# WORLD YEAR OF PHYSICS 2005: OPPORTUNITY TO LOOK IN THE FUTURE OF PHYSICAL INVESTIGATIONS AND SOCIETY CHALLENGES FOR PHYSICS

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Last year the 32nd session of the General Conference of UNESCO adopted a resolution supporting the initiative of 2005 as the World Year of Physics (WYP2005). The reasons of the General Conference of UNESCO for that were the following:

- **Recognising** that Physics provides a significant basis for the development of understanding of nature,
- **Stressing** that education in Physics provides women and men with the tools to build the scientific infrastructure essential for development,
- **Considering** that research in Physics and its applications has been and continues to be a major driving force to scientific and technological development, and remains a vital factor in addressing the challenges of the 21st century,
- **Being aware** that the year 2005 marks the 100th anniversary of a series of great scientific advances by Albert Einstein,
- Welcomes the resolution of the International Union of Pure and Applied Physics (IUPAP), at the initiative of the European Physical Society, to declare the year 2005 the World Year of Physics and carry out, within this framework, activities to promote physics at all levels world-wide;
- **Decides** to support the initiative of the World Year of Physics 2005;
- **Invites** the Director-General to request the United Nations General Assembly to declare 2005 the International Year of Physics.

On this basis the General Assembly of the United Nations firstly in its history on 10 June 2004 has declared 2005 the World Year of Physics.

This act is clear recognition that physics, in particular, and science, in general makes important contributions to society. From electricity and transport to computers and the Internet, physics has laid the foundation for numerous transforming technologies over the past 200 years. Especially physicists are proud of their central role in science and society in the twentieth Century. The advances and breakthroughs of 20th-century physics have enriched all the sciences and opened a new era of discovery. They have touched nearly every part of our society, from health care to national security to our understanding of Earth's environment. They have led us into the information age and fuelled broad technological and economic development. The pace of discovery in physics has quickened over the past two decades. New microscopic devices are being developed with a host of potential applications, and instruments of unprecedented sensitivity and reach are being created and employed. Physics at the tiniest distances is being linked to the origin and fate of the universe itself.

The WYP2005 marks also the 100th anniversary of Albert Einstein's "miraculous year" in which he published five important papers describing ideas that have since influenced all of modern physics. These scientific papers have provided the basis for three fundamental fields in physics: the theory of relativity, quantum theory and the theory of Brownian motion. Therefore this year provides the opportunity to celebrate Einstein, his great ideas, and his influence on life in the 20th century.

Thus the WYP 2005 is a world-wide celebration of physics and its importance in our everyday lives. Physics not only plays an important role in the development of science and technology but also has a tremendous impact on our society. WYP aims to raise the world-wide awareness of physics and physical science.

However recognising the great achievements of physical sciences in the past it is more important to look to the future.

The huge technological developments of the 20<sup>th</sup> century, of course, have come with a price tag. In particular, our use of the Earth's finite resources - triggered by the insatiable demands of the world's increasing population - has escalated. Managing these resources without depleting them for good - a concept known as "sustainable development" - is one of the most urgent challenges we face today. Physics will play a crucial role in solving the global problems of the society, which are classified in four main areas:

- Economic Development
- Energy production
- Environmental protection
- Public health.

Society has other urgent needs, which modern physics is poised to address. How will we meet our energy needs as Earth's environment changes and its natural resources become depleted? Physicists' involvement in molecular biophysics, solar energy collection and conversion, or laser fusion may contribute to a solution. Health threats are likely to increase on our interconnected and highly populated planet, and rapid response to new contagions requires the development of ways to detect biomolecules remotely through advanced laser technique.

Now we live in an era of astounding technological transformation of economy in which change, not stability, has become the norm. All around us are now-familiar technologies, heir present state of development-or very existence- would have seemed extraordinary just a generation ago. In 1776 when Adam Smith published his massive four-volume study An Inquiry Into the Nature and Causes of the Wealth of Nations, he noted that the specialization of labor had vastly increased industrial productivity. He then observed that as workers become more skilled, businesses become more efficient, which leads inexorably to "the invention of a great number of machines which facilitate and abridge labour and enable one man to do the work of many". So was born the idea that "innovation" is an important ingredient in economic development. By 20th century, econometric measures of innovation revealed a clear link between industrial performance and investment in science, education and technology. As century progressed, those nations that learned to develop and exploit innovation were rapidly transformed from agrarian subsistence economies to wealthy technological states. From wireless telephones and handheld GPS units to video games, DVD, and digital television; to genetic engineering, decoding of the human genome, and combinatorial drug design; to MRIs, CT scans, laser eye surgery, and robotic hip replacement surgery; to polymeric materials for inline skates, tennis rackets, and skis; to superalloys for jet engine turbine blades; to lightweight, fuel-efficient automobiles and aircraft; to computers, the Internet, and the World Wide Web-technology is everywhere and touching all of us in ever more pervasive ways. All of this technology does not just happen. It arises from innovation based on decades of research in the underlying basic science, of which physics is a major component in essentially every case. Some of concludent illustrations of physics involvement in the economic development are related to:

• information and communication technologies (ICT), which move from the developed world to lower cost centres of production, thus requiring local expertise;

- emerging field of nano-science and nanotechnology, which allow for the first time, to break free from traditional raw material-based production infrastructures and move into knowledge-based and modern economic, political and social systems;
- transport, where physics provides solutions to difficult problems;
- modern, knowledge-based agriculture and food production and a range of further areas.

ICT has created a new way of viewing the ways in which different industrial, agricultural, and service elements link together so that more than just the economic contribution of these different growth segments can be identified. These technologies challenge us to find new ways in which human efforts can enhance institutional life and sustain technological learning in developing economies. Today's computers are doubling in performance every year or two. This will end when the ever-shrinking size of electronic components approaches the level of individual molecules and atoms. Quantum physics offers a radically different approach to information processing, whereby single atoms and photons could be the new hardware. This could lead to computers capable of solving problems that are intractable on any imaginable extension of today's computers but that are important in areas from basic science to national security. Quantum communication might provide some security against interception beyond anything possible in today's cyber infrastructure. These applications are based on the strangest and least intuitive concepts of quantum physics, such as Einstein's action-at-a-distance, which allows teleportation and the remote transfer of information without physical contact. Quantum computing is forcing us to explore both theoretical and experimental quantum mechanics at their deepest levels.

Nanotechnology is the study, design, creation, synthesis, manipulation, and application of functional materials, devices, and systems through control of matter at the atomic and molecular levels and the exploitation of novel phenomena and properties of matter at that scale. Nanotechnology can contribute new tools to address sustainable development problems, and it can strengthen the technologies already available and make them more efficient. It will coexist with rather than replace established technologies. Its impact will be felt in multiple ways, depending on how other technologies converge and align themselves around it. Nanotechnology is likely to be particularly important in the developing world as it is R.Moldova today, because it involves little labor, land, or maintenance; it is highly productive and inexpensive; and it requires only modest amounts of materials and energy.

We are now in the early stages of a second "quantum revolution" in which we can see and control tiny clusters of atoms and indeed even individual atoms. This second revolution is bringing together two central strands of the physics endeavor: atomic and condensed matter physics. The nanoworld lies in the transition region between our familiar classical world of relatively well-behaved macroscopic objects and the quantum world of atoms and molecules. These nanostructures have counterintuitive but useful optical properties that come from their subwavelength dimensions. Scientists see unique opportunities to tailor material properties for efficient optical switches, light sources, or photoelectric power generators. Negative index nanomaterials could dramatically improve optical microscopes or reduce the feature size in chip fabrication. Other applications include photonic crystals, single photon sources and detectors, environmental monitoring, and biomedical optics, with applications such as killing cancerous cells via localized optical absorption and heating.

With the needs to develop cleaner energy and mitigate the adverse effects of climate change, for example, society will increasingly depend on physics to understand and solve the problems of energy production and environmental protection. Taking clean water as an example, membranes that are made from carbon nanotubes - rolled-up 2D sheets of graphite -

can be used to block the passage of bacteria, viruses, heavy metals and other pollutants. They can therefore be used as effective filters for purifying water. Carbon nanotubes can also withstand relatively high temperatures, which means the filter could be unclogged periodically by heating it; conventional polymer-based water filters, in contrast, are destroyed if heated. Meanwhile, natural tracers such as tritium, helium-3 and carbon-14 - in conjunction with chemical and hydrological measurements - can be used to determine where ground water has come from and whether it has been contaminated with pollutants. Such information is critical for determining if the water is safe to drink. Other applications of physics include the development of recyclable polymeric nanocomposites that may replace metals and other materials that are currently used in industrial manufacturing.

Harnessing renewable energy sources through cleaner, more affordable, and more reliable technologies can prevent the dependency of developing countries on fossil fuels and avert potential energy crises and environmental degradation brought about by the depletion of oil and coal. Improved access to clean energy could play a role in improving health and increase the efficiency of agricultural production. Applications of nanotechnology such as solar cells, fuels cells, and novel hydrogen storage systems based on nanostructured materials promise to deliver clean energy solutions. Nanophotovoltaic devices, such as those based on quantum dots or ultrathin films of semiconducting polymers, can significantly reduce the costs associated with conventional solar cells. Carbon nanotubes can be used in composite film coatings for flexible solar cells. A major expense associated with hydrogen as a source of energy is its generation from water, a process that requires energy. Photo- and thermochemical nanocatalysts can be used to generate hydrogen from water at low costs. Electricity can also be cheaply produced using green technology from artificial systems that incorporates energy transduction proteins into an engineered matrix. Organic light-emitting devices based on semiconducting nanospheres can be developed to improve rural lighting.

Much of the improvement in human welfare over the past century can be accounted for by technological innovation in public health, nutrition, and agriculture. These improvements have reduced mortality rates and increased life expectancy. Telemedicine links, using broadband communication, could bring healthcare services to remote areas of the developing world. Novel recyclable materials could be produced by nanotechnology and self-assembly of molecules, while genetic engineering could help to develop foods and plants such as cotton that are resistant to harmful insects.

All above shortly mentioned aspects are related to "external" challenges of physics in connection with society and global problems. However, what are "internal" challenges of physics at the beginning of the new millennium in the WYP2005? What new answers do we seek? What knowledge must we obtain?

Physical community has identified, from many important and relevant issues, six broad grand challenges that succinctly describe key scientific opportunities available to physical science:

- 1. Developing Quantum Technologies;
- 2. Understanding Complex Systems;
- 3. Exploring the Universe;
- 4. Unifying the Forces of Nature;
- 5. Creating New Materials and Products;
- 6. Applying Physics to Biology and Medicine.

1. Due to all that was discovered in the 20<sup>th</sup> century about the nature of quantum physics, scientists are now at the dawn of a new kind of quantum revolution, in which *coherence* and *control* are the watchwords. The ability to manipulate individual atoms and

molecules will lead to new quantum technologies with applications ranging from the development of new materials to the analysis of the human genome. A new generation of technology will be developed with construction and operation entirely at the quantum level. Measurement instruments of extraordinary sensitivity, quantum computation, quantum cryptography, and quantum-controlled chemistry are likely possibilities. As the structures being explored for new electronic devices become smaller than the wavelength of light, one enters the realm of nanoscale physics, a field that is rapidly evolving and expanding as the size of structures decreases and the quality and complexity increase. New tools for material fabrication have now emerged that permit cutting and pasting almost on the atomic scale. The nanofabrication challenge for the future is to achieve control in all three dimensions like the layer precision of Molecular Beam Epitaxy in one dimension. Many structures in nature are well self-organized on the nanoscale. A challenge for artificial self-assembly is to reach the perfection often required for specific physical properties. A related and important new direction for the coming future is called "molecular electronics." Fundamentally, quantum mechanics is a theory of information. A realistic quantum computer must be based on switches built out of electrons and nuclei of individual atoms, or nanoscopic condensed matter systems.

2. The rapid advances of massively parallel computing, coupled with equally impressive developments in theoretical analysis, have generated an extraordinary growth in our ability to model and predict complex and nonlinear phenomena and to visualize the results. Problems that may soon be rendered tractable include the strong nuclear force, turbulence and other nonlinear phenomena in fluids and plasmas, the origin of large-scale structure in the universe, and a variety of quantum many-body challenges in condensed-matter, nuclear, atomic, and biological systems. In the study of complex systems, physicists are expanding the boundaries of their discipline: They are joining forces with biologists to understand life, with geologists to explore Earth and the planets, and with engineers to study crack propagation. Much progress is being made in applying the quantitative methods and modeling techniques of physics to complex systems, and instruments developed by physicists are being used to better measure the behavior of those systems.

3. The universe is still a mysterious place. The universe itself is now a laboratory for the exploration of fundamental physics. New instruments through which stars, galaxies, dark matter, and the Big Bang can be studied in unprecedented detail will revolutionize our understanding of the universe, its origin, and its destiny. New measurements will test the foundations of cosmology and help determine the nature of dark matter and dark energy, which make up 95 percent of the mass-energy of the universe. Questions such as the origin of the chemical elements and the nature of extremely energetic cosmic accelerators will be understood more deeply.

4. Determining of the basic constituents of matter is an important step toward an historic goal: the discovery of a unified theoretical description of all the fundamental forces of nature—the strong nuclear force, the electroweak forces, and gravity. This challenge was a great dream of A.Einstein. The most promising and exciting framework for unifying gravity with the other forces is string theory, which proposes that all elementary particles behave like strings at very tiny distances.

5. The discovery of materials such as high-temperature superconductors and new crystalline structures has stimulated new theoretical understanding and led to applications in technology. Several themes and challenges are apparent—the synthesis, processing, and understanding of complex materials composed of more and more elements; the role of molecular geometry and motion in only one or two dimensions; the incorporation of new

materials and structures in existing technologies; the development of new techniques for material synthesis. The ability to create new materials and structures is inextricably linked to advances in the understanding of fundamental phenomena in material physics. These advances, along with improvements in synthesis and processing, have led to an astonishing array of new materials with unexpected properties and to dramatic improvements in the properties of established materials. New materials allow entirely new device concepts to be realized or lead to a dramatic change in scale, such as single-molecule wires made of carbon nanotubes.

6. Like all aspects of the modern world, medicine has been transformed by discoveries in physics during the past century. Modern medicine is unthinkable without modern chemistry, and modern chemistry could never have existed without the fundamental understanding of atoms and molecules provided by the revolution in physics that started just about 100 years ago. The basis for medical practice resides in an understanding of how the body functions. Physics has contributed to this knowledge in essential ways through biophysical research and through the development of enabling technologies for the biological sciences. At the level of molecules, structure and function are inseparable. Understanding the structure of complex biological molecules is also the key to developing new pharmaceuticals by an approach that is more rational than the hit-and-miss approach of the past.

