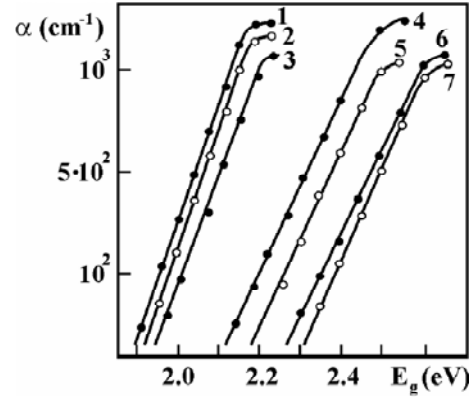


Figure 30. Absorption coefficients for (1) $\text{Ge}_{20}\text{As}_{14}\text{Se}_{52}\text{I}_{14}$; (2) $\text{Ge}_{20}\text{As}_{14}\text{Se}_{48}\text{S}_4\text{I}_{14}$; (3) $\text{Ge}_{20}\text{As}_{14}\text{Se}_{42}\text{S}_{10}\text{I}_{14}$; (4) $\text{Ge}_{20}\text{As}_{14}\text{Se}_{32}\text{S}_{20}\text{I}_{14}$; (5) $\text{Ge}_{20}\text{As}_{14}\text{Se}_{18}\text{S}_{34}\text{I}_{14}$; (6) $\text{Ge}_{20}\text{As}_{14}\text{Se}_2\text{S}_{50}\text{I}_{14}$; (7) $\text{Ge}_{20}\text{As}_{14}\text{S}_{52}\text{I}_{14}$ (values obtained by taking into account the correction for regular reflection).

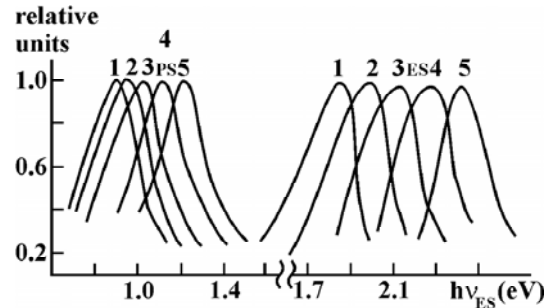


Figure 31. Excitation luminescence spectra (ES) and photoluminescence (PS) spectra for (1) $\text{Ge}_{20}\text{As}_{14}\text{Se}_{52}\text{I}_{14}$, (2) $\text{Ge}_{20}\text{As}_{14}\text{Se}_{40}\text{S}_{12}\text{I}_{14}$, (3) $\text{Ge}_{20}\text{As}_{14}\text{Se}_{26}\text{S}_{26}\text{I}_{14}$, (4) $\text{Ge}_{20}\text{As}_{14}\text{Se}_{12}\text{S}_{40}\text{I}_{14}$, (5) $\text{Ge}_{20}\text{As}_{14}\text{S}_{52}\text{I}_{14}$.

of the bandgap value. On the other hand, a comparison of these spectra with those of the corresponding two- and three-component glasses indicates that these complex glasses contain structural units of the type As_2S_3 , As_2Se_3 , GeS_2 , As-SeI and AsSI [40].

On the basis of the experimentally established behavior of the absorption coefficient (Figure 32) it was possible to determine the optical bandgap for the system $\text{Ge}_{20}\text{As}_{14}(\text{Se}_{0.5}\text{S}_{0.5})_{66-x}\text{I}_x$. The corresponding analytical form of the functional dependence of the energy bandgap E_g on the parameter x is:

$$E_g(\text{eV}) = 1.968 + 0.0087 \cdot x \quad (10)$$

The values of energy bandgap are in the range from 1.97 to 2.08 eV.

The experimentally established behavior of the absorption coefficient (Fig. 33) [36] served as the basis for determining the values of optical bandgap for the glasses from the system $\text{Ge}_x\text{As}_{34-x}\text{Se}_{26}\text{S}_{26}\text{I}_{14}$.

The corresponding analytical expression of the functional dependence of the energy bandgap E_g on the parameter x is of the form:

$$E_g(\text{eV}) = 1.843 + 0.0046 \cdot x \quad (11)$$

The obtained energy bandgap values are in the range from 1.84 to 1.94 eV.

In Fig. 34a is presented the dispersion of the absorption coefficient of the glasses from the system $(\text{As}_2\text{S}_3)_x(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_{100-x}$, and in Fig. 34b the behavior of the optical bandgap as a function of the As_2S_3 content [41]. The corresponding analytical expression of the functional dependence of the energy bandgap E_g on the parameter x is of the form:

$$E_g(\text{eV}) = 0.16 + 1.89 \cdot x \quad (12)$$

The values of the energy bandgap range from 1.44 to 2.10 eV.

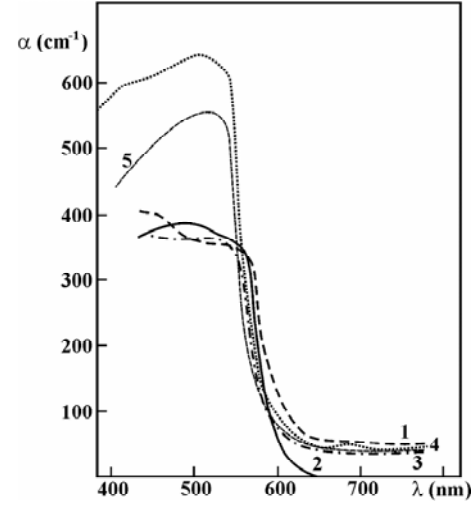


Figure 32. Absorption coefficients for $\text{Ge}_{20}\text{As}_{14}(\text{Se}_{0.5}\text{S}_{0.5})_{66-x}\text{I}_x$ glasses: (1) $x = 0$; (2) $x = 2$; (3) $x = 6$; (4) $x = 10$; (5) $x = 14$.