For today global society challenges of physics is characteristics its covering both world and inside country levels. Physical investigations today are structured in international research network. Therefore, the linkages of "external" challenges for physics to the national needs of R.Moldova as well as the linkages of "internal" challenges of physics to national research and development goals are evident. In the context of this short review physics should be a priority for science of Moldova. The WYP2002 is not only an opportunity for us to join the International community for physics celebration, but it is an opportunity to raise public awareness of physics and physical science in our developing country, to attract a new generation of scientists and to find the linkages of physical researches to the needs of our country. National priorities of R.Moldova are stipulated in different programs and strategies of development such as Strategy of poverty eradication and economic growth. Physics can contribute to these national priorities being involved in:

- Advancing fundamental investigations to develop scientific platform of qualitative economic growth and to improve the quality of life.
- Enabling technological innovations that spur economic competitiveness and job growth.
- *Providing knowledge and tools to assure energetic and informational development of the country.*
- Contributing to the development of therapies and diagnostic medical systems that enhance the health of the nation's people.
- Educating in science, mathematics, and engineering to ensure a scientifically literate population and qualified technical personnel who can meet national needs,
- Enhancing our ability to understand and respond to global and local environmental issues.
- Participating in International and European partnerships that foster the advancement of scientific frontiers and accelerate the progress of science across borders.
- Contributing to the mission adviser goals of government and departments.

In order to allow physics to contribute strongly to areas of national need, the government and the physics community should develop and implement a strategy for long-term investment in basic physics research. Key considerations in this process should include

the overall level of innovative infrastructure necessary to assure economic growth driven by new physics-based technologies.

An essential part of maintaining the physics leadership in the science of R.Moldova and international competitiveness as well as deeper involving in solution of society needs is to train and to equip the next generation of physical scientists. Physics and other related departments

should review and revise their curricula to ensure that they are engaging and effective for a wide range of students and that they make connections to other important areas of science and technology.

# SUPERCONDUCTIVITY AND FERROMAGNETISM IN NONADIABATIC SYSTEM WITH STRONG ELECTRON CORRELATIONS AND MAGNETIC IMPURITY

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The theory of superconductivity in non-adiabatic system with strong electron correlations and paramagnetic impurity was constructed in [1] - [3].

The obtained results allow one to make the following conclusions:

- **a.** Both the non-adiabatic effects and strong electron correlations, violating Migdal's theorem [4], are enhancing superconductivity.
- **b.** These effects reduce the influence of the exchange interaction in the paramagnetic phase of the system with magnetic impurities. As a result, the decrease of  $T_c$  with impurity concentration is slowed down compared to the conventional superconductors. The critical impurity concentration corresponding to the collapse of superconductivity is increased and the region of ungapped states is substantially enlarged.
- c. The coefficient of the isotope effect  $\alpha$  increases with impurity concentration and decreases with increase in Migdal's parameter m. At m > 0,2 the coefficient  $\alpha$  can be less than 0,5 for both pure and doped superconductors, depending on the value of the impurity concentration.

At low temperatures, the coexistence of superconductivity and ferromagnetic arrangement of impurity spins is possible. This arrangement is due to mediated exchange interaction of ions through the conduction electrons, which gives as a feedback the spatial density of electron spin defined by the paramagnetic susceptibility. This quantity is not zero in superconductor even at T = 0 by virtual of the exchange scattering of electrons on paramagnetic impurity. These effects as well as spin-orbital interaction give rise to the spin flip of electrons, and the mixing of electronic states with opposite spin directions, thus weakening the effect of the shift of the Fermi surfaces and gives rise to the possibility of coexistence of superconductivity and ferromagnetism.

The article aims to study the influence of non-adiabatic effects and strong electron correlation on the superconducting transition temperature  $T_c$  and the temperature of ferromagnetic arrangement of impurity  $T_k$  as functions of concentration of chaotically distributed magnetic impurity and , therefore, on the coexistence of superconductivity and ferromagnetism (see also [5], [6]).

The Hamiltonian of the system is

$$H = H_0 + H_1 + H_2,$$
(1)

where  $H_0$  is Hamiltonian of free electrons and phonons,  $H_1$  is electron-phonon interaction,  $H_2$  is interaction of electrons with chaotically distributed magnetic impurity.

In order to study superconducting properties of the system we have to obtain the equations for Greens's functions (normal and anomalous) taking into account the electron-phonon and electron-impurity interactions. For this purpose we will go to the interaction representation and write the perturbation theory for Green functions over interactions  $H_1+H_2$ . After having performed averaging over chaotically distributed impurity and orientations of their spins, we obtain

$$\overline{V_{\alpha_{1}\beta_{1}}(\vec{x}_{1})V_{\alpha_{2}\beta_{2}}(\vec{x}_{2})} = \frac{c}{V}\sum_{\vec{q}} e^{-i\vec{q}(\vec{x}_{1}-\vec{x}_{2})} \left\{ V_{1}(\vec{q})V_{1}(-\vec{q})\delta_{\alpha_{1}\beta_{1}}\delta_{\alpha_{2}\beta_{2}} + \left\langle S_{z}\right\rangle \left[ V_{1}(\vec{q})V_{2}(\vec{q})\delta_{\alpha_{1}\beta_{1}}\sigma_{\alpha_{2}\beta_{2}}^{z} + V_{2}(\vec{q})V_{1}(-\vec{q})\delta_{\alpha_{2}\beta_{2}}\sigma_{\alpha_{1}\beta_{1}}^{z} \right] + V_{2}(\vec{q})V_{2}(-\vec{q}) \left[ \left\langle S_{x}^{2}\right\rangle \sigma_{\alpha_{1}\beta_{1}}^{x}\sigma_{\alpha_{2}\beta_{2}}^{x} + \left\langle S_{y}^{2}\right\rangle \sigma_{\alpha_{1}\beta_{1}}^{y}\sigma_{\alpha_{2}\beta_{2}}^{y} + \left\langle S_{z}^{2}\right\rangle \sigma_{\alpha_{1}\beta_{1}}^{z}\sigma_{\alpha_{2}\beta_{2}}^{z} \right] \right\}, \quad (2)$$

where *c* is the concentration of impurity  $\sigma_{\alpha\beta}$  are Pauli matrices. V<sub>1</sub> (**q**), V<sub>2</sub> (**q**) are the Fourier components of the potential of impurity scattering. **S** is spin of impurity atom, and  $\langle .... \rangle$  means averaging over orientations of spins of impurity atoms. Hereinafer direct hat line means averaging over chaotically distributed impurity and orientations of their spins. Note that formula (2) can possibly account for ferromagnetic arrangement ( $\langle S_z \rangle \neq 0$ ). Internal field I = c V<sub>2</sub> (0)  $\langle S_z \rangle$  arises as well. In the derived series of perturbation theory we take in consideration all diagrams, inherit to the doped adiabatic systems with  $\langle S_z \rangle \neq 0$ , and additional diagrams, containing intersection of two lines of electron-phonon with electron-impurity interactions, in similar way as in the case of paramagnetic phase ( $\langle S_z \rangle = 0$ ) [1, 2]. These additional diagrams determine to first order the effect of nonadiabaticity.

For the sake of simplicity we are choosing Einstein spectrum and write the phonon Green's function in the form

$$D(\vec{p} - \vec{p}_1 \Omega - \Omega_1) = -|g_{\vec{p}\vec{p}_1}|^2 \frac{\omega_0^2}{(\Omega - \Omega_1)^2 + \omega_0^2} = |g_{\vec{p}\vec{p}_1}|^2 D(\Omega \Omega_1).$$
(3)

Investigations of the influence of strong electron correlations on electron - phonon or electron- impurity interaction [7, 8] show that as the exchange momentum q increases, these quantities increase weakly with the next dramatic drop. These results allow one to get an approximate form of the above - mentioned quantities

$$\left|g_{\vec{p}\vec{p}_{1}}\right|^{2} = \left(\frac{2k_{F}}{q_{c}}\right)^{2} g^{2}\theta\left(q_{c} - |\vec{p} - \vec{p}_{1}|\right),$$

$$V_{i}\left(\vec{p} - \vec{p}_{1}\right)V_{j}\left(\vec{p}_{1} - \vec{p}\right) = V_{i}V_{j}\left(\frac{2k_{F}}{q_{c1}}\right)^{2}\theta\left(q_{c1} - |\vec{p} - \vec{p}_{1}|\right).$$
(4)

In order to derive analytical expression for vertex functions we consider the weak coupling approximation  $T_c / \omega_0 \ll 1$  and I / E, I /  $\omega_0 \ll 1$  and use the method of direct calculation [4], [9].

Generalizing the method of Grin functions and mass operators determinations [2], [3] for a case  $\langle S_Z \rangle \neq 0$  and also the method of calculation of superconducting transition temperature in adiabatic systems [10], we obtain the equation:

$$\ln \frac{T_{c}}{T_{c0}} = \Psi\left(\frac{1}{2}\right) - \frac{1}{2} \left[1 - \frac{\overline{b}}{\sqrt{\overline{b}^{2} - I^{2}}}\right] \Psi\left(\frac{1}{2} + \rho_{+}\right) - \frac{1}{2} \left[1 + \frac{\overline{b}}{\sqrt{\overline{b}^{2} - I^{2}}}\right] \Psi\left(\frac{1}{2} + \rho_{-}\right), \quad (5)$$

where  $T_{C0}$  is the temperature of superconducting transition for the pure nonadiabatic system:

$$T_{C0} = \frac{2\omega_{0}\gamma}{\sqrt{e}(1+m)\pi} \exp\frac{1}{2} \left(\frac{m}{m+1}\right) \exp\left(-\frac{Z}{\lambda_{\Delta}}\right), \qquad (6)$$
  
$$\lambda_{\Delta} = \lambda \left[1+2\lambda P_{V}^{0}\left(Q_{c} \ 0 \ \omega_{0}\right) + \lambda P_{c}^{0}\left(Q_{c} \ 0 \ \omega_{0}\right)\right], \qquad \lambda_{z} = \lambda \left[1+\lambda P_{V}^{0}\left(Q_{c} \ 0 \ \omega_{0}\right)\right], \qquad (7)$$

$$Z = 1 + \lambda_z \frac{1}{1+m}, \qquad m = \frac{2\omega_0}{E}, \qquad Q_c = \frac{q_c}{2K_E}.$$

Here  $P_v^0$  and  $P_c^0$  are vertex and crossing functions for pure system.  $\Psi$  is Euler's psifunction, m is Migdal's parameter,  $\rho_{\pm}$  are parameters of impurity scattering, determined by relationships

$$\rho_{\pm} = \frac{1}{Z} \frac{\left[\overline{a} + \sqrt{\overline{b} - I^{2}}\right]}{2\pi T_{c}}, \qquad \overline{a} = \frac{2}{3} \overline{\Gamma}_{S0} + \overline{\Gamma}_{ex} S(S+1) + \overline{\Gamma}_{ex} \langle S_{z}^{2} \rangle;$$
  
$$\overline{b} = \frac{2}{3} \overline{\Gamma}_{S0} - \overline{\Gamma}_{ex} \left( \langle S_{x}^{2} \rangle + \langle S_{y}^{2} \rangle \right), \qquad \overline{\Gamma} = \Gamma \left[ 1 + 2\lambda P_{v} \left( Q_{c} 00 \right) \right], \qquad (8)$$

 $\overline{\Gamma}_{s_0}$  is damping caused by the spin - orbital interaction :

$$\overline{\Gamma}_{S0} = \Gamma_{S0} \left[ 1 + 2\lambda P_V \left( Q_c 00 \right) \right]; \qquad \Gamma_{S0} = \pi N_0 c_{S0} V_{S0}^2, \qquad I = c V_2 \left( 0 \right) \left\langle S_z \right\rangle, \tag{9}$$
the concentration of non-magnetic impurity  $V_z$  is the potential of impurity scattering

 $c_{S0}$  is the concentration of nonmagnetic impurity,  $V_{S0}$  is the potential of impurity scattering.

Equation (5) describes the superconducting transition temperature in the phase of ferromagnetic arrangement of impurity's atoms and attributes the paramagnetic effect of internal field to the influence of electron scattering on the impurity atoms. By the form this equation coincides with the corresponding equation of the adiabatic theory. But for all that the remarkable redetermination of the quantities  $T_{C0}$  and  $\rho_{\pm}$  have taken place. The quantity  $T_{C0}$  increases owing to the effects of non-adiabaticity and can achieve the values inherent to high- $T_{C}$  materials at intermediate values of coupling constant but the parameters of impurity scattering  $\overline{a}$  and  $\overline{b}$  decrease in comparison with the case of the adiabatic systems.

In the limit  $T_C \rightarrow 0$  on the basis of (25) expression for the critical concentration of impurity can be easily derived ( $\Gamma_{cr}$ )

$$\ln\frac{\Gamma_{cr}}{\Gamma_{cr}^{p}} = \ln\frac{2\overline{\Gamma}}{\sqrt{\overline{a}^{2} - \overline{b}^{2} + I^{2}}} + \frac{\overline{b}}{2\sqrt{\overline{b}^{2} - I^{2}}} \ln\frac{\overline{a} + \sqrt{\overline{b}^{2} - I^{2}}}{\overline{a} - \sqrt{\overline{b}^{2} - I^{2}}} , \qquad (10)$$

where  $\overline{\Gamma} = \overline{\Gamma}_{ex} S(S+1)$ ,  $\Gamma_{cr}^{p}$  is the critical concentration of impurity in the paramagnetic phase, determined by the relationship:

$$\Gamma_{cr}^{p} = \frac{\pi T_{C0}}{2\gamma f_{c}}; \ f_{c} = f_{c}(m) = \frac{1}{Z} \left[ 1 - 2\lambda \frac{m}{1 + m} \right].$$
(11)

The last formula shows a significant increase of the critical concentration of impurity in non-adiabatic systems at I = 0 than in usual superconductors due to large values of  $T_{C0}$  and  $f_c(m) < 1$ . The temperature of superconducting transition  $T_C$  in the ferromagnetic phase is determined by equation (5) and the critical concentration of impurity by relationships (10).

Besides that, to obtain explicit dependence of  $T_C$  on the concentration of impurity is too difficult a task because we have to know temperature dependence of the quantities  $\langle S_z \rangle$  and  $\langle S_z^2 \rangle$ . In order to obtain qualitative picture how the quantity  $T_C$  behaves in the ferromagnetic phase we are studying the behavior of this quantity near the temperature of magnetic arrangement  $T_k$ , determining the slope of curve  $T_C(\Gamma)$  and values of the critical concentrations of impurity in two limit cases:  $\Gamma_{S0}/\Gamma >>1$  and  $\Gamma_{S0}/\Gamma <<1$ . In order to perform these calculations we approach used at study of the adiabatic systems. We proceed from the statement that the quantity  $T_C$  decreases and the temperature  $T_k$  increases as the concentration of impurity increases. From this point of view the curves  $T_C$  and  $T_k$  as functions of impurity concentration intersects on the phase diagram (T,  $\Gamma$ ) or (temperature, concentration of impurity) at the point (T<sup>\*</sup>,  $\Gamma$ <sup>\*</sup>). Near this point equation (5) can lead to

$$\frac{T_{C} - T^{*}}{T^{*}} = \frac{Y}{Y - 1} \frac{\overline{\Gamma} - \overline{\Gamma}^{*}}{\Gamma^{*}} = \frac{Y}{Y - 1} \frac{\Gamma - \Gamma^{*}}{\Gamma^{*}} , \qquad (12)$$

where

$$Y = \frac{3f_c}{2} \Psi' \left(\frac{1+3f_c}{2}\right) - \frac{15}{2f_c} \frac{1}{\left(S+1\right)^2 + S^2} \left(\frac{1}{2\pi N_0 V_2}\right)^2 \left(1 - \frac{\overline{\Gamma}_{S0}}{\overline{\Gamma}^*}\right)^{-1} \times \left\{\Psi' \left(\frac{1+3f_c}{2}\right) + \frac{1}{f_c} \left(1 - \frac{\overline{\Gamma}_{S0}}{\overline{\Gamma}^*}\right)^{-1} \times \left[\Psi\left(\frac{1}{2} + \frac{f_c}{2}\left(1 + \frac{2\overline{\Gamma}_{S0}}{\overline{\Gamma}^*}\right)\right) - \Psi\left(\frac{1+3f_c}{2}\right)\right]\right\}.$$
(13)

The value of the quantity  $T_c$  in the ferromagnetic phase near  $\Gamma^*$  depends on the parameters  $\Gamma_{S0} / \Gamma$ ,  $V_2$ ,  $N_0$  and  $f_c$  (m). Effects of non-adiabaticity in this formula are revealed in  $f_c$  (m) < 1 at nonzero Migdal's parameter (m  $\neq$  0). At m = 0  $f_c$  (m) = 1 we obtain results of adiabatic theory for the case of isotropic scattering of impurity. We consider the most interesting case: strong spin-orbital interaction ( $\Gamma_{S0} / \Gamma >> 1$ ). In this limit we derive

$$Y = \left\{ \frac{3f_c}{2} + \frac{15S(S+1)}{2f_c \left[ \left( S+1 \right)^2 + S^2 \right]} \left( \frac{1}{2\pi N_0 V_2} \right)^2 \frac{\Gamma}{\Gamma_{S0}} \right\} \Psi' \left( \frac{1+3f_c}{2} \right).$$
(14)

On the basis of (10) we obtain also expressions for the critical concentration of impurity in the ferromagnetic phase for the  $\Gamma_{s0} / \Gamma >> 1$ . This expression has the following form

$$\ln \frac{\Gamma_{cr}}{\Gamma_{cr}^{p}} \approx -\frac{3\overline{\Gamma}_{cr}}{2\overline{\Gamma}_{S0}k^{2}(S+1)^{2}} \left[ 1 + \frac{\overline{\Gamma}_{cr}}{\frac{2}{3}\overline{\Gamma}_{S0}} \ln \frac{\overline{\Gamma}_{cr}}{\frac{2}{3}\overline{\Gamma}_{S0}} \right],$$
(15)

where  $k = 2 \pi N_0 V_2 f_c Z$ .

We obtain  $\Gamma_{cr} < \Gamma_{cr}^{P}$  and with increase of  $\Gamma_{S0}$  the critical concentration coincides with the critical concentration  $\Gamma_{cr}^{P}$  in the paramagnetic phase. The same procedure like in the case of the adiabatic systems can be performed for the case of low values of the spin orbital ( $\Gamma_{S0} / \Gamma <<1$ ). In this case in non-adiabatic system  $\Gamma_{cr} << \Gamma_{cr}^{P}$  but is greater than the same value in usual superconductors.

To determine Curie's  $T_k$  temperature we calculate spin density of electron  $\langle \sigma_z \rangle$  determined by the relationship:

$$\left\langle \sigma_{z} \right\rangle = \frac{1}{\beta V} \sum_{\vec{p} \Omega} \left[ \overline{G}_{\uparrow\uparrow} \left( \vec{p} \Omega \right) - \overline{G}_{\downarrow\downarrow} \left( \vec{p} \Omega \right) \right]$$
(16)

where  $\overline{G}$  is the complete Green function averaged over chaotically distributed positions of impurity atoms and orientation of their spins.

In result of calculations we obtain:

$$\left\langle \sigma_{z} \right\rangle - \left\langle \sigma_{z} \right\rangle_{n} = -N_{0} i\pi \sum_{\Omega} \left[ \frac{1}{\sqrt{1 + U_{1+}^{-2} + U_{2+}^{-2}}} - \frac{1}{\sqrt{1 + U_{1-}^{-2} + U_{2-}^{-2}}} \right] \varphi \left( \Omega \right) , \qquad (17)$$

where

$$\left\langle \sigma_{z}\right\rangle_{n} = -\frac{2N_{0}I}{Z}$$

 $U_{1\pm}$  and  $U_{2\pm}$  are determined by complex system of equations [5], [6].

We consider behavior of the quantities  $T_k$  near the temperature of superconducting transition  $T_C$ . In the weak coupling approximation ( $\Delta / E \ll 1$ ) and for concentrations of impurity ( $\Gamma / E \ll 1$ ), which is not too large, using the same approach as in the case of adiabatic systems [10] with insignificant improvement in the case of electron-phonon interaction for Curie temperature  $T_k$ , we derive near the intersection point ( $T^*$ ,  $\Gamma^*$ ) the following expression

$$\frac{T_{\kappa} - T^{*}}{T^{*}} = \frac{1 - \alpha \frac{3f_{c}}{2} \Psi'\left(\frac{1}{2} + \frac{3f_{c}}{2}\right)}{1 + \alpha \left[1 - \frac{3f_{c}}{2} \Psi'\left(\frac{1}{2} + \frac{3f_{c}}{2}\right)\right]} \frac{\Gamma - \Gamma^{*}}{\Gamma^{*}} , \qquad (18)$$

where

$$\alpha = \frac{2}{f_c b_1 \left(\frac{3f_c}{2}\right)} \left[ 1 - \frac{\Gamma_{s0}}{\Gamma^*} \right]^{-1} \left\{ \Psi' \left(\frac{1}{2} + \frac{3f_c}{2}\right) + \frac{1}{f_c} \left[ 1 - \frac{\Gamma_{s0}}{\Gamma^*} \right]^{-1} \times \left[ -\Psi \left(\frac{1}{2} + \frac{3f_c}{2}\right) + \Psi \left(\frac{1}{2} + \frac{f_c}{2} + \frac{\Gamma_{s0}}{\Gamma^*} f_c\right) \right] \right\},$$

$$b_1 \left(\frac{3f_c}{2}\right) = -\frac{1}{2} \Psi'' \left(\frac{1}{2} + \frac{3f_c}{2}\right) - \frac{3f_c}{2} \frac{1}{6} \Psi''' \left(\frac{1}{2} + \frac{3f_c}{2}\right).$$
(19)

Formula (18) can possibly allow one to determine  $T_k$  near the superconducting transition temperature  $T_C$  and the slope of the curve  $\left(\frac{d T_k}{d \Gamma}\right)$ . So, we can present the qualitative behavior of  $T_k$  as a function of concentration of impurity in the superconducting phase. The

behavior of  $T_k$  as a function of concentration of impurity in the superconducting phase. The common examination of (12) and (18) allows by an uneasy way to obtain the phase diagram  $(T_C, \Gamma)$ .

The dependence of the temperature of superconducting transition  $T_C$  is given In fig. 1 at the ferromagnetic arrangement as well as of Curie temperature  $T_k$  in superconducting state at different values of Migdal's parameter  $m = 2\omega_0 / E$  for systems large values of spin-orbital interaction ( $\Gamma / \Gamma_{S0} \ll 1$ ). Curves 1 - 3 correspond to  $T_C$  and the curves 1' - 3' correspond to  $T_k$ . We obtain favorable conditions for coexistence of superconductivity and ferromagnetism. We have derived that both the exchange interaction and the spin-orbital interaction lower the «splitting» of Fermi surface by conservation of the spin of electron. The quantities  $T_C$  as a function of concentrations of impurity at given m (m = 0, 1; 1, 0; 0) go to the corresponding curves of paramagnetic phase with the critical concentrations  $\Gamma_{cr} = \Gamma_{cr}^p$ .



Fig.1. The critical temperature  $T_C$  and the temperature of ferromagnetic arrangement  $T_k$  plotted as functions of inverse relaxation time  $\Gamma$  at  $\Gamma_{S0} / \Gamma >> 1$ .

Fig.2. The critical temperature  $T_C$  and  $T_k$  plotted as fuction of inverse relaxation time  $\Gamma$  at  $\Gamma_{S0}/\Gamma <<1$ .

The value  $T_k$  as function of concentration of impurity increases and has the form of curve with convexity down. But from all of that the field with coexistence of superconductivity and ferromagnetism is arisen between the curves of  $T_C$  and  $T_k$ . In this figure m = 0,1 the field with coexistence is bounded by curves 1 and 1<sup>/</sup>, at m = 1 by curves 2 and 2<sup>/</sup>, at m = 0 and by curves 3 and 3<sup>/</sup>. Therefore, maximum field of coexistence corresponds to the value m = 0.1 and is lessened with increase of m. For arbitrary m (0.1 < m < 1) this field is greater than in the case of adiabatic systems (m = 0). The quantities T\* and  $\Gamma$ \* in the non-adiabatic system are greater than in adiabatic systems at different values of m.

Figure 2 corresponds to the case of low values of the spin-orbital interaction  $(\Gamma_{S0}/\Gamma \ll 1)$ . As can be seen from the figure in this case the coexistence of superconductivity and ferromagnetism is possible at low temperatures and small concentrations of impurity. Extent of this field depends greatly on the parameter m. It has minimum value at m = 0 (adiabatic systems), maximum one at m = 0.1, then it decreases with increase of m remaining greater than the field inherent to adiabatic systems.

Such picture is determining by the maximum in  $T_{\rm C}$  dependence on m at the point  $m\approx 0.1.$ 

In fig.1 and fig.2 we show crosshatched region corresponding to the coexistence of superconductivity and ferromagnetism: we have first field between curves 3 and 3' with m = 0 (adiabatic systems), second field between curves 2 and 2' with m = 1 (non-adiabatic systems) and third between curves 1 and 1' with m = 0.1. Due to the nonadiabaticity this field of coexistence expands with increase of concentration of impurity. We observe also increase of the temperature T\* and the concentration of impurity  $\Gamma^*$ , at which the ferromagnetic arrangement arises in non-adiabatic systems in comparison to adiabatic ones.

We make the following conclusions:

1. Upon doping a non-adiabatic system with magnetic impurities, a ferromagnetic spin ordering of impurity ions can set in at low temperatures. In such regions superconductivity

and ferromagnetism coexist. The decisive role is then played by the competition of the following mechanisms: on one band the splitting of the Fermi surfaces by the internal magnetic field destroying superconductivity and on the other hand the exchange and spin-orbital interactions which produce spin-flips and favor the formation of Cooper pairs.

2. The extent of the coexistence region of superconductivity and magnetism on (T, c) phase diagram is determined by the ratio of exchange ( $\Gamma_{ex}$ ) and spin-orbital ( $\Gamma_{S0}$ ) interactions.

For  $\Gamma_{s0} / \Gamma_{ex} \ll 1$  the phase coexistence exists only at very low temperature and impurity concentrations. For  $\Gamma_{s0} / \Gamma_{ex} \gg 1$  the coexistence region is substantially enlarged and the critical concentration coincides with that of a paramagnetic phase.

3. Non-adiabatic effects lead to the increase of the coexistence region of superconductivity and ferromagnetism for the above-mentioned values of the ratio  $\Gamma_{S0}/\Gamma_{ex}$ . In this region the behavior is determined by the Migdal's parameter m: the region is maximal for m ~ 0.1 and for the rest of the interval 0.1 < m < 1 it still remains larger than for adiabatic systems.

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# POLARON STATES AT ARBITRARY COUPLING REGIMES IN RECTANGULAR POTENTIAL WELL

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#### Abstract

We report here a new approach to the confined polaron problem at arbitrary coupling regimes. It is shown, that developed theory permits calculation of polaron energy without use of parabolic potential barriers.

## **1. Introduction**

Modern optoelectronic technologies permit fabrication of low-dimensional structures in which electron is confined within narrow quantum wells. In their fabrication, besides Si and Ga crystals, polaronic compounds of type  $A_3B_5$  and  $A_2B_6$  and alkali-haloid's crystals are widely used. In future it is not inconceivable use of liquid components with great values of permittivity. In this situation redefinition of electron's parameters due to polaronic effect becomes of a great importance. Taking into consideration polaronic states is necessary in all fundamental problems of optoelectronics, like laser emission. luminescence. electroconductivity and others. Final goal of the theoretical investigations in this direction is to find effective methods of calculation of polaronic states and their optimization.

Today we have a great number of publications devoted to polaron effect investigation in different structures. Polaron states at arbitrary coupling regimes were investigated in [1] for the bulk crystals and in [2] for 2D and 1D systems. The polaron ground-state energy and the polaron effective mass were obtained in [3] at arbitrary values of the electron-phonon coupling constant  $\alpha$ . A great interest is shown to more realistic quasi-2D (quantum well), quasi-1D (quantum wire) and quasi-0D (quantum dot) structures. Polarons in a slab of a finite width for the weak coupling regime were considered in [4, 5]. Polarons in a cylindrical quantum wire were considered in [6]. In all the above-mentioned papers, the increase of the polaron ground-state energy and of the effective mass with confinement strengthening was obtained. Thus, polaron effect role increases in nanostructures as compared with 3D systems.

Most of work on polarons is based on Feynman variational theory founded on path integration, which allows one to investigate polaron parameters at arbitrary coupling regime. However Feynman variational method possibilities are strictly confined by the parabolic potentials. In the present paper we are trying to surmount this restriction, extending variational procedure over non-parabolic potentials.

For showing the essence of this new approach we shall simplify the model, although in principle these simplifications are not necessary and we shall not use them in future. Fundamental is that we can use potential wells of different confinements and real phonon spectra.

In this paper we examine a quasi-2D structure – quantum layer with infinite barriers. Electron motion is described by x, y coordinates (in layer's plane) and z coordinate (in the direction perpendicular to layer's plane). We consider that "fictitious" particle moves in

layer's plane and is described only by x, y coordinates. We apply bulk-phonon approximation (3D phonons).