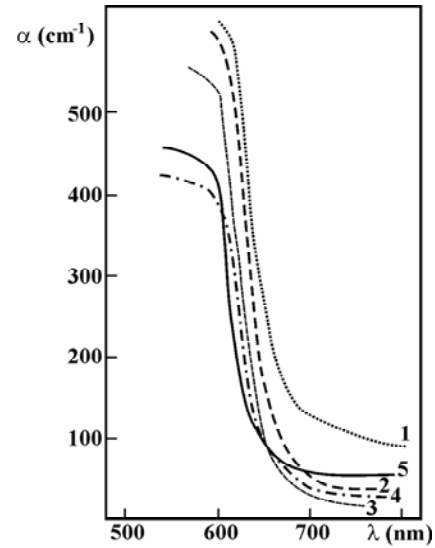


Figure 33. Absorption coefficients for: (1) $\text{Ge}_x\text{As}_{34-x}\text{Se}_{26}\text{S}_{26}\text{I}_{14}$ glasses: (1) $x = 2$; (2) $x = 6$; (3) $x = 10$; (4) $x = 14$; (5) $x = 20$.

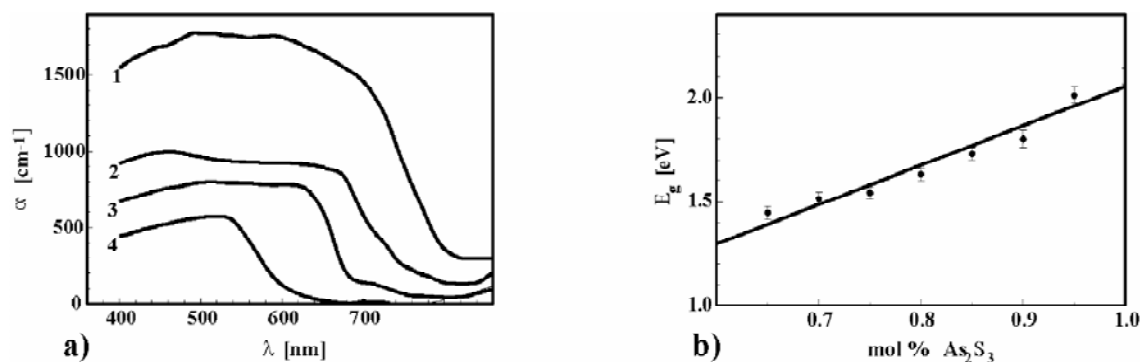


Figure 34. Frequency dependence of the absorption coefficient for bulk glasses in the $(\text{As}_2\text{S}_3)_x(\text{AsSe}_{0.5}\text{Te}_{0.5}\text{I})_{1-x}$ system: (a) - (1) $x = 0.70$; (2) $x = 0.80$; (3) $x = 0.90$; (4) $x = 0.95$; (b) - Dependence of energy gap on content of As_2S_3 .

Acknowledgments

This work was supported by the Provincial Secretariat of Science and Technological Development, Autonomous Province of Vojvodina, Project "Technology of obtaining and characterization of disordered semiconductors" No. 114-451-01397/2006-01.

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The Influence of Some D-Seco-Estrone Derivatives on the Phase Transitions of Binary Mixtures of Cholesteric Liquid Crystals

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Received: December 22, 2005

Abstract

We have studied the influence of the new chiral non-mesogenic seco-estrone derivatives 2 and 4, synthesized in several synthetic steps starting from estrone, on the physical characteristics of the binary mixtures of cholesteric liquid crystals. We have examined the phase transitions of the mixture of cholesteryl laurate and cholesteryl enantate with addition of chiral non-mesogenic additives 2 and 4 (45 % – 45 % – 10 %; Mix.1 and Mix.2, respectively). X-ray diffraction data enabled the determination of the molecular structures of the compounds 2 and 4, the crystal lattice parameters of the new chiral additives and their molecular length (l) and width (d^*), as well as some parameters of the mixtures: the thickness of smectic layers and the longitudinal spacing distance in the cholesteric phase (d), and the average distance between the long axes of neighbouring molecules (D). Using molecular-mechanic calculations, based on the solved molecular structures, the most probable conformation of the compound 2 was determined.

Key words: X-ray diffraction, D-seco-estrone derivatives, cholesteric liquid crystals

1. Introduction

This work represents the continuation of our studies [1, 2] of binary and multicomponent mixtures of cholesteric liquid crystals, undertaken with an aim to obtain the systems with stable mesophase transitions and transition temperatures close to room temperature. Taking into account the suitable steroidal configuration of investigated D-seco-estrone derivatives, as well as their antiestrogenic activity with no estrogenic effect [3, 4], we have undertaken the study of a binary mixture of cholesteryl laurate and cholesteryl enantate with these derivatives. These chiral additives do not have any liquid crystalline phases.

The addition of some of the D-seco-estrone derivatives to cholesteric compounds or their binary mixtures in different concentrations resulted in significant shift of the temperature of phase transitions towards lower temperatures with respect to that of the initial components [5]. Comparing the results of optical microscopy and X-ray diffraction data from unoriented sample we have identified the type and temperature of the phase transition and outlined the phase diagrams. The layer spacing (d) in SmA* phase and the average intermolecular distance (D) (i.e. the mean distance between the long axes of neighbouring parallel molecules) were determined using the Bragg law: $\lambda = 2x \sin \theta$, where the distances $x = d$ and $x = D$ were calculated from the positions of the small angle and the large angle diffraction peak, respectively. In the case of a cholesteric phase, d corresponds to the average longitudinal (along the director) spacing distance, which is approximately equal to the length of the molecule. X-ray diffraction data enabled the determination of the crystal lattice parameters, molecular structures and the molecular length (l) and width (d^*) of some new chiral additives. On the basis of the solved molecular structures, using molecularmechanic calculations, the most probable conformation of compound 2 was also determined.