#### 2. Feynman variational theory

The Lagrange function of the polaron problem under consideration has the form

$$L = -\frac{m}{2\hbar^2} \left( \dot{z}_{\tau}^2 + \dot{\rho}_{\tau}^2 \right) - V(z_{\tau}) - \frac{1}{2} \sum_{\vec{k}} \left[ \frac{\dot{q}_k^2}{\hbar^2} + \omega_k^2 q_k^2 \right] + \sum_{\vec{k}} \gamma_k \left( \rho, z \right) q_{\vec{k}} , \qquad (1)$$

where  $\overline{\rho} = (x, y)$  and z are coordinates of an electron,  $q_{\overline{k}}$  are the vibrational normal coordinates for LO phonons of wave vector  $\vec{k}$  with frequency  $\omega_0$ ,  $V(z_{\tau})$  is quantum potential well. Amplitudes of the electron-phonon interaction are given by the expression

$$\gamma_{\vec{k}}(\vec{r}) = 2\sqrt{\frac{2\pi\hbar\omega_0\alpha_F}{V}} \frac{\omega_0}{k} \left(\frac{\hbar}{2m\omega_0}\right)^{1/4} e^{i\vec{k}\vec{r}} = \gamma_{\vec{k}}^0 e^{i\vec{k}\vec{r}}, \qquad (2)$$

where the Fröhlich coupling constant is

$$\alpha_F = \frac{e^2}{2\hbar\omega_0} \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0}\right) \left(\frac{2m\omega_0}{\hbar}\right)^{1/2},\tag{3}$$

 $\varepsilon_{\infty}$  and  $\varepsilon_0$  are high-frequency and static dielectric constants, respectively.

According to Feynman variational theory (FVT), the electron-phonon interaction is simulated by an elastic interaction of the electron with a "fictitious" particle of  $M_f$  mass. The trial Lagrange function is written as

$$L_{0} = -\frac{m\dot{\rho}^{2}}{2\hbar^{2}} - \frac{M_{f}\dot{R}^{2}}{2\hbar^{2}} - \frac{M_{f}\omega_{f}^{2}}{2} \left(\vec{\rho} - \vec{R}\right)^{2} - \frac{m\dot{z}^{2}}{2\hbar^{2}} - V_{0}(z), \qquad (4)$$

where  $M_f$  and  $\omega_f$  are the variational parameters, R(x, y) are the coordinates of a "fictitious" particle,  $V_0(z)$  is approximating quantum well potential function that includes, in principle, polaron effect and therefore depends on variational parameters.

We shall consider motion in x, y plane using standard Feynman approach. Following the path-integral method, statistical sum is written as

$$Z = Sp \int e^{S} D\vec{r} Dq = Sp \int e^{S_0} D\vec{r} Dq \frac{Sp \int e^{S-S_0} D\vec{r} Dq}{Sp \int e^{S_0} D\vec{r} Dq} = Z_0 \left\langle e^{S-S_0} \right\rangle_{S_0},$$
(5)

where

**f** a

and

$$Z_0 = Sp \int e^{S_0} D\vec{r} Dq , \qquad (6)$$

$$\left\langle F[\vec{r},q]\right\rangle_{S_0} = \frac{Sp\int F[\vec{r},q]e^{S_0}D\vec{r}Dq}{Sp\int e^{S_0}D\vec{r}Dq}$$

Using Jensen-Feynman inequality

$$\left\langle e^{S}\right\rangle_{S_{0}} \geq e^{\left\langle S\right\rangle_{S_{0}}},$$
(7)

from Eqs. (5) and (7) we find

$$Sp\int e^{S}D\vec{r}Dq \geq Z_{0}e^{\langle S-S_{0}\rangle}$$
(8)

Finding the logarithm of Eq. (7) we obtain

$$\ln Z \ge \ln Z_0 + \left\langle S[\vec{r}] - S_0[\rho, z] \right\rangle_{S_0}.$$
<sup>(9)</sup>

Thus, statistical sum is given by Eq. (9) where  $Z_0$  is a statistical sum of a system with Lagrangian  $L_0$ , S and  $S_0$  are the exact and trial electron action functionals obtained as a result of the elimination of the phonon coordinates and the coordinates of the "fictitious" particle, respectively.

Path integral with action  $S_0$  can be obtained accurately

$$Sp\int e^{S_0[\rho,R,z]}D\vec{\rho}D\vec{R}Dz = \frac{L^2m\alpha^2}{2\pi\hbar^2\lambda} \cdot \left(2 \quad sh\frac{\lambda\hbar\nu}{2}\right)^{-2}Sp\int e^{S_0[z]}Dz ,$$

where

$$\alpha^2 = \frac{M_f + m}{m}, \quad v = \alpha^2 \omega_f, \quad \lambda \equiv 1/T,$$

and

$$Sp\int e^{S_0[z]}Dz = Sp\int \exp\left(\int_0^{\lambda} \left[-\frac{m\dot{z}_{\tau}^2}{2\hbar^2} - V_0(z_{\tau})\right]Dz\right) = \sum_n e^{-\lambda E_n}$$

Here  $E_n$  are the eigenvalues of the Hamiltonian derived from  $L_0(z)$ . In case of low temperatures  $(T \to 0)$ ,  $\lambda \to \infty$ 

$$Sp\int e^{S_0[z]}Dz = e^{-\lambda E_0},$$

where  $E_0$  is the ground state of an electron in  $V_0(z)$  potential. As a result we obtain

$$\ln Z_0 = \ln \left[ \frac{L^2 m \alpha^2}{2\pi \hbar^2 \lambda} \cdot \frac{1}{\left(2 s h \frac{\lambda \hbar v}{2}\right)^2} \right] - \lambda E_0.$$

In order to derive  $S_0[\vec{r}]$  it is necessary to integrate  $Z_0 = Sp \int e^{S_0[\vec{r},R]} D\rho Dz D\vec{R}$  by paths *R* of the "fictitious" particle. Having integrated we obtain

$$S_{0}[\vec{\rho},z] = \int_{0}^{\lambda} \left[ -\frac{m\dot{\rho}^{2}}{2\hbar^{2}} - \frac{M_{f}\omega_{f}^{2}\rho_{\tau}^{2}}{2} \right] d\tau + \int_{0}^{\lambda} \left[ -\frac{m\dot{z}^{2}}{2\hbar^{2}} - V_{0}(z_{\tau}) \right] d\tau + \Phi_{0}[\rho_{\sigma},\rho_{\tau}] - 2\ln\left[ 2sh\frac{\lambda\hbar\omega_{f}}{2} \right],$$

where

$$\Phi_{0}[\rho_{\sigma},\rho_{\tau}] = \frac{\hbar M_{f}\omega_{f}^{3}}{4} \int_{0}^{\lambda} \vec{\rho}_{\tau}, \vec{\rho}_{\sigma} \frac{ch[\hbar\omega_{f}(|\tau-\sigma|-\lambda/2)]}{sh(\lambda\hbar\omega_{f}/2)}.$$

Functional  $S[\vec{r}]$  could be found integrating by path the phonons  $q_k(\tau)$ 

$$S[\vec{\rho}, z] = \int_{0}^{\lambda} \left[ -\frac{m\dot{\rho}^{2}}{2\hbar^{2}} - -\frac{m\dot{z}^{2}}{2\hbar^{2}} - V(z) \right] d\tau + \Phi\left[\vec{r}_{\tau}, \vec{r}_{\rho}\right].$$

Here

$$\Phi\left[\vec{r}_{\tau},\vec{r}_{\rho}\right] = \sum_{\vec{k}} \Phi_{k}\left[\vec{r}_{\tau},\vec{r}_{\rho}\right],$$

$$\Phi_{k}\left[\vec{r}_{\sigma},\vec{r}_{\tau}\right] = \frac{\hbar}{4\omega_{k}} \left(\gamma_{k}^{0}\right)^{2} \int_{0}^{\lambda} e^{i\vec{k}(\vec{r}_{\tau}-\vec{r}_{\sigma})} \frac{ch\left[\hbar\omega_{\vec{k}}\left(|\tau-\sigma|-\lambda/2\right)\right]}{sh\left(\lambda\hbar\omega_{\vec{k}}/2\right)} d\tau d\sigma.$$

$$\langle \Phi_k \left[ \vec{r}_{\sigma}, \vec{r}_{\tau} \right] \rangle_{S_0} = \frac{\hbar}{4\omega_k} \left( \gamma_k^0 \right)^2 \int_0^{\lambda} \langle e^{i\vec{\eta}(\vec{\rho}_{\tau} - \rho_{\sigma})} \rangle_{S_0[\rho]} \frac{ch \left[ \hbar \omega_{\vec{k}} \left( \left| \tau - \sigma \right| - \lambda/2 \right) \right]}{sh \left( \lambda \hbar \omega_{\vec{k}}/2 \right)} \langle e^{ik(z_{\tau} - z_{\sigma})} \rangle_{S_0[z]} d\tau d\sigma .$$

A particular feature of our new approach consists in the integral calculation method by z paths. Due to a non-parabolic potential well in  $L_0(z)$ , there are no standard representations for output (exact) calculations of

$$\left\langle e^{i\kappa(z_{\tau}-z_{\sigma})}\right\rangle_{S_{0}} \equiv \frac{Sp\int e^{i\kappa(z_{\tau}-z_{\sigma})} e^{S_{0}[z]} Dz}{Sp\int e^{S_{0}[z]} Dz}.$$

We shall make use of transition amplitude representation for a time-independent Hamiltonian, suitable at any shape of potential well, using  $\psi_n(z)$  eigenfunctions of trial Hamiltonian

$$\int_{z_{\sigma}}^{z_{\tau}} e^{S_0[z_{\tau'}]} Dz_{\tau'} = K_0[z_{\tau},\tau; \ z_{\sigma},\sigma] = \sum_n \psi_n(z_{\tau}) \ \psi_n^*(z_{\sigma}) e^{-(\tau-\sigma) E_n} .$$
(10)

By  $\tau$  and  $\sigma$  points  $\lambda - 0$  interval is divided into three parts  $\lambda - \tau$ ,  $\tau - \sigma$  and  $\sigma - 0$ , and on each of them electron moves in a potential well without interacting with phonons and can be described by amplitude of transition  $K_0[z_{\tau},\tau;z_{\sigma},\sigma]$  (10), determined by that potential well. Interaction with phonons occurs in points of time  $\tau$  and  $\sigma$ .

Convolving path integrals on each of these segments in transition amplitudes, and integrating by  $z_0$  and  $z_{\lambda}$  one can obtain

$$\left\langle e^{i\kappa(z_{\tau}-z_{\sigma})} \right\rangle_{S_{0}} = \int \delta(z_{\lambda}-z_{0}) dz_{\lambda} dz_{0} \int dz_{\tau} dz_{\sigma} \times \\ \left( \sum_{m} \psi_{m}(z_{\lambda}) \psi_{m}^{*}(z_{\tau}) e^{-(\lambda-\tau)E_{m}} \right) \left( \sum_{n} \psi_{n}(z_{\tau}) \psi_{n}^{*}(z_{\sigma}) e^{-(\tau-\sigma)E_{n}} \right) \times \\ \sum_{l} \psi_{l}(z_{\sigma}) \psi_{l}^{*}(z_{0}) e^{-\sigma E_{l}} e^{i\kappa(z_{\tau}-z_{\sigma})} \left/ \int e^{S_{0}} Dz = \\ \sum_{n} \left| \left\langle \psi_{n}^{*}(z_{\tau}) \right| e^{i\kappa z_{\tau}} \left| \psi_{0}(z_{\tau}) \right\rangle \right|^{2} e^{-(\tau-\sigma)(E_{n}-E_{0})}$$

$$(11)$$

Wave functions  $\psi_n$  are here the eigenfunctions, and  $E_n$  - eigenvalues of the Schrödinger equation with a variational potential

$$\left(\frac{p_z^2}{2m} + V_0(z)\right)\psi_n = E_n\psi_n.$$

We shall choose a potential well with infinite barriers

$$V(z) = \begin{cases} 0, \ |z| \le L/2; \\ \infty, \ |z| \ge L/2. \end{cases}$$

Under such conditions polaron effect couldn't influence the shape and the height of potential well, therefore  $V(z) = V_0(z)$ . As a result, we obtain

$$\left\langle S-S_{0}\right\rangle_{S_{0}}=\left\langle \Phi\left[\vec{r}_{\sigma},\vec{r}_{\tau}\right]\right\rangle_{S_{0}}-\left\langle \Phi_{0}\left[\vec{r}_{\sigma},\vec{r}_{\tau}\right]\right\rangle_{S_{0}}+\frac{M_{f}\omega_{f}^{2}}{2}\int_{0}^{\lambda}\left\langle \rho_{\tau}\right\rangle^{2} d\tau+2\ln\left[2sh\frac{\lambda\hbar\omega_{f}}{2}\right].$$

Using the following thermodynamic formula

$$E = -\frac{\partial}{\partial \lambda} \ln Z ,$$

in case of  $\lambda \rightarrow 0$ , polaron energy is found to be

$$E = \int \psi_{0}^{*} \hat{H}(z) \psi_{0} dz + \frac{h\nu}{2} \left( 1 - \frac{1}{\alpha} \right)^{2} - \frac{\hbar}{2\omega_{0}} \sum_{\vec{k}} \left( \gamma_{\vec{k}}^{0} \right)^{2} \sum_{n} \left| \left\langle \psi_{n} \right| e^{i\kappa z} \left| \psi_{0} \right\rangle \right|^{2} \int_{0}^{\infty} d\tau \, e^{-(E_{n} - E_{0} + \hbar\omega_{0})\tau} e^{-\eta^{2} A(\tau)},$$
(12)

where

$$\gamma_{\bar{k}}^{0} = 2\sqrt{\frac{2\pi\hbar\omega_{0}\alpha_{F}}{V}}\frac{\omega_{0}}{k}\left(\frac{\hbar}{2m\omega_{0}}\right)^{1/2},$$

and

$$A(\tau) = \frac{\hbar^2 a_1}{2m} \tau + \frac{\hbar a_2}{2m\nu} \left( 1 - e^{-\hbar\nu\tau} \right), \ \left( a_1 = 1/\alpha^2, \ a_2 = 1 - 1/\alpha^2 \right).$$

## 3. Analytical analysis

We shall turn to the non-dimensional variables. For the energy we have  $\varepsilon = \frac{E}{\hbar\omega_0}$ . For coordinates and variational parameters  $\overline{z} = \frac{z}{R_p}$ ,  $\overline{\kappa}_z = \kappa_z R_p$ ,  $\overline{\eta} = \eta R_p$ ,  $\overline{v} = \frac{v}{\omega_0}$  and  $t = \hbar\omega_0 \tau$ .