2. Experimental details

General

The optical study was performed using a polarization microscope Carl Zeiss (Jena) in the transparent light with special additional facility for the controlled heating and cooling of the sample, Mettler FP5.

Unoriented samples were investigated by X-ray diffraction in the transmission geometry by means of a conventional powder diffractometer, Seifert V-14, using CuK α radiation at 0.154 nm, with an automatic high temperature kit Paar HTK-10.

The molecular and crystal structure of the chiral additive 4 in crystal phase was determined by the standard procedures of the single crystal structure determination. Because of the poor crystal quality of 4, the crystal structure refinement was limited to isotropic stage. For this crystal the molecular energy minimum conformation was determined by the molecularmechanic calculations (MMC) (PCMODEL, Serena Software, 1989), starting from the rough molecular model. From the additive 2 no single crystals could be grown, therefore a structure determination by X-ray was not possible. Instead, MMC was used to obtain the minimal energy conformations of this molecule.

Synthesis of the new chiral additives

The starting compound, 3-benzyloxy-17-oxo-16,17-secoestra-1,3,5(10)-trien-16-nitrile (1, Scheme 1) was synthesized in several steps, starting from estrone. The sodium borohydride reduction of compound 1 afforded 3-benzyloxy-17-hydroxy-16,17-secoestra-1,3,5(10)-trien-16-nitrile (2). Tosylation of the 17-hydroxy function of derivative 2, carried out in dry pyridine, yielded 3-benzyloxy-17-tosyloxy-16,17-secoestra-1,3,5(10)-trien-16-nitrile (3). Further, under reaction conditions of hydrogenolysis, this compound gave 3-hydroxy-17-tosyloxy-16,17-secoestra-1,3,5(10)-trien-16-nitrile (4).

The phase sequences of the synthesized chiral additives (2 and 4) are given in Table 1.

Table 1. The phase sequence of initial substances.

Substances	Phases and transition temperature (°C)
Cholesteryl laurate	I 93 Ch 90 SmA* 83.5 Cr
Cholesteryl enantate	I 114 Ch 99.5 SmA* 72.9 Cr
2	Cr 137-138 I
4	Cr 138-140 I

3. Results and discussion

The molecular structure of compound 4 (Scheme 1) was determined by X-ray diffraction and it is presented in Figure 1. The basic crystallographic data are given in Table 2.

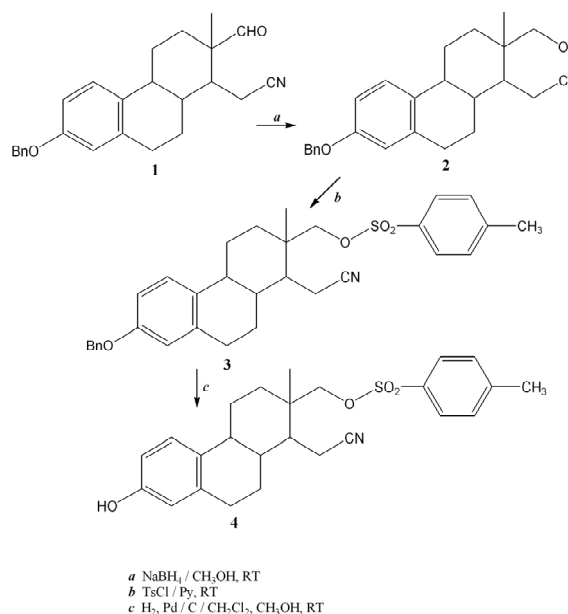
The X-ray measurement of 4 was aborted after collecting about 50 % of data because the check reflections had fallen below 50 % of their initial intensity. Therefore the structure of 4 could be solved with partial data only and isotropically refined to $R = 0.103$. This analysis has shown that the asymmetric unit contains two independent molecules of 4 and the water molecule (see Fig. 1b).

In spite of the poor data and less precisely defined molecular parameters, the revealed structure enabled us to define its minimum energy conformation by the MMC.

The combinations of the energy minimum molecular structures of 4 enabled us to generate the minimum energy structures of molecule 2 by MMC, which is given in Figure 1a.

Table 2. The basic crystallographic data.

Compound	4
Radiation	MoK α
System	Monoclinic
Space group	P2 ₁
a (Å)	10.1937(8)
b (Å)	7.7656(6)
c (Å)	30.158(2)
β (°)	99.343(7)
R	0.1026
	3512 ref. $F_o > 4\sigma(F_o)$

**Scheme 1.**

The molecular length of compound 4 was determined as the distance between the O atom on the C-3 and the CH₃ group from the 17-tosyloxy moiety ($l \sim 17$ nm). The molecular width was estimated as the distance between the O atoms of the SO₂ group and the nitrile N atom ($d^* \sim 4.5$ nm). The l and d^* values of compound 2 were determined in the same way taking the terminal atoms in the molecules ($l \sim 14.5$ nm, $d^* \sim 8.1$ nm).

The optical microscopic studies have been started with checking the pure substances: cholesteryl laurate and cholesteryl enantate. The properties of the cholesteric

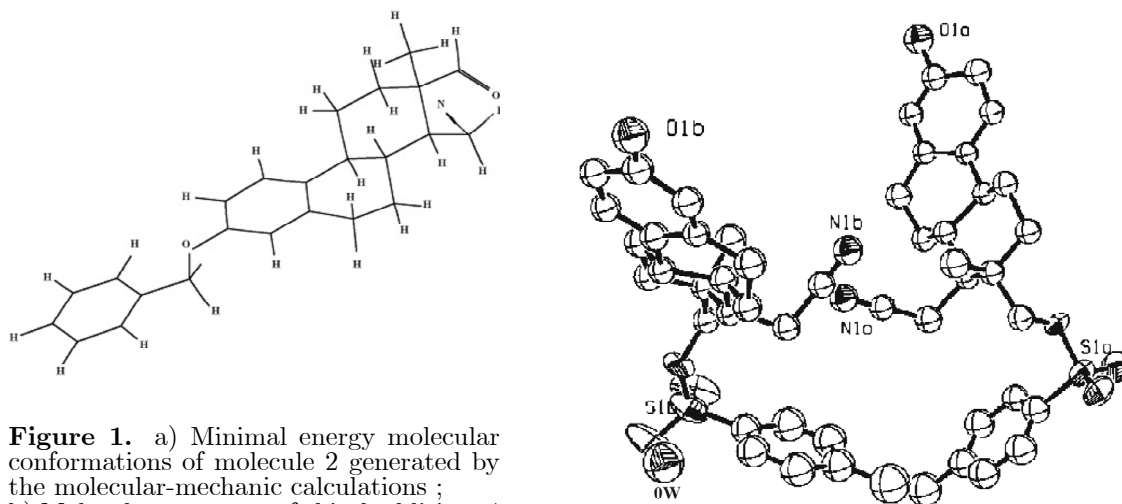


Figure 1. a) Minimal energy molecular conformations of molecule 2 generated by the molecular-mechanic calculations ;
b) Molecular structure of chiral additives 4

substances have shown good agreement with existing literature data [6]. Then the melting points of the new chiral additives 2 and 4 were determined. The phase transition temperatures of pure substances are listed in Table 1. After that we prepared the binary mixture, Mixbin, which contained cholesteryl enantate and cholesteryl laurate, 50 % – 50 % by weight. This binary mixture was used as the reference compound for testing the chiral additives. Therefore threecomponent mixtures (Mix.1 and Mix.2), containing Mixbin (90 %), and one of the chiral derivatives (2 and 4, 10 %) were prepared. Phase sequences of the investigated mixtures are presented in Table 3.

Analysis of the phase sequences of the threecomponent mixture Mix.2, and comparison with the binary mixture (Mixbin) have shown that the addition of chiral non-mesogenic additive, 4, resulted in shifts of the temperatures of the isotropiccholesteric (I-Ch) phase transition by 3.5°C and of the cholestericsmectic A* (Ch-SmA*) one by ~ 2.3°C. In the case of Mix.1, the shifts of the I-Ch and Ch-SmA* phase transition temperatures were 10.4°C and 7.9°C, respectively.

Table 3. The phase sequence of investigated mixtures. The transition temperatures are given in °C.

Mixture	Transition temperature			Phase temperature range		ΔT		
	I→Ch	Ch→SmA*	SmA*→Cr	Ch	SmA*	I→Ch	Ch→SmA*	SmA*→Cr
Mixbin	76.8	69.1	35	7.7	34.1			
Mix.1	66.4	61.2	30	5.2	31.2	10.4	7.9	5
Mix.2	73.3	66.8	24	6.5	42.8	3.5	2.3	11

On the basis of the collected experimental data, we have performed the study of un-oriented samples by X-ray diffraction. X-ray diffraction studies were carried out on the binary (Mixbin) and on ternary mixtures (Mix.1 and Mix.2). Relevant parameters of investigated mixtures, obtained from X-ray diffraction data, are presented in Table 4. Diffraction profiles of unoriented samples of some of the ternary mixtures, as well as of

Mixbin, at different temperatures, are given in Figure 2.

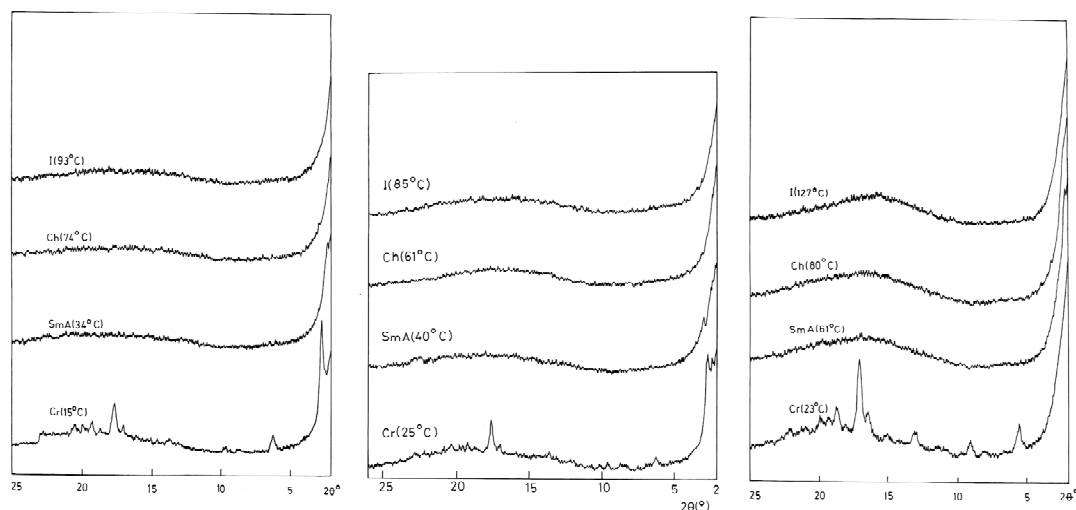


Figure 2. X-ray diffraction profiles for: a) Mixbin, b) Mix.1 and c) Mix.2.

Table 4. Molecular parameters of investigated mixtures for all observed phases at a fixed temperature T : angles corresponding to the reflection peaks 2θ , effective layer thickness d (error of measurements δ_d was about ± 0.1 Å), average repeat distance D (error of measurements δ_D was about ± 0.03 Å).

Mixture	T (°C)	2θ (°)	d (Å)	D (Å)
Mixbin	93(I)	16.6		5.33
		2.9	30.4	
		3.1	28.5	
	74(Ch)	17.0		5.21
		2.2	40.1	
Mix.1	34(SmA*)	17.8		4.98
		15		5.90
	77(I)	3.2	27.6	
		16.5		5.57
		2.75	32.1	
Mix.2	42(SmA*)	16.0		5.53
		15.7		5.64
	86(I)	3.5	25.2	
		16.5		5.37
		2.2	40.1	
	52(SmA*)	17.0		5.21

The analysis of X-ray diagrams of the SmA* phase showed the presence of a strong reflection at small angles, indicating the presence of a layer structure, and the diffuse broad peak appearing in the range of $2\theta \sim 10 - 25^\circ$, with the maximum at $2\theta \sim 17.0^\circ$, corresponding to the average intermolecular distance (D).