Dimensionless formula of energy is

$$\mathcal{E}(\alpha, \overline{\nu}, \alpha_F) = \mathcal{E}_0 + \frac{\overline{\nu}}{2} \left( 1 - \frac{1}{\alpha} \right)^2 + \mathcal{E}_{e-ph}(\alpha, \overline{\nu}, \alpha_F), \qquad (13)$$

Where electron-phonon part has the form

$$\mathcal{E}_{e-ph} = -\frac{\alpha_F}{\pi} \sum_{n=0}^{\infty} \int_{-\infty}^{\infty} \left| \left\langle \psi_n \left| e^{i\overline{\kappa}\,\overline{z}} \left| \psi_0 \right\rangle \right|^2 d\overline{\kappa} \int_{0}^{\infty} e^{-(\varepsilon_n - \varepsilon_0 + 1)t} dt \int_{0}^{\infty} \frac{\overline{\eta}e^{-\overline{\eta}^2 \overline{A}(t)}}{\overline{\eta}^2 + \overline{\kappa}^2} d\overline{\eta} \right|. \tag{14}$$

In (13) and (14) energy depends on non-dimensional variational parameters  $\alpha$  and  $\overline{v}$ , as well as on Fröhlich coupling constant  $\alpha_F$ . Integration variables are also dimensionless. Function  $\overline{A}(t)$  has the form

$$\overline{A}(t) = a_1 t + \frac{\overline{a}_2}{\overline{v}} \left( 1 - e^{-\overline{v}t} \right).$$

Using the well known expressions for energy levels and eigenfunctions for a particle in V(z) potential [8], one can obtain the matrix element  $\langle \psi_n | e^{i\overline{\kappa}\,\overline{z}} | \psi_0 \rangle$  in an explicit form

$$\left\langle \psi_n \left| e^{i\overline{\kappa}\,\overline{z}} \left| \psi_0 \right\rangle \right\rangle = \frac{4}{\overline{L}^2} \left( I_1^2 + I_2^2 \right),$$

where

$$I_{1} = -\frac{4\overline{L}^{2}\pi^{2}n\,\overline{\kappa}\sin^{2}n\pi/2\sin\overline{L}\overline{\kappa}/2}{\left((n-1)\pi - \overline{L}\overline{\kappa}\right)\left(\pi + n\pi - \overline{L}\overline{\kappa}\right)\left((n-1)\pi + \overline{L}\overline{\kappa}\right)\left(\pi + n\pi + \overline{L}\overline{\kappa}\right)},$$
  
$$I_{2} = -\frac{4\overline{L}^{2}\pi^{2}n\,\overline{\kappa}\cos^{2}n\pi/2\cos\overline{L}\overline{\kappa}/2}{\left((n-1)\pi - \overline{L}\overline{\kappa}\right)\left(\pi + n\pi - \overline{L}\overline{\kappa}\right)\left((n-1)\pi + \overline{L}\overline{\kappa}\right)\left(\pi + n\pi + \overline{L}\overline{\kappa}\right)}.$$

In order to calculate the double integral

$$J(\overline{\kappa}^{2}) = \int_{0}^{\infty} e^{-(\varepsilon_{n} - \varepsilon_{0} + 1)t} dt \int_{0}^{\infty} \frac{\overline{\eta} e^{-\overline{\eta}^{2} \overline{A}(t)}}{\overline{\eta}^{2} + \overline{\kappa}^{2}} d\overline{\eta} , \qquad (15)$$

we introduce the notation  $\beta = \varepsilon_n - \varepsilon_0 + 1$  and make the following transformations of variables:  $\overline{\eta} = \overline{\kappa} y$ ,  $x = y^2 \overline{A}(t)$ . Accordingly, (15) takes the form

$$J\left(\overline{\kappa}^{2}\right) = \int_{0}^{\infty} e^{-\beta t} \int_{0}^{\infty} \frac{e^{-\overline{\kappa}^{2} x}}{x + \overline{A}(t)} dx dt .$$
(16)

Taking into account, that asymptotical behavior of  $\overline{A}(t)$  in the explicit form is

$$\overline{A}(t) = a_1 t + \frac{\overline{a}_2}{\overline{v}} \left( 1 - e^{-\overline{v}t} \right) \approx t , \quad (t << 1)$$

we can write  $\overline{A}(t) \equiv t + (\overline{A}(t) - t)$ , and represent

$$\frac{1}{x+\overline{A}(t)} = \frac{1}{x+t} + \left(\frac{1}{x+\overline{A}(t)} - \frac{1}{x+t}\right) = \frac{1}{x+t} - \frac{\overline{A}(t) - t}{(x+t)(x+\overline{A}(t))}.$$
(17)

Since  $\overline{A}'(t) = a_1 + a_2 e^{-\overline{v}t} > 0$ ,  $\overline{A}(t)$  is a monotone increasing function. So, integral (16) using decomposition (17) can be represented in the form

$$J(\bar{\kappa}^{2}) = \frac{1}{2} \int_{0}^{\infty} e^{-\beta t} \int_{0}^{\infty} \frac{e^{-\bar{\kappa}^{2} x}}{x+t} dx dt - \frac{1}{2} \int_{0}^{\infty} e^{-\beta t} \left(\bar{A}(t) - t\right) \int_{0}^{\infty} \frac{e^{-\bar{\kappa}^{2} x}}{(x+t)(x+\bar{A}(t))} dx dt .$$
(18)

The first integral in (18) can be derived in an explicit form and is equal to

$$J_1\left(\overline{\kappa}^2\right) = \frac{1}{2} \int_0^\infty e^{-\beta t} \int_0^\infty \frac{e^{-\overline{\kappa}^2 x}}{x+t} dx dt = \frac{1}{2} \frac{\ln \overline{\kappa}^2 - \ln \beta}{\overline{\kappa}^2 - \beta}.$$
 (19)

As for the second integral in (18)

$$J_2\left(\overline{\kappa}^2\right) = \frac{1}{2} \int_0^\infty e^{-\beta t} \left(\overline{A}(t) - t\right) \int_0^\infty \frac{e^{-\overline{\kappa}^2 x}}{(x+t)(x+\overline{A}(t))} dx dt$$

we notice that it do not have any singularity by  $\bar{\kappa}^2$ . In particular, at  $\beta = 1$  and  $\bar{\kappa}^2 = 0$ 

$$J_2(0) = \frac{1}{2} \int_0^\infty e^{-t} \left( t - \overline{A}(t) \right) \int_0^\infty \frac{dx}{(x+t)(x+\overline{A}(t))} dx dt = \int_0^\infty e^{-t} \ln \frac{t}{\overline{A}(t)} dt \neq 0.$$

It means the uniform convergence of integral by x and we can change the integration order. For numerical calculations it is convenient to represent  $J_2(\overline{\kappa}^2)$  in the following form

$$J_2\left(\overline{\kappa}^2\right) = \frac{1}{2} \int_0^\infty e^{-\overline{\kappa}^2 x} \int_0^\infty \frac{\left(t - \overline{A}(t)\right) e^{-\beta t}}{\left(x + t\right) \left(x + \overline{A}(t)\right)} dt dx \,. \tag{20}$$

As a result we obtain the following expression for  $J(\overline{\kappa}^2)$ 

$$J\left(\overline{\kappa}^{2}\right) = \frac{1}{2} \left( \frac{\ln \overline{\kappa}^{2} - \ln \beta}{\overline{\kappa}^{2} - \beta} - \int_{0}^{\infty} e^{-\overline{\kappa}^{2} x} \int_{0}^{\infty} \frac{\left(t - \overline{A}(t)\right) e^{-\beta t}}{\left(x + t\right) \left(x + \overline{A}(t)\right)} dt dx \right).$$
(21)

Collecting all together, we derive the final form for polaron energy

$$\mathcal{E} = \mathcal{E}_{0} + \frac{\overline{\nu}}{2} \left( 1 - \frac{1}{\alpha} \right)^{2} - 16\alpha_{F} \overline{L}^{2} \pi^{3} \sum_{n=1}^{\infty} n^{2} \int_{-\infty}^{\infty} d\overline{\kappa} \frac{\overline{\kappa}^{2} \left( 1 + (-1)^{n} \cos \overline{\kappa} \overline{L} \right)}{M^{2}} \times \left\{ \frac{\ln \overline{\kappa}^{2} - \ln \beta}{\overline{\kappa}^{2} - \beta} - \int_{0}^{\infty} e^{-\overline{\kappa}^{2} x} \int_{0}^{\infty} \frac{\left( t - \overline{A}(t) \right) e^{-\beta t}}{\left( x + t \right) \left( x + \overline{A}(t) \right)} dt dx \right\}.$$
(22)

The further calculations can be performed only in the numerical form.

# 4. Numerical results and discussions

Results of numerical calculations of polaron energy  $\Delta \varepsilon = \varepsilon - \varepsilon_0$  using (22) are represented in Fig.1. The function  $\Delta \varepsilon (\alpha_F)$  is plotted at different values of well width  $\overline{L}$ . Curves corresponding to 3D and 2D limiting cases are also plotted here. It is clearly seen, that with confinement strengthening, curves are moving away from 3D limit case and draw near 2D limit case.



Fig.1. Dependences  $\Delta \varepsilon(\alpha_F)$  plotted at different values of well width



Fig. 2. Polaron energy dependences in weak-coupling limit.

In the weak-coupling limit, polaron energy is proportional to  $\alpha_F$  for any confinement. But  $\alpha_F$  factor depends on confinement. Polaron energy in weak-coupling limit for finite confinement is obtained using (22) and presented in Fig. 2. Dotted lines are plotted using perturbation theory. Firm lines denote results obtained using formula (22). Comparing these results one can see that for small  $\alpha_F$  they coincide. In the linear approximation formula (22) can be written as  $\Delta \varepsilon = -C(\overline{L})\alpha_F$ . Numerical values of the coefficients of the linear terms are C(1,0) = 1,02, C(0,5) = 1,31, C(0,2) = 1,43. Comparing these values to the one obtained for 2D polarons in weak coupling limit  $\left(\Delta\varepsilon = -\frac{\pi}{2}\alpha_F - 0,06397\alpha_F^2\right)$ , we can clearly see

theirs correct arrangement.

Thus we have: 1) our general formula (22) gives a correct weak-coupling limit; 2) expected dependence of weak-coupling region on confinement strength is obtained. It is observed that as coupling increases, straight-line region for energy shortens depending on coupling constant. It is worth noting the correct order of  $\Delta \varepsilon(\alpha_{E}, \overline{L})$  curves.

#### 5. Conclusions

A new approach to the polaron energy problem at arbitrary coupling regimes is proposed. Coupling energy for a polaron in a rectangular potential well with infinite barriers is calculated at different well widths. Thus, it is shown that developed theory permits calculation of polaron energy without use of parabolic potential barriers, for all electronphonon coupling regimes.

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# PROBLEM OF IMPURITY STATES IN NARROW-GAP IV-VI SEMICONDUCTORS

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Starting from mid-70th, a great deal of both experimental and theoretical efforts has been attracted to the unexplained puzzle of impurity states arising in the IV-VI narrow-gap cubic semiconductors doped with some of the group III elements, and to the unusual effects observed in these materials. We review the experimental results obtained in the field: the electrical activity of impurity centers, persistent photoconductivity and related effects, unusual optical, dielectric and magnetic phenomena. Some of the features of these semiconductors, such as possibility of realization of the semiinsulating state with the persistent photoresponse, possibility of fast quenching of persistent photoconductivity, microwave stimulation of the quantum efficiency up to 100, and some others, have made it possible to construct the far-infrared photodetector with extremely high characteristics. The theoretical models proposed so far to account for the physical picture of the processes involved are discussed in view of the recent advances in the field.

Many of the sensitive photodetecting systems operating in the far infrared wavelength range (20-200)  $\mu$ m are based on germanium or silicon doped with shallow impurities [1]. The highest cutoff wavelength reported  $\lambda_{co} \approx 220 \ \mu$ m corresponds to the uniaxially stressed Ge(Ga) [2].

An alternative possibility for construction of sensitive far-infrared photodetectors is provided by unique features of a narrow-gap semiconductor - indium-doped  $Pb_{1-x}Sn_xTe$ . Exciting results of fundamental research on the group III - doped lead telluride - based alloys [3] provided possibilities for construction of far-infrared photodetectors based on new physical principles [4].

Doping of the lead telluride with indium in amount exceeding concentration of other impurities and defects results in the Fermi level pinning effect [5]. A consequence of this effect is homogenization of electrical properties of the semiconductor. This feature results in almost absolute reproducibility of sample parameters independent of the growth technology. High sample homogeneity gives rise to enhanced carrier mobility reaching  $10^5$ - $10^6$  cm<sup>2</sup>/V·s at low temperatures.

Position of the pinned Fermi level  $E_0$  may be tuned by alloying [6]. It crosses the gap in the tin content range (0.22 < x < 0.28) providing the semiinsulating state of the semiconductor for this range of alloy compositions. Conductivity of material in the semiinsulating state (0.22 < x < 0.28) is defined by activation from the impurity local level  $E_0$ , and therefore the free carrier concentration is very low n,p <  $10^8$  cm<sup>-3</sup> at temperatures T < 10 K. So we have a very unusual situation, when a heavily doped narrow-gap semiconductor with high number of growth defects acts as an almost ideal semiconductor with practically zero background free carrier concentration and very high electrical homogeneity. This makes very attractive the idea to use this material as an infrared photodetector.

External infrared illumination leads to the substantial increment of material conductivity at the temperatures T < 25 K reaching several orders of magnitude [7]. High amplitude of photoresponse at the low temperatures is a consequence of the persistent photoconductivity effect: the photoresponse increases linearly in time providing a kind of «internal integration»

of the incident radiation flux. When the radiation is switched off, the conductivity relaxes very slowly. The characteristic relaxation time  $\tau > 10^4$  s at 4.2 K < T < 10 K. The effect is defined by the specifics of impurity states that form DX-like centers [8].

If sample temperature is so that  $\tau$  is higher that the operation time required, then a photoresistor may operate only if there exists a possibility to return to the initial "darkness" state, i.e. to quench quickly the persistent photoconductivity. The most efficient way of quenching of the persistent photoconductivity in Pb<sub>1-x</sub>Sn<sub>x</sub>Te(In) is application of strong microwave pulses to sample contacts [4]. Using this technique the long-living photoexcited free electrons may be localized for 10 µs. Therefore it is possible to operate in the regime of periodical accumulation and successive fast quenching of photoresponse. Moreover, application of microwave pulses in some special regime results in giant increment of the quantum efficiency up to ~ 100 [4].

A laboratory model of the IR-radiometer based on  $Pb_{1-x}Sn_xTe(In)$  operating in the regime of periodical accumulation and successive fast quenching of the persistent photoconductivity, has been demonstrated in [4]. Despite low sensitivity of the measuring electronics used, the photon flux with  $\lambda = 18 \ \mu m$  detected in [4] was as low as  $N \approx 2 \cdot 10^4 \ s^{-1}$  that corresponds to NEP  $\approx 2 \cdot 10^{-16} \ W$  for the detector area of 0.3.0.2 mm<sup>2</sup> and the operating rate 3 Hz.