The calculation of the longitudinal spacing distance (d) in the cholesteric phase gives the value of 30.4 Å and 25.2 Å for Mixbin and Mix.2, respectively. The shortest longitudinal spacing distance was observed in the Ch phase of Mix.2. It is probably due to the steric influence of the long tosyloxy group in position 17 of compound 2, and the higher number of single bonds, which enabled better packing in the mixture.

One can notice that the thickness of smectic layers (d) in the SmA* phase of investigated mix-

ture with chiral additive 2 is smaller than in Mixbin. It is probably due to the conformation of the additive, that the packing of the host molecules in ternary mixtures is altered compared to that in Mixbin. Chiral additive 2 has a OH group at the position 17. On the other hand, chiral additive 4 possesses a longer tosyloxy group at the same position. It may be a consequence of this sterical modification and the presence of more single bonds in the case of chiral additive 4 is that the d layer thicknesses of Mixbin and Mix.2 in the SmA* phase are practically the same, while in Mix.1 they are nearly 25 % smaller.

As can be seen from Table 4, the maximum of the broad peak, corresponding to D in the SmA* mesophase, shifted towards larger angle values in Mix.1 and Mix.2, than in Mixbin. This indicates that in chiral-containing additives a higher packing density of the molecules is energetically more favourable, than in the pure cholesteric binary mixture.

Comparing Mix.1 and Mix.2 it was established that the phase transitions temperatures $I \rightarrow Ch$ and $Ch \rightarrow SmA^*$ decrease with the increasing width of molecules (d^*), as well as with the decreasing molecular length (l) of the chiral additives.

4. Conclusion

The results of the studies on the ternary mixtures of cholesteric liquid crystals with new, non-liquid crystalline, chiral seco-estrone derivatives 2 and 4 have shown a significant shift of the mesomorphic phase transitions toward lower temperatures, with respect to the ones of the pure cholesteric binary mixture. The molecular structure of derivative 4 was solved by the standard procedure of single crystal structure determination, while molecularmechanical calculations were used to obtain similar data for derivative 2 forming poor quality crystals. The molecular length and width (l and d^* values, respectively) of the compounds were determined taking terminal atoms in the molecules. On the basis of X-ray diffraction data on the crystalline powder of unoriented samples we have determined the intermolecular distance, D , and the layer spacing or the longitudinal spacing distance, d . It was shown that the thickness of smectic layers, d , in the SmA* phase of the investigated mixtures with chiral additive 2 is smaller than in the binary mixture, while in Mix.2 was practically the same. The maximum of the broad peak, corresponding to the intermolecular distance in the SmA* mesophase, shifts towards smaller angle values in Mix.1 and Mix.2 than in Mixbin, which indicates that a highest packing density of the molecules is in the binary mixture. It was found that the phase transition temperatures decrease with increasing molecular length of the chiral additives.

Acknowledgments

This work was supported by research Grant No. 1578 and No. 1896 from the Ministry of Science and Enviromental Protection of the Republic of Serbia and Hungarian National Science Funds OTKA T 030401, T 032667 and T 037336. D. Ž. O., M. G., A. V. and N. É. are grateful for the hospitality provided within the framework of an exchange project of the Serbian Academy of Sciences and Arts and the Hungarian Academy of Sciences.

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Tunelling of Davydov's Soliton through the Barrier in the Linear Polymer Chain with Impurity

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Received: December 23, 2005

Abstract

The influence of the impurity on the propagation of Davydov's soliton in a linear polymer chain was studied. Impurity is treated as an entity which has different excitation energy and different value of resonance dipole-dipole interaction energy from all the other monomer units of the chain. Numerical results show that the higher value of the exciton energy at the impurity site is unsurmountable potential barrier for soliton propagation. However, there is a borderline in the rise of the resonance dipole-dipole interaction energy where the barrier becomes permeable again.

Key words: Davydov's soliton, nonideal chain, impurity

1. Introduction

The fact that the Davydov soliton model [1] was a subject of intensive theoretical investigations during the last three decades [2] confirms its importance in the attempts to understand and describe the energy transport process in α -helix proteins. In this relatively simple model, the analysis of these processes has been reduced to the analysis of Frenkel's excitons [3] in the soft one-dimensional polymer chain, which are amide-I vibrational quantum exciton in protein [4]. Due to the nonlinear and strong exciton-lattice interaction, autolocalized excitations - soliton appear in the system. Thus, these are in fact the excitonic polarons. In other words, the propagation of the exciton (amide-I quanta) along the chain is followed by local chain deformation, which means that the real excitation is the "dressed" exciton, i.e. autolocalized solitary wave.

Davydov's model is of methodological importance since it explains transport of energy in α -helix proteins. Davydov's model uses the α -helix protein made of identical monomer units, which is not true in reality. A real α -helix protein is composed of different monomer units. Namely, the proteins are macromolecules composed of 20 different amino acids. In this paper a nonideal polymer chain (i.e. a chain with implanted one different monomer unit which is treated as "impurity") is considered.

As far as we know, in previous papers on Davydov's model, only an ideal infinite translationally invariant chain without impurities has been considered. Taking into account the

above complexity of the protein structure (there is the impurity which disturbs its translational invariance), we propose an approach which allows analyzing a nonideal chain with only one impurity. The disturbance of the structure caused by the impurity is considered as a particular perturbation of the Hamiltonian of the ideal chain. This approach, which is also numerically verified, allows adjusting the theoretical method used for the analysis of an ideal chain and applying it easily to a nonideal chain (with impurity).

2. System Hamiltonian

In order to obtain the Hamiltonian of the disturbed polymer chain, i.e. the chain consisting of weakly interacting monomers, we start from standard Davydov's Hamiltonian of the ideal polymer chain, designated below as H_d , to which the term H_a describing supposed disturbance due to the existence of the impurity in the chain, shall be added and explained in detail later. The Hamiltonian H_d consists of three parts. Hamiltonian H_e describes monomer amide-I quantum excitations. They will be considered, in accordance with Davydov's approach, as Frenkel's excitons [4, 5] in the so-called two level approximation, which means that only the ground and the first excited levels are taken into account, because the higher excited levels are supposed to be sufficiently far away from the first excited level [3]. Hamiltonian H_p describes vibrations of monomer units. Hamiltonian H_i describes exciton-phonon interaction. Thus, the Hamiltonian of the disturbed nonideal polymer chain is given as

$$H_s = H_d + H_a = H_e + H_p + H_i + H_a \quad (1)$$

The Hamiltonian H_e , in the usual nearest neighbours approximation, is of the following form:

$$H_e = \sum_n (\Delta + D_n) B_n^+ B_n + \sum_{n,m} J_{n,m+1} B_n^+ (B_{n+1} + B_{n-1}) \quad (2)$$

where B_n^+ and B_n are the Bose operators which create and annihilate the excitation on the n -th chain site having the on-site energy $\Delta + D_n$, where Δ is the exciton energy of the isolated monomer and D_n is the contribution to the on-site energy arising due to the resonance dipole-dipole interaction of the considered monomer unit with other monomer units. The matrix element $J_{n,m}$ characterizes the exciton-exciton interaction which enables the exciton propagation along the chain.

H_p is taken in the harmonic approximation, which means that

$$H_p = \frac{1}{2} \sum_n \left[\frac{1}{M} p_n^2 + k (u_n - u_{n-1})^2 \right] \quad (3)$$

where M is the mass of the monomer unit; u_n is the n -th monomer unit displacement and p_n is the corresponding conjugate momentum; k is the lattice elasticity coefficient.

The Hamiltonian H_i of the exciton-lattice interaction could be easily derived starting from the exciton Hamiltonian H_e . It is necessary to expand the quantities D_n and $J_{n,m+1}$ in terms of monomer unit displacement u_n up to the first-order term. In this way one obtains

$$\begin{aligned} D_n &= -D + \chi_1 (u_{n+1} - u_{n-1}), \\ J_{n,m+1} &= -J + \chi_2 (u_n - u_{n-1}) \end{aligned} \quad (4)$$

where χ_1 and χ_2 are the exciton-phonon coupling parameters. It should be noticed that in the original Davydov's theory only the constant χ_1 in the one-dimensional polymer chain is included, while χ_2 is omitted. However, more detailed analysis shows that χ_2 should not be neglected. Rough estimation is given by Takeno et al [6].

After the substitution of the expansions (4) in (2), the obtained Hamiltonian may be divided into two parts. The first one, which does not include monomer unit displacements u_n corresponds to the exciton Hamiltonian, while the other one, with the term containing the monomer unit displacements, corresponds to the exciton-lattice interaction H_i which is given as

$$H_i = \chi_1 \sum_n B_n^+ B_n (u_{n+1} - u_{n-1}) + \chi_2 \sum_n B_n^+ (B_{n+1} + B_{n-1}) (u_n - u_{n-1}) \quad (5)$$

Now, it is obvious that the Hamiltonian H_i consists of two parts with two coupling parameters χ_1 and χ_2 . The first part determines the change of on-site exciton energy caused by the lattice vibrations, while the second term reflects the influence of these vibrations on exciton propagation along the chain.

The particular manner in which we include the disturbance caused by the impurity has affected some of the previously considered Hamiltonian terms. Namely, although the chain has the impurity the Hamiltonian H_d (which is in fact the Hamiltonian of ideal Davydov's model) describes an ideal polymer chain with no impurity. As we have the chain with impurity at some place in the chain, this means that to H_d some nonexistent terms have been added and therefore these terms must be extracted and the terms corresponding to the impurities included too. In order to solve this problem we follow the usual theory of a single impurity in the crystal lattice, where it is taken that the presence of impurity on some lattice site is equivalent to the presence of a local potential on that site. In other words, this means that impurity affects the coupling constant and the other relevant parameter, mainly near the impurity position and, consequently, H_a may be extracted from the Hamiltonian H_d in which the constants Δ , J , k , χ_1 , χ_2 have been renormalized in an appropriate way. However, the correction of all these constants need not be considered because some of them are negligible quantities. We have found out that the corrections of the exciton energy Δ and the constant of resonance energy dipole-dipole interaction J are the only ones that, although in somewhat different manner, should be included. These quantities should be substituted by the new ones $\Delta + \tilde{\Delta}Y(na)$, and $J + \tilde{J}Y(na)$, where $\tilde{J}Y(na) \equiv Y_n$ is the function of the lattice position "vector" na which has the following form

$$Y_n = \sum_{n_i} e^{-\beta a(n-n_i)^2} \quad (6)$$

that has its maximum at n_i , the lattice site where the impurity is placed. As can be seen, Y_n is chosen to be sufficiently fast decreasing (exponentially). The constant β depends on the potential induced by the impurity effects and will be obtained from the physical condition that the impurity affects only several nearest neighbors.

Taking into account the previous facts, which indicate that only the exciton parameters are corrected, it is easy to show that the exciton Hamiltonian of the nonideal chain can be expressed as a sum of aforementioned exciton Hamiltonian of the ideal chain H_e and Hamiltonian of the residue H_a which is of the form

$$H_a = \sum_n \tilde{\Delta} Y_n B_n^+ B_n - \sum_n \tilde{J} Y_n (B_{n+1} + B_{n-1}) \quad (7)$$

The nonzero terms in the above sums are only due to the lattice points at which the impurities are present.