Direct comparison of the  $Pb_{0.75}Sn_{0.25}Te(In)$  photodetector, the Si(Sb) BIB structure and the Ge(Ga) photodetector using the same cryogenic equipment and measuring electronics has been performed in [9].The responsivity S<sub>1</sub> of the  $Pb_{0.75}Sn_{0.25}Te(In)$  photodetector at 116 µm was of the order of 10<sup>3</sup> A/W at 40 mV bias, that is by 2-3 orders of magnitude higher than the S<sub>1</sub> value obtained for a state of the art Ge(Ga) photodetector in the same measuring conditions.

The same authors have directly observed persistent photoresponse in the  $Pb_{0.75}Sn_{0.25}Te(In)$  photodetector at the wavelengths of 90 and 116 µm that are considerably longer than the wavelength corresponding to the thermal activation energy of the ground impurity state. Indications exist that the red cutoff wavelength for this photodetector may exceed 220 µm - the highest  $\lambda_{co}$  observed so far. Later this conclusion was confirmed by a direct experiment: the persistent photoresponse has been detected at the wavelengths of 176 and 241 µm [10].

Specifics of impurity states may make very easy construction of a focal-plane array on  $Pb_{1-x}Sn_xTe(In)$ . Local infrared illumination leads to local generation of nonequilibrium free electrons, i.e. the persistent photoconductivity effect is observed only in the illuminated part of the sample, and the photoexcitation does not propagate into the darkened regions [11]. The characteristic time of the excitation propagation is at least more than  $10^4$  s at T = 4.2 K. The spatial characteristic scale is ~ 10 µm.

Therefore the distribution of the radiation exposure over the sample surface reflects in a distribution of the concentration of long-living free electrons. In other words, it is possible to construct a focal plane "continuous" array, in which the signal is internally integrated in every effective element.

Readout technique is a special problem. The approach proposed in [4] seems to be the most promising. Let us consider a thin slice of  $Pb_{1-x}Sn_xTe(In)$  with a semitransparent electrode deposited on one side (Figure 1). The investigated radiation flux illuminates the sample from the same left side in Figure 1. A buffer insulating fluoride layer is deposited on another side of the sample followed by a thin layer of silicon or some other semiconductor with a relatively wide gap, and a second semitransparent electrode. If the sample is

illuminated by a shortwavelength laser from the right side, it is possible to generate a local highly conductive region in the wide-gap semiconductor. If then a bias between the electrodes is applied, the current is defined by the  $Pb_{1-x}Sn_xTe(In)$  sample conductivity in the region of the laser spot, because the thickness of the semiinsulating wide-gap semiconductor layer is be much less in this point. Another advantage of such a readout technique is heavy damping of the dark current in such a structure. It is analogous to certain extent to the ideas involved in BIB structures. If the recombination rate in the wide-gap semiconductor is high enough, it is easy to reconstruct the conductivity distribution over the  $Pb_{1-x}Sn_xTe(In)$  sample simply by scanning the laser beam over the structure surface and by measuring the respective current. Unfortunately this idea is not realized in practice so far.



**Fig.1.** Device for readout of information from the "continuous" focal-plane array on  $Pb_{1-x}Sn_xTe(In)$ . 1 - semitransparent electrodes, 2 - active  $Pb_{1-x}Sn_xTe(In)$  layer, 3 - fluoride buffer layer, 4 - layer of a silicon (or other semiconductor with a relatively wide gap), 5 - short-wavelength laser, 6 - incident infrared radiation flux [4].

High radiation hardness is one more advantage of the photodetectors based on  $Pb_{1-x}Sn_xTe(In)$ . This is a consequence of a very high density of impurity states (~  $10^{18} - 10^{19}$  cm<sup>-3</sup>) that pin the Fermi level. The fast electron irradiation with fluencies up to  $10^{17}-10^{18}$  cm<sup>-2</sup> does not affect the photoresponse [12]. This value is at least by 4 orders of magnitude higher than for Hg<sub>1-x</sub>Cd<sub>x</sub>Te, doped Ge and Si.

In summary, application of the lead-tin tellurides doped with the group III impurities as base elements for the infrared photodetectors gives a challenging opportunity to produce universal and sensitive systems. They have a number of advantageous features that allow them to compete successfully with the existing analogs: internal accumulation of the incident radiation flux, possibility of effective fast quenching of an accumulated signal, microwave stimulation of the quantum efficiency up to  $10^2$ , possibility of realization of a "continuous" focal-plane array, possibility of application of a new readout technique, high radiation hardness. In our opinion, these features make the Pb<sub>1-x</sub>Sn<sub>x</sub>Te(In)-based photodetectors ideal for the space-borne applications, for example, in the infrared astronomy.

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# OPTICAL PROPERTIES OF LANTHANIDE-STRONTIUM FLUORIDE SOLID SOLUTIONS

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# Abstract

The results of the refraction study of two-component solid solution single crystals grown on the basis of rare-earth element (REE) fluorides with different content of strontium fluoride ( $R_{1-x}Sr_xF_{3-x}$ , where R = La, *Ce*, *Pr*, *Nd*;  $0 \le x \le 0,15$ ) are presented. Experimentally obtained values of refractive indices and density have given the possibility to calculate some refraction characteristics of the crystals investigated: molar (Lorenz–Lorentz) refraction, polarizability, molar volume, and to analyze all the data obtained in two directions: with the increase of  $SrF_2$  content *x* for each binary system and according to the REE atomic number for one and the same *x*.

## 1. Introduction

The wide use of fluoride materials in scientific experiments and modern technologies set up the problem of searching for the possibility of the fluoride-crystal characteristic variation. It was found that this problem can be successfully solved by using the multicomponent fluoride systems instead of single-component ones.

## 2. Experiments and data processing

Our work is just devoted to the investigation of the physical properties (optical characteristics and density) of such complex crystals. The objects of our study were the solid solutions of the  $RF_3$ - $SrF_2$  (R – rare-earth elements (REE)) binary systems. The  $R_{1-x}Sr_xF_{3-x}$  ( $R = La, Ce, Pr, Nd; 0 \le x \le 0.15$ ) single crystals with tysonit structure were grown from the melt by the Stockbarger method in the Institute of Crystallography of the Russian Academy of Sciences [1].

The samples for investigations had the form of a cylinder with the diameter of 10 mm and the height of 2-5 mm. The axis of the cylinder practically coincided with the optical axis of the crystal. The crystal density  $\rho$  was measured by hydrostatic weighting method with an accuracy of  $\pm 10^{-3}$  g/cm<sup>3</sup>; the refractive indices  $n_o$ ,  $n_e$  were measured with the help of the Pulfrich refractometer to the nearest  $\pm 10^{-3}$ .

From the experimental data obtained some crystal characteristics were calculated. These ones were the molar volume —  $V_{mol} = M/\rho$  (*M* is the molecular weight of the compound); the number of molecules in the unit volume  $N = N_{Av}/V_{mol}$  ( $N_{Av}$  is the Avogadro number); the Lorenz-Lorentz molecular refraction  $R_{mol}$  and molecular polarizability  $\alpha_{o,e}$ ; the last two

parameters were obtained with the help of the formula

$$R_{mol\ o,e} = \frac{n_{o,e}^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} = \frac{4\pi}{3} \cdot N_{Av} \cdot \alpha_{o,e}.$$
 Here  $n = (2n_o + n_e)/3$  is the average refractive index of

the medium and  $\alpha_{o,e}$  are the polarizability components of the anisotropic molecule.

The experimental data obtained and the refraction parameters calculated were analyzed in two directions: in dependence on the  $SrF_2$  content x for each binary system (composition range) and versus the REE atomic number Z for the crystals with one and the same x (lanthanide series).

## 3. Results and discussion

#### **3.1.** Composition range

Earlier [2,3] we have already obtained the  $n_o$ ,  $n_e$  and  $\rho$  values for the  $La_xSr_{1-x}F_{3-x}$  single crystals as functions of x. All three parameters are linearly decreasing with the x increase. It was revealed that for the  $CeF_3$ - $SrF_2$ ,  $PrF_3$ - $SrF_2$ ,  $NdF_3$ - $SrF_2$  binary systems the regularities of the measured characteristic alterations were maintained.

For all four types of single crystals the tendency of the calculated parameter changes with the x increase are identical (see [2,3]). Firstly, this is the  $\alpha_{o,e}$  decrease in the range of binary system compositions. As to molar volume  $V_{mol}$  and the value of N, these parameters are practically independent of  $SrF_2$  content in the  $R_{1-x}Sr_xF_{3-x}$  single crystals, or change very slightly. Thus, for  $NdF_3$ - $SrF_2$ -system crystals the increase of  $V_{mol}$  is no more than 1-2 % when x varies from 0 to 0.15. For the  $PrF_3$ - $SrF_2$  solid solutions the change of  $V_{mol}$  is yet smaller. The N values of this crystal systems are changed in the same manner. From the above reported it can be concluded that the decrease of refractive indices with x in the composition range is caused only by the decrease of the polarizability.

#### 3.2. Lanthanide series

Having studied the set of the solid-solution crystals with the systematic lanthanide substitution we obtain the possibility to follow the refraction parameter variations versus the rare-earth element (REE) atomic number. Unfortunately we have the fluoride single crystals only with four first elements of lanthanide series, namely La, Ce, Pr, Nd. The second component of solid solution in all cases was  $SrF_2$  as it was already mentioned.



Fig. 1. Density  $\rho$  of the  $R_{1-x}Sr_xF_{3-x}$  single crystals as functions of the REE atomic number Z(R) at x = 0 (1); 0.05 (2) and 0.10 (3) The experimental values of density  $\rho$  and of refractive index  $n_o$  of the crystals under study with  $SrF_2$  contents equal to 0, 5 and 10 mol.% are presented in fig. 1 ( $\rho$ ) and fig. 2 ( $n_o$ ). As it can be seen the density of all compounds is practically linearly increasing according to



REE atomic number Z. This increase is caused evidently by the REE molecular weight rise.

We observe that the refractive index in lanthanide series behaves in a different way: at first the value of  $n_o$  (and  $n_e$  also) increases and then (at R=Pr) stops its increase. The refractive index is a complex function of several physical parameters, but the main ones are the number N of polarizing particles, that is the number of  $R_{1-x}Sr_xF_{3-x}$ -molecules in the unit volume, and their polarizability  $\alpha$ .

The value of *N*, as it was already mentioned, was calculated from the molar volume magnitude. Within each binary system the value of  $V_{mol}$  remains approximately constant, i.e. it does not noticeably depend on the  $SrF_2$  content *x* in the compound. But in REE series  $V_{mol}$  is decreasing, namely for the single crystals with R = La, *Ce*, *Pr*, *Nd* the molar volume  $V_{mol} = 33.00, 32.20, 31.65, 31.10 \text{ cm}^3$ , consequently. The *N* value change with REE atomic number is demonstrated in fig. 3.



It is necessary to note that the invariability of the molar volume  $V_{mol}$  with x takes place

exactly only for the crystals of two systems: with R = La and Ce. For crystals with R = Pr and Nd such independence of  $SrF_2$  content x is disturbed. However, these deviations are so slight that they cannot distort the common image of  $V_{mol}$  and N variations in the lanthanide series for the binary systems, studied in this work.

The polarizability  $\alpha$  of the  $R_{1-x}Sr_xF_{3-x}$  molecule is monotonically decreasing with REE atomic number increase for all values of x (fig. 3). Such a change of  $\alpha$  is caused by the decrease of the polarizability of trivalent ion  $R^{3+}$  [4] with the REE atomic number. This behavior, in turn, is conditioned by the well known effect of the lanthanide contraction.

Thus, two parameters — N and  $\alpha$ , which, finally, determine the variation of refractive index in the REE series are changing in two contrary directions: N is increasing and  $\alpha$  is decreasing with Z increase. Namely these competing tendencies define the nonmonotonic variation of the  $R_{1-x}Sr_xF_{3-x}$  single-crystal refractive indices with the REE atomic number. Formerly in [5] it was reported about the change of optical parameters of *R*-*Na*-fluoride crystals with hexagonal structure. The results of the present work do not contradict the character of the  $n_{o,e}$  change for the  $Na_{0.4}R_{0.6}F_{2.2}$  single crystals, where *R* in given case [5] is a REE-ion of the second part of the lanthanide series from  $Dy^{3+}$  to  $Lu^{3+}$ .

## 4. Conclusion

Thus, the analysis of the refractive index behavior in the  $R_{1-x}Sr_xF_{3-x}$  single crystals carried out both for x-dependence (with the invariable R) and depending on R (when x = const.), reveals some refraction peculiarities for these complex compounds.

The effect of lanthanide contraction (inherent only to the members of the REE series) results finally in a complex character of the refractive index variation of the two-component systems under study. This effect is responsible also for the rarely found antibateness in the change of the density  $\rho$  and refractive index *n* of the solid solution single crystals with respect to the REE atomic number. In practice, the set of data presented extends the possibility of the searching of the materials with the performance characteristics required.

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# INFLUENCE OF HIGH-TEMPERATURE TREATMENT IN NITROGEN ATMOSPHERE ON PHOTOLUMINESCENCE OF ZnSe SINGLE CRYSTALS

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The present paper is devoted to the investigation of photoluminescence (PL) spectra of ZnSe crystals annealed at high-temperature in nitrogen atmosphere. The pressure of nitrogen atmosphere was varied from 2 up to 16 atm. The influence of the presence of zinc vapour in the annealing medium on PL spectra is also discussed. The zinc vapour density corresponds to the saturated vapour density at the annealing temperature of 1050°C.

# 1. Experimental conditions

The doping of ZnSe crystals was carried out in the process of crystal annealing at the temperature of  $1050^{\circ}$ C during 50 hours in quartz ampoules of about 5 cm<sup>3</sup> volume. Ampoules were evacuated up to the pressure of  $4 \cdot 10^{-4}$  torr, warmed at the temperature about 300°C during 10 minute and then filled with nitrogen. The nitrogen atmosphere was obtained from the liquid nitrogen vapour of technical purity; the pressure was controlled by both manometer and ampoule temperature. The nitrogen vapour was purified of oxygen using the fine copper deposited on a silica gel. The length of the tube filled with copper was about 25 cm; its inside diameter was about 8 mm. During the process of nitrogen vapour passing, the temperature of copper was equal to 200°C. After the purification, the nitrogen vapour was drained in a coil pipe cooled by the liquid nitrogen.

The rectangular samples, the volume of which was equal to  $20\div30 \text{ mm}^3$ , were treated in K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>: H<sub>2</sub>SO<sub>4</sub> and Br: CH<sub>3</sub>OH solutions and boiled in NaOH solution before the loading in the ampoule. The mass of zinc loaded in the ampoules for the annealing in Zn vapour was the same, equal to 200 mg.

Luminescence was excited by radiation of nitrogen impulse laser with 337.1 nm wavelength. The PL spectra in the wavelength range from 430 nm to 1002 nm were studied by means of a monochromator with reciprocal dispersion of 1.4 nm/mm. The investigations were carried out in the temperature range from 88K to 350K.