3. Dynamic equations of the solitary waves in the chain with the impurity

As is known from the theory of Davydov's model, described here by the Hamiltonian H_d , in the case of strong exciton-lattice coupling and small longitudinal elasticity coefficient ("soft" polymer chain), the solitonic excitations can arise in the system. The following calculation, which treats the nonideal chain with impurity, is completely based on the presumptions of Davydov's soliton theory and therefore it will be given in short. The only differences in our case, which do not change the calculation procedure, are the following: the presence of H_a in the system Hamiltonian and, as mentioned above, we included the parameter χ_2 also, contrary to the usual approach (for one-dimensional polymer chain), in which only coupling parameter χ_1 was taken into account. The calculation procedure given here is the derivation of basic dynamic equations of the theory of Davydov's model. The first step is to write down the averaged equation of motion of the lattice and the time dependent Schrödinger equation of the whole system, using the system Hamiltonian H_s and following one-quasi-particle wave function

$$|\Psi\rangle = e^{-\frac{i}{\hbar}S(t)} \sum_n [A_n(t)B_n^+|0\rangle], \quad S(t) = \sum_n [\alpha_n(t)p_n - \pi_n(t)u_n],$$

$$\alpha_n(t) = \langle\Psi|u_n|\Psi\rangle, \quad \pi_n(t) = \langle\Psi|p_n|\Psi\rangle \quad (8)$$

where $|0\rangle$ is the vacuum-state function, $\exp[S(t)]$ is the unitary operator, usually used in the theory of lattice vibrations in the presence of external forces, while $A_n(t)$ determines the probability of creating the exciton at the lattice site n , which means that

$$\sum_n |A_n(t)|^2 = 1. \quad (9)$$

The averaged equation of motion of the lattice, i.e. of the quantity α_n is of the form

$$M \frac{d^2\alpha_n}{dt^2} = k[\alpha_{n+1} + \alpha_{n-1} - 2\alpha_n] + \chi_1 [|A_{n+1}|^2 - |A_{n-1}|^2] +$$

$$+ \chi_2 [A_n^*(A_{n+1} - A_{n-1}) + (A_{n+1}^* - A_{n-1}^*)A_n] \quad (10)$$

On the other hand, by substituting $|\Psi\rangle$ (Eq. 8) into the time-dependent Schrödinger equation, where the total system Hamiltonian H_s has been used, we obtain:

$$i\hbar \frac{\partial A_n}{\partial t} = [\Lambda + \varepsilon Y_n + \chi_1(\alpha_{n+1} - \alpha_{n-1})] A_n - (J + \tilde{J}Y_n)(A_{n+1} + A_{n-1} - 2A_n) +$$

$$+ \chi_2 [(\alpha_{n+1} - \alpha_n)A_{n+1} + (\alpha_n - \alpha_{n-1})A_{n-1}], \quad (11)$$

$$\Lambda = \Delta - D + \frac{1}{2} \sum_n \left[\frac{1}{M} \pi_n^2 + k(\alpha_n - \alpha_{n-1})^2 \right] - 2J, \quad \varepsilon = \tilde{\Delta} - 2\tilde{J}$$

Since our main aim was to carry out the numerical analysis of the last two equations, it is useful to write down these equations in the continual approximation ($na \rightarrow x$; $(n \pm 1)a \rightarrow x \pm a$; $A(na, t) \rightarrow A(x, t) \cdots$), in which we have

$$A_{n\pm 1} \cong A(x, t) \pm a \frac{\partial A(x, t)}{\partial x} + \frac{1}{2} a^2 \frac{\partial^2 A(x, t)}{\partial x^2},$$

$$\alpha_{n\pm 1} \cong \alpha(x, t) \pm a \frac{\partial \alpha(x, t)}{\partial x} + \frac{1}{2} a^2 \frac{\partial^2 \alpha(x, t)}{\partial x^2} \quad (12)$$

After substituting the expansions (12) into (11) we obtain the following equation

$$\left(\frac{\partial^2}{\partial t^2} - v_0^2 \frac{\partial^2}{\partial x^2} \right) \rho(x, t) + v_0^2 \frac{2k}{\chi} \frac{\partial |B(x, t)|^2}{\partial x} = 0 ,$$

$$\left[i\hbar \frac{\partial}{\partial t} - \Lambda + \frac{\hbar^2}{2m_{ex}} \frac{\partial^2}{\partial x^2} + 2ak\rho(x, t) \right] B(x, t) = \varepsilon Y(x) B(x, t) \quad (13)$$

where a is the lattice constant and

$$B(x, t) = \frac{1}{\sqrt{a}} A(x, t) e^{\frac{i}{\hbar} \Lambda t} , \quad \rho = -\frac{\partial \alpha}{\partial x} \quad v_0^2 = \frac{ka^2}{M} ,$$

$$\chi = \chi_1 + \chi_2 , \quad m_{ex} = \frac{\hbar^2}{2a^2[J + \tilde{J}Y(x)]} \quad (14)$$

v_0 is the sound velocity in the unperturbed phonon system; m_{ex} is the exciton mass. As can be seen, the expression for the exciton mass in the disturbed chain with impurity contains the additional term $2a^2[J + \tilde{J}Y(x)]$, which means that the exciton is, in some sense, dressed in the additional local potential, due to the presence of the impurity.

4. Results of the numerical analysis

Equations (10) and (11), which determine the dynamics of the considered disturbed nonideal chain, have been analyzed numerically. The results are presented graphically in the figures given below, all of them representing the time-dependent quantity $|A_n(t)|^2$, which is the density of probability to obtain the excitation at the given lattice site n in the given time t . In all presented cases, it was assumed that the cyclic boundary conditions can be applied, the chain has 200 monomer units, the first chain monomer unit is excited, the monomer unit mass is $M = 1.9 \cdot 10^{-25}$ kg (interval of mass) α -amino acids is $(1.17 - 1.91) \cdot 10^{-25}$ kg, the elasticity coefficient is $k = 20$ N/m [7, 8] and $J = 1.55 \cdot 10^{-22}$ J [9, 10, 11] resonance energy of dipole-dipole interactions between neighboring peptide groups. In this paper, the constant $\chi_1 = 6.0 \cdot 10^{-11}$ N [12, 13], $\chi_2 = 0.2 \cdot 10^{-11}$ N [6], while the constant β , which appears in Y_n is taken to be equal to 1.8 .