## 2. Experimental results

The PL intensity for the as-grown ZnSe crystal is rather weak for the whole investigated wavelength region (Fig. 1, curve 1). The edge PL band with a maximum at 447.0 nm (2.779 eV) and a half-width of 42 meV and less-intensive bands of long-wave (630 nm, 1.971 eV) and infra-red (IR) (894 nm, 1.389 eV) luminescence are observed in the PL spectrum at 100K.

The annealing of the as-grown sample in vacuum at 1050°C during 50 hours results in an increase of the edge and IR PL intensity and a slight shift of these PL bands towards longwavelengths (Fig. 1, curve 2). A slight asymmetry of the edge PL band appears too. The temperature dependence of the edge PL intensity for the vacuum-annealed sample is characterized by two linear slopes, which correspond to the values of temperature quenching activation energy, equal to ~ 20 and 100 meV. The same values for the IR PL band are equal to 8 and 25 meV.

The thermal treatment of ZnSe crystal in the nitrogen atmosphere under the pressure of 2 atm does not change essentially the PL spectrum (fig. 1, curve 3). The increase of the annealing medium pressure up to 4 atm leads to both an increase of the luminescence intensity in the whole investigated wavelength region and an essentially shift of the IR PL band towards long wavelengths (Fig. 1, curve 4). The edge PL band becomes narrower (~ 29.5 meV) and more symmetric. The activation energy of temperature quenching for this band is characterized by two values, equal to 12.7 and 81 meV (Fig. 1, inset a, curve 1). The corresponding values for the IR PL band are equal to 12 and 44 meV (Fig. 1, inset b, curve 3).



Fig. 1. PL spectra of ZnSe crystals annealed in the nitrogen atmosphere. T = 100K. Curves: 1 - asgrown; 2 - annealed in vacuum; 3, 4, 5, 6 - annealed in the N<sub>2</sub> atmosphere under the pressure $<math>P(N_2) = 2, 4, 8, 16$  atm, respectively.

Inset: PL band intensity in the maximum versus temperature for: a) edge PL band; b) IR PL band. Curves: 1, 3 – the pressure  $P(N_2) = 4$  atm; 2, 4 –  $P(N_2) = 8$  atm. The increase of the nitrogen pressure up to 8 atm results in the further increase of the edge and IR PL intensity and the further shift of these bands towards long-wavelengths (fig. 1, curve 5). The half-width of the edge PL band increases up to 38 meV and its asymmetry becomes less-marked. The low-temperature value of the temperature quenching activation energy for this band decreases down to 4.9 meV (fig. 1, inset a, curve 2), while the character of the IR band corresponding dependence is practically unchanged (fig. 1, inset b, curve 4).

The edge and IR PL spectra of the sample annealed in the nitrogen atmosphere under the pressure  $P(N_2)=16$  atm practically coincide with the corresponding spectra for the sample annealed at 8 atm (fig. 1, curve 6). The low-temperature value of the temperature quenching activation energy for the edge PL band decreases down to 3,8 meV, while the corresponding value for the IR luminescence does not change essentially.

The difference in the positions of the PL band maxima is the most apparent at the temperatures of 100K and above. At lower temperatures, this difference becomes smaller.

The annealing of the as-grown ZnSe crystal at the temperature of  $1050^{\circ}$ C during 50 hours in the saturated Zn vapour (~3.5 atm) leads to a decrease of PL intensity in the whole investigated wavelength region (fig. 2, curve 1; arbitrary units for the PL intensity in fig. 1 and fig. 2 coincide). The maximum of the edge PL band at 100K is localized at 449.0 nm (2.766 eV), while the maximum of the IR PL band is localized at ~896 nm (~1.386 eV).



Fig. 2. PL spectra of ZnSe crystals annealed in the nitrogen and saturated zinc vapour atmosphere. T = 100K. Curves: 1 - annealed in the atmosphere of saturated zinc vapour P(Zn) = 3.5 atm; 2, 3, 4 - annealed in the nitrogen and saturated zinc vapour atmosphere,  $P(N_2) = 4$ , 8, 16 atm, respectively.

Inset: PL band intensity in the maximum versus temperature for the samples: 1 - annealed in Zn vapour;  $2 - \text{annealed in zinc and nitrogen atmosphere at P(N_2)=16 atm.}$ 

The thermal treatment in the atmosphere of 3.5 atm of Zn and 4 atm of  $N_2$  (the validity of Dalton's law of partial pressures and the weak chemical interaction between molecular nitrogen and zinc are supposed) results in an essential intensity increase of all the PL bands and their shift towards short-wavelengths (fig. 2, curve 2). The temperature quenching of PL intensity in the maximum of the edge PL band is characterized by two values of the activation energy, equal to 8.3 meV and 26 meV (fig. 2, inset, curve 1).

The increase of the nitrogen vapour pressure up to 8 atm (P(Zn) = 3.5 atm) leads to the further increase of PL intensity for all the bands and a weak shift of them towards a long-wavelength region. We can note that the long-wave slope of a "green" luminescence band becomes less steep (fig.2, curve 3).

The increase of the nitrogen vapour pressure from 8 to 16 atm does not lead to an increase of the edge PL intensity, as well as in the case of annealing in the atmosphere of pure nitrogen. The intensity of the visible long-wave luminescence band increases and the long-wave component of this band becomes more prominent. The positions of maxima of the edge and IR PL bands are shifted towards long-wavelengths (fig.2, curve 4). The comparison of the curves of the edge luminescence temperature quenching for the samples annealed in the atmosphere of saturated zinc vapour and the atmosphere of zinc and nitrogen under the pressure  $P(N_2) = 16$  atm shows that the addition of nitrogen in the thermal treatment medium does not change the character of this dependence (fig. 2, inset).

#### 3. Discussion

The relatively large value of the half-width of the edge PL band for the as-grown crystal (about 42 meV) indicates a complex structure of the corresponding band. The position of the edge PL band maximum is in a good agreement with the spectral position of a radiation line of acceptor-bound excitons. These acceptors, which have the energy depth of 300 meV, can be the  $V_{Zn}$  native defects. The centers responsible for the IR radiation can be attributed to the  $(V_{Zn}^{-1}D^{+})^{-}$  associative complexes, which consist of both doubly ionized defects of zinc vacancy and singly ionized shallow uncontrollable donors. As is known, the annealing in vacuum results in an increase of the  $V_{Zn}$  defect concentration. The intensity of the edge and IR luminescence increases after this annealing (fig. 1, curve 2). This fact shows that the radiation attributed to the  $V_{Zn}$  defects dominates in the edge PL spectrum. The annealing in Zn vapour promotes the filling of zinc vacancies with zinc atoms and, as a consequence, leads to a decrease of the edge and IR luminescence intensity (fig. 2, curve 1).

The changes in the edge and IR PL spectra, observed after the thermal treatment of ZnSe crystals in the nitrogen atmosphere (P(Zn)=0), can be explained by both the increase of the concentration of deep  $V_{Zn}$  native defects and the appearance of shallow  $N_{Se}$  acceptors responsible for the shift of the edge PL band towards a long-wavelength region. The concentration of  $N_{Se}$  acceptors increases with increasing nitrogen pressure.

Simultaneous annealing of the crystals in zinc and nitrogen vapours obviously leads to the appearance of several types of the centers, which are responsible not only for a complex structure of the visible long-wave luminescence, but also for relatively high intensity of the edge and IR luminescence. The high intensity of the edge and IR PL bands cannot be stipulated by an increase of  $V_{Zn}$  defects due to the sample annealing in the saturated zinc vapour.
# **EFFECTIVE MASSES OF ELECTRONS IN CADMIUM ARSENIDE**

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#### Abstract

The effective masses of the conductivity electrons were explored within the framework of simplified band model and for cadmium arsenide without the center of symmetry. It appeared that effective masses are distinguished in different spin sub-bands. The energy dependences of the effective masses are nonlinear with the clearly expressed minimum close to the bottom of the band. Anisotropy of the effective masses as the stronger as the less is the energy of carriers. These features are explained by the influencing of the narrow band of heavy electrons, almost degenerated with the bottom of the conductivity band.

# Introduction



Fig. 1. The surfaces of equal energy of the electrons in the cadmium arsenide (the phase without inversion center).  $\epsilon = 0.03 \text{ eV}.$ 

the following compact form:

The low temperature modification of  $Cd_3As_2$  is the purpose of this paper. The phase belongs to spatial group with  $4_1cd(C_{4v}^{12})$  – symmetry, i.e. with no symmetry center.

Nevertheless, it should be noted that real crystals are not so far from cubic symmetry. The ordering process mainly affects the metallic sublattice, whereas the cubic face centered (FCC) sublattice of the anions is left almost undisturbed. The tetragonal distortion of the lattice is rather small:  $\eta = c/2a \le 1,00565$ . Therefore, the tetragonal cell of ordered crystals can be considered as a slightly stretched aggregate of few, almost identical cubic cells [1].

The simplified band model for this approach has been presented earlier in [2] within the framework of the so-called «pseudocubic approximation». The exact dispersion law can be expressed in

$$\gamma(\varepsilon) = f_1(k_x^2 + k_y^2) + f_2k_z^2 \pm 2f_3\sqrt{k_x^2 + k_y^2}, \qquad (1)$$

where

$$\mathbf{f}_{1} = \mathbf{P}^{2} \left( \left( \varepsilon + \Delta / 3 \right) \left( \varepsilon + \delta + \Delta / 3 \right) - \eta^{-2} \Delta^{2} / 9 \right), \tag{2}$$

$$f_2 = \eta^{-4} P^2 \varepsilon (\varepsilon + 2\Delta/3), \qquad (3)$$

$$\mathbf{f}_3 = (1/3)\eta^{-1} \varepsilon \mathbf{P} \mathrm{d}\Delta \,, \tag{4}$$

$$\gamma = \varepsilon \left(\varepsilon - \varepsilon_{g}\right) \left[ \left(\varepsilon + 2\Delta/3\right) \left(\varepsilon + \delta + \Delta/3\right) - 2\eta^{-2}\Delta^{2}/9 \right) - d^{2} \left(\varepsilon + 2\Delta/3\right) \right],$$
(5)

and  $\varepsilon$  is the energy of electrons, counted off from the bottom of the conductivity band, ( $\varepsilon_g$ , P,  $\Delta$ ) are the three known parameters of Kane [3],  $\delta$  is parameter proposed by Kildal [4], d is the parameter entered by us [2], which takes into account absence of the symmetry center,  $\eta$  is Pikus-Polubotko's parameter, which takes into consideration the lattice deformation [5].

The two signs ("+" and "-") in equation (1) correspond to two branches of energy spectrum. It may be pointed out, that a dispersion law similar to (1) has been found also in wurtzite-type bulk crystals and in some two-dimensional systems (e.g. heterojunctions and inversion layers) [6].

Equation (1) looks as biquadrate in the spherical system of co-ordinates:

$$\mathbf{k}^{4} - \lambda(\varepsilon, \theta)\mathbf{k}^{2} + \mu(\varepsilon, \theta) = 0.$$
(6)

Two different solutions of (6) are:

$$k_{\alpha,\beta}^{2}(\varepsilon,\theta) = \frac{\lambda(\varepsilon,\theta)}{2} \left( 1 \pm \sqrt{1 - \frac{4\mu(\varepsilon,\theta)}{\lambda(\varepsilon,\theta)^{2}}} \right), \tag{7}$$

where  $\alpha,\beta$  are the spin states indicators, corresponding to two signs in (1 and 7), and:

$$\lambda(\varepsilon, \theta) = \frac{2\left[\gamma\left(f_1 \sin^2 \theta + f_2 \cos^2 \theta\right) + 2f_3^2 \sin^2 \theta\right]}{\left[f_1 \sin^2 \theta + f_2 \cos^2 \theta\right]^2},$$
(8)

$$\mu(\varepsilon, \theta) = \frac{\gamma^2}{\left[f_1 \sin^2 \theta + f_2 \cos^2 \theta\right]^2},$$
(9)

These equations turn to the Kildal's model [4] with the assuming, that d = 0,  $\eta = 1$ . If that is right  $\delta = 0$  additionally, it would transform itself to the classical equations of Kane [3] model. The most suitable numerical values of the parameters  $\varepsilon_g$ , P,  $\Delta$ ,  $\delta$  for Cd<sub>3</sub>As<sub>2</sub> are:

	$\epsilon_{g} = -0.13 \text{ eV}, P = 7.2 \cdot 10^{-10} \text{ eV} \cdot m,$	$\Delta = 0.3 \text{ eV},$	$\delta = 1,00565 \text{ eV},$	d = 0,035  eV [7].
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# **Results and analyses**

The surfaces of equal energy are almost spherical within the limits of the model mentioned above [2] and with these numeral parameters. It is as more right as the energy of electrons is higher. In fig. 1 two surfaces are shown. Each of them belongs to one of the two states with the opposite spins. Parts of surfaces are cut out for the comfortable consideration.



Rather weak anisotropy of surfaces allows approximate studying the effective masses of electrons. It is possible to assume that the known expression [8] for isotropic, but non-parabolic bands is the suitable approaching:

$$\mathbf{m}_{\alpha,\beta}(\varepsilon,\theta) = \frac{\hbar^2}{2} \left( \frac{\partial k_{\alpha,\beta}^2(\varepsilon,\theta)}{\partial \varepsilon} \right), \tag{10}$$

Some results of numeral calculations in accordance with (10) are presented in fig. 2, 3.

Fig. 2 shows dependence of the effective masses on energy for different directions  $(\theta = \frac{\pi}{9}(1), \theta = \frac{\pi}{4}(2), \theta = \frac{\pi}{2}(3))$  and for two opposite spin states (solid and dot lines). The spin breaking up of curves is well traced. In addition, one can see that these dependences are linear only on the right of the clearly expressed minima. The linear dependences of the effective mass on the energy are the well-known result in the Kane model. However, such linear dependence evidently does not take place near to the bottom of the conductivity band. Thus, the necessity of taking into account the influence of the band of heavy electrons is obvious for this range of energies.

Fig.3 presents the dependence of the averaged effective mass (so called "the effective mass of the density of states") [9]. This value is independent of directions and of the spin states. It was obtained by the changing of the equal energy surfaces by spheres with the same number of electronic states. It is evident that this curve has minima also.



The angular dependences of the effective masses are shown by fig. 4 for both spin subbands. It is seen that the effective masses have the minima at  $\theta = \frac{\pi}{2}$  and the maxima along some drections, which are close to direction of main axis of crystal ( $\theta = \pi/2$ ). The following values of energies are presented by numbers from {1 to 6}: {0.08, 0.04, 0.02, 0.01, 0.005 and 0.0025} eV. Only first two curves can be acknowledged as more or less isotropic. Therefore, the states near the bottom of the conductivity band are considerably anisotropic in regard to the effective masses. It seems to be somewhat unexpected, as for fig.1, where there are no noticeable features in directions of maxima of the effective masses. Nevertheless, they should be existing, as it appears from fig.4.

#### Conclusions

Our results show that the effective masses of electrons demonstrate non-trivial features close to the bottom of the band. These peculiarities are explained by presence of the extremely narrow band of the heavy electrons, which is almost degenerated with bottom of the conductivity band.

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# STUDY OF OPTICAL SPECTRA OF SEMICONDUCTING COMPOUND CuInSe<sub>2</sub> IN WIDE ENERGY REGION

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# Abstract

The precise reflectivity spectra of copper indium diselenide are obtained in energy range 1 to 5 eV at 80 K for polarized light ( $\mathbf{E}\perp\mathbf{c}, \mathbf{E}\parallel\mathbf{c}^*$ ). For the first time the spectra for pure polarization  $\mathbf{E}\parallel\mathbf{c}$  are evaluated. Optical functions in energy range 1- 23 eV are calculated using Kramers–Kronig transformations.

## Introduction

CuInSe<sub>2</sub> crystals belong to I-III-VI<sub>2</sub> group of semiconducting compounds and are characterized by a large reduction in the energy band gap  $E_g$  and in spin–orbit splitting  $\Delta_{so}$  as compared to their binary analog (see review [1]). These crystals reveal chalcopyrite structure (space group  $D_{2d}$ ). The different methods were used for growing of these crystals [2-4].

The optical properties of copper indium diselenide were investigated by different methodic (reflection, electroreflection, electron loss spectra) [5-10]. Electron band structure of CuInSe<sub>2</sub> was envisaged in [1,7,8]. The band structure calculations with the pseudopotential method were carried out in [11]. The value of  $E_g$  obtained experimentally is equaled to 1.0 - 1.3 eV. Theory predicts the value from 0.8 to 1.6 eV [11,12]. The top of the valence band is located at  $\Gamma$  point and consists of three levels. So three exciton-like series of transitions are registered in experimental spectra. From energy positions of these three excitonic peaks parameters of spin-orbit and crystal field splitting may be evaluated.

# **Reflectivity spectra**

In this work the polarized reflection spectra of CuInSe<sub>2</sub> measured in the energy interval 1 to 5 eV are presented. The specimens were grown by iodine transport and had developed mirror-like surfaces of  $(10\overline{1}), (01\overline{1})$  and  $(11\overline{2})$  types.

The reflectance spectra measurements were made at the installation built on base of DFS-12 monochromator, working in the first order of diffraction [13]. The installation was supplied with the glass cryostat with quarts window, in which the samples were cooled with liquid nitrogen through the copper bulk finger, and with a Glan-Thompson polarizing prism as a polarizer. For the measurements the more developed faces of  $(11\overline{2})$  type were used. The optical axis does not lie on the surface of any face of crystal but constitutes the angle near  $35.1^{\circ}$  with the surface of face  $(11\overline{2})$ . So the measured spectrum at polarization  $\mathbf{E} \| \mathbf{c}^*$  ( $\mathbf{c}^*$  is the

projection of optical axis on the reflective plane) contains admixture of spectrum related with the polarization  $E \perp c$ .

# Determination of "pure" polarization

The simple method [14,15], based on the recalculation of optical functions, was used for obtaining of the optical functions related with the pure polarization  $\mathbf{E} \| \mathbf{c}$ . For this method we do not need any additional measurements. It is based on the simple relationship [16] between the optical permittivities for extraordinary beams expanding in uniaxial absorbing crystal in different directions and parameters of tensor of complex permittivity of compound:

$$\frac{1}{\hat{\varepsilon}_{\alpha}} = \frac{\cos^2(\alpha)}{\hat{\varepsilon}_o} + \frac{\sin^2(\alpha)}{\hat{\varepsilon}_e} \quad , \tag{1}$$

where  $\hat{\varepsilon}_{\alpha} = n_{\alpha}^2 - k_{\alpha}^2 - 2in_{\alpha}k_{\alpha}$  is equivalent complex permittivity,  $n_{\alpha}$  is refractive index and  $k_{\alpha}$  is extinction index, relating to the beam of light expanding in absorbing uniaxial crystal in direction forming angle  $\alpha$  with the optical axis;  $\hat{\varepsilon}_{o} = n_{o}^{2} - k_{o}^{2} - 2in_{o}k_{o}$  is parameter of tensor of complex permittivity of compound for  $\mathbf{E} \perp \mathbf{c}$  (ordinary beams of light);  $\hat{\varepsilon}_{e} = n_{e}^{2} - k_{e}^{2} - 2in_{e}k_{e}$  is parameter of tensor of complex permittivity of compound for  $\mathbf{E} \parallel \mathbf{c}$  (extraordinary beams of light). So for obtaining of data related with optical properties of compound for the polarization  $\mathbf{E} \parallel \mathbf{c}$  we need only to calculate optical functions, relating to polarizations  $\mathbf{E} \parallel \mathbf{c}^{*}$  and  $\mathbf{E} \perp \mathbf{c}$ , and to calculate all that we desire using relationship (1). The FORTRAN program for the calculating of optical functions of uniaxial crystals with the optical axis, forming finite angle  $\alpha$  with the surface under investigation, using the Kramers-Kronig transformations, was developed.

#### Optical functions in wide energy interval

For the calculating of optical functions of CuInSe<sub>2</sub> on the base of our experimental data in region 1 to 5 eV we used the data of other authors in the range 4 –23 eV [5,6]. The full complex  $(R, \varepsilon_1, \varepsilon_2, n, k, \mu, \varepsilon_2 E^2, n_{ef}, \varepsilon_{ef}, \text{Im}(\varepsilon^{-1}), \text{Im}(1+\varepsilon)^{-1}, \alpha, \beta, \theta)$  of optical functions has been calculated for polarizations  $\mathbf{E} \perp \mathbf{c}$ ,  $\mathbf{E} \parallel \mathbf{c}^*$  and  $\mathbf{E} \parallel \mathbf{c}$  at 80K. The technique of calculations is described in [13,17,18].

The optical functions in the investigated region exhibit strong anisotropy (Fig.1 to 4). At the low energy edge of fundamental absorption band near 1eV one can find the doublet exciton-like structure in polarization  $\mathbf{E} \perp \mathbf{c}$ , which in polarizations  $\mathbf{E} \parallel \mathbf{c}^*$  and  $\mathbf{E} \parallel \mathbf{c}$  becomes the triplet. These peculiarities are connected with direct transitions excited between top of valence band triply splitted by noncubic crystalline field and spin-orbit interaction and the lowest state at a bottom of conduction band. Exciton spectra have been investigated earlier in [19-21].

Three polarized maxima in R spectra in the energy range 2 to 4 eV may be connected with excitons from Cu 3d subband, which is included in chemical interaction in the copper based compounds [9].

At energies higher than 4 eV the strong broad band of absorption with complicated polarization dependence is found. All spectra exhibit the pronounced polarization dependence. Some maxima in R at  $\mathbf{E} \perp \mathbf{c}$  have notable shift or absent in comparison with  $\mathbf{E} \parallel \mathbf{c}$  (Fig.1). Energies of prominent reflectance features of CuInSe<sub>2</sub> between 2 and 6 eV are following: 2.94, 3.24, 3.72, 4.80 and 5.40 eV ( $\mathbf{E} \perp \mathbf{c}$ ), 2.91, 3.72, 4.89, 5.4 eV ( $\mathbf{E} \parallel \mathbf{c}^*$ ), 2.91,

3.74, 4.27, 4.95, 5.39 eV ( $\mathbf{E} \| \mathbf{c}$ ). The authors of article [5] have published other data: 2.92, 3.24, 3.72, 4.85, 5.43 (5.38) eV. These results are obtained due to a contribution of about 35% of  $\mathbf{E} \perp \mathbf{c}$  to the spectrum with nominal  $\mathbf{E} \| \mathbf{c}^*$ .



**Fig.1.** Reflectivity spectra *R* of CuInSe<sub>2</sub> at temperature 80K for polarizations  $\mathbf{E} \perp \mathbf{c}$  (*1*),  $\mathbf{E} \parallel \mathbf{c}^*$  (*2*) and  $\mathbf{E} \parallel \mathbf{c}$  (*3*).



**Fig.2.** Real part of dielectric function  $\varepsilon_1$  of CuInSe<sub>2</sub> at temperature 80K for polarizations  $\mathbf{E} \perp \mathbf{c}$  (1),  $\mathbf{E} \parallel \mathbf{c}^*$  (2),  $\mathbf{E} \parallel \mathbf{c}$  (3).



**Fig.3**. Optical functions k(1,2) and  $\varepsilon_2(3,4)$  of CuInSe<sub>2</sub> at 80K and polarizations  $\mathbf{E} \perp \mathbf{c}(1,3)$  and  $\mathbf{E} \parallel \mathbf{c}(2,4)$ .



**Fig.4**. Optical functions  $-Im\varepsilon^{-1}(1,2)$  and  $-Im(\varepsilon+1)^{-1}(3,4)$  of CuInSe<sub>2</sub> at 80K and polarizations  $\mathbf{E} \perp \mathbf{c} (1,3) \mathbf{E} \parallel \mathbf{c} (2,4)$ .

The functions  $\varepsilon_1$  (see Fig.2),  $\varepsilon_2$ , k,  $Im(\varepsilon^{-1})$ ,  $Im(1+\varepsilon)^{-1}$  (see Fig.3,4) exhibit different behavior in polarizations  $\mathbf{E}\perp\mathbf{c}$  and  $\mathbf{E}\parallel\mathbf{c}$ . The spectra k,  $\varepsilon_2$  are looking like spectrum R, especially in case of  $\mathbf{E}\perp\mathbf{c}$ . The form of spectra  $\varepsilon_1$  differs significantly from those of R. The absorption index  $\mu$  at energy 6 eV reaches  $0.8 \cdot 10^{-6} \text{ sm}^{-1}$  ( $\mathbf{E}\perp\mathbf{c}$ ),  $0.9 \cdot 10^{-6} \text{ sm}^{-1}$  ( $\mathbf{E}\parallel\mathbf{c}$ ). The functions of surface and bulk plasmons have noticeable structures at energies 8-11 eV and 13-14 eV. The function  $\varepsilon_{ef}$  reaches saturation at 9 eV, but  $n_{ef}$  doesn't reach saturation at 21 eV.

The results obtained give the most total information about band structure of  $CuInSe_2$  and the reliable basis for the more precise determination of band structure of this compound.

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# **OPTICAL DEFORMATION POTENTIALS FOR PbSe AND PbTe**

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The values of optical deformation potentials ( $D_u$  and  $D_d$ ) for PbSe and PbTe are analyzed using absorption, luminescence and X-ray diffraction data on high quality, deep quantum well PbSe/PbSrSe and PbTe/PbEuTe structures. It is important for these evaluations to use the value of isotropic deformation potential ( $D_{iso}$ ) which is determined from the low temperature hydrostatic pressure experiments and the intervalley splitting which was determined from differential absorption spectroscopy. The fitting procedure was done using an accurate **k**·**p** model for the band structure near the fundamental gap including anisotropy, multi-valley, and band nonparabolicity effects. We find the new optical deformation potential values at 4 K:  $D_u = -0.2$  and -0.5 eV, and  $D_d = 5.3$  and 3.5 eV for PbSe and PbTe, respectively.

#### 1. Introduction

There is a considerable interest to the energy spectrum changes due to strain in semiconductor multi-quantum well (MQW) heterostructures. It is especially important in the case of IV-VI semiconductors because good lattice matching is restricted to four-component solid solutions and in view of the lack of good substrates, particularly for PbSe. As a result, the most common IV-VI MQW structures are strained and, as optical experiments have shown, the elastic strains in this case result in noticeable spectral changes (up to 20 meV or  $\sim$  10 % of the energy gap). Energy spectra depend on the strain and deformation potential values, which in their turn are not well known for the Pb salts. So far, the theoretically and experimentally determined deformation potentials are spread over a wide range. In Table I, we have listed the obtained theoretical values [1-3] together with those obtained experimentally [4-7] by different groups. The mentioned large variation is clearly seen and calls for both more calculations and measurements.

In particular, considerable discrepancies still remain among the data for the optical deformation potentials  $D_d$  and  $D_u$ . With a few exceptions [6], most  $D_d$  and  $D_u$  values do not agree with the isotropic (volume) deformation potential  $D_{iso} = 3 D_d + D_u$ , determined with good accuracy from hydrostatic pressure experiments at different temperatures [6,8]. On the other hand, previous optical studies of IV-VI strained structures [6,9] were based on the model that in these structures the lowest energy transition belongs to the normal (longitudinal) valley. Recent differential transmission spectroscopy of PbSe/PbSrSe/BaF<sub>2</sub>(111) MQW structures clearly demonstrates this validity at well widths up to 30 nm [10]. An important aspect of this work is that the authors [10] were able to measure

the intervalley splitting which results directly in one  $(D_u)$  of deformation potential constants and the next one  $(D_d)$  can be obtained from the  $D_{iso}$  relation.

Presented here is a detailed analysis of the absorption and PL spectra of high quality PbSe/PbSrSe and PbTe/PbEuTe MQW structures at different sample temperatures.

Table 1. Acoustic  $(D_d^{c,v})$  and  $D_u^{c,v}$  and  $D_u^{c,v}$  and  $D_d^{c,v} = D_d^c - D_d^v$  and  $D_u^c = D_u^c - D_u^v$  deformation potential values for the IV-VI semiconductors (in eV)

Material	$D_d^c$	$D_u^c$	$D_d^v$	$D_u^v$	$D_d$	$D_{u}$	$D_{iso}$	References	
	- 2.67	2.56	- 9.15	4.67	6.48	- 2.11	17.24	Rabii [2]	
		1.06		3.14		- 2.08		Enders [3]	
					6.5	- 3.7	15.8	Valeiko [6]	
PbSe					6.1	- 1.3	17.0	Wu [7]	
					5.3	-0.2	15.7	4 K	
					5.33	-0.6	15.4	77 K $\}$ this work	
					4.9	-0.7	14.0	300 K	
	- 4.36	8.29	-8.93	10.46	4.57	- 2.17	11.55	Ferreira [1]	
		0.297		2.48		- 2.18		Enders [3]	
РbТе	- 1.09	2.07	- 2.23	2.62	1.14	- 0.55	2.87	Kriechbaum [4]	
			4.9	5.4	1.9	- 0.5	6 (5.2)	Singleton [5]	
					4.3	- 2.8	10.1	Valeiko [6]	
		$\pm 0.5$		1	3.53	- 0.5	10.1	$\sim$ 4 K, this work	

Published data for PbTe/BaF<sub>2</sub> strained structures were also used. Based on the experimentally determined  $D_{iso}$  and the unambiguously determined well-width dependent intervalley