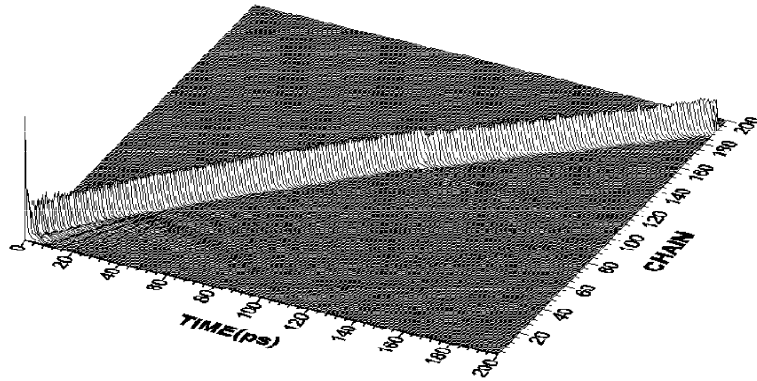


Figure 1. Solitary wave tunneling through the exciton barrier (impurity is at the 120th site. The value of increased exciton energy is $\tilde{\Delta} = 0.3 \cdot 10^{-22}$ J.

Fig. 1 shows the propagation of the solitary wave in the monomer chain with one impurity at the lattice site $n = 120$ is presented. In this case the only exciton energy at the impurity site is changed by the value $\tilde{\Delta} = 0.3 \cdot 10^{-22}$ J. We see from Fig. 1 that a small increase in the exciton energy at the impurity site is not a barrier to the solitary wave propagation.

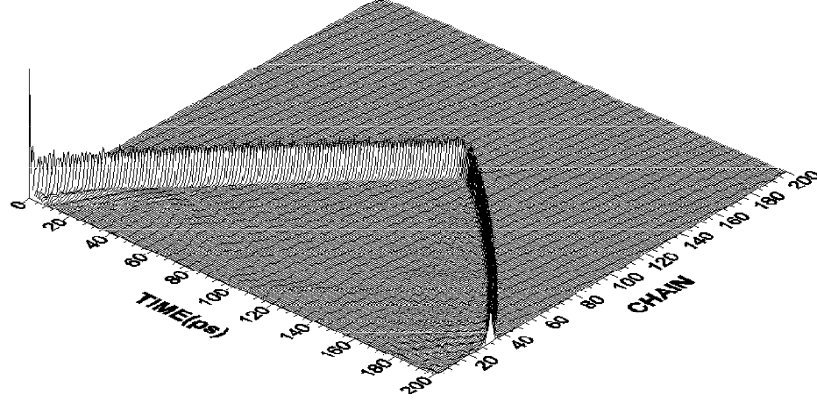


Figure 2. Total reflection of the solitary wave at one impurity site (at the 120th site) The value of increased exciton energy is $\tilde{\Delta} = 0.5 \cdot 10^{-22}$ J.

However, if we increase the exciton energy by a value of $\tilde{\Delta} = 0.5 \cdot 10^{-22}$ J (at the impurity site $n = 120^{\text{th}}$), as can be seen in Fig. 2, then the impurity becomes a nonpermeable potential barrier and soliton wave is reflected.

On the other hand, if we increase the resonance dipole-dipole interaction energy, we come to the border value of about $\tilde{J} = 0.05 \cdot 10^{-22}$ J, when the barrier at the impurity site becomes permeable again, as we can see from Fig. 3.

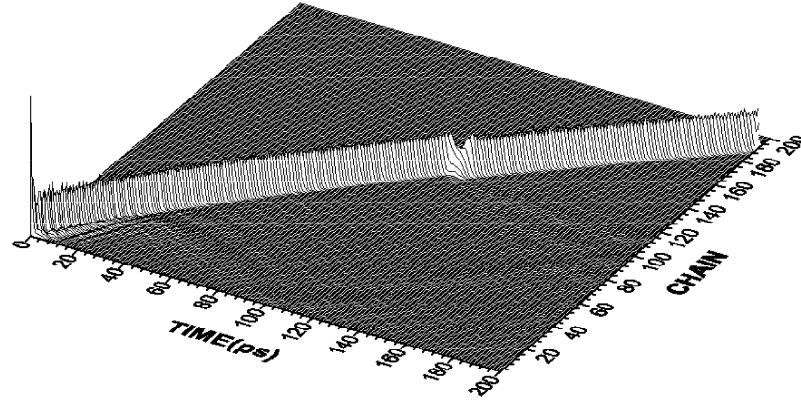


Figure 3. Solitary wave tunnelling through the potential barrier (impurity is at the 120th site). The value of increased exciton energy is $\tilde{\Delta} = 0.5 \cdot 10^{-22}$ J and the value of increased resonance energy of dipole-dipole interaction is $\tilde{J} = 0.05 \cdot 10^{-22}$ J.

According to Eq. (14), the exciton mass decreases. The internal energy of the exciton and soliton is increased and the region involved in the excitation is expanded [4].

5. Concluding remarks

We have shown, by the numerical analysis of equations of motion (10) and (11), that is possible that the soliton wave is tunnelling through the potential barrier when the resonance dipole-dipole interaction energy is increased at the impurity site. In this case the inner energy is increased and the excitation region becomes dissipated, which then enables the soliton wave to tunnel through the barrier.

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Journal of Research in Physics

Volume 30 Number 2 September 2006

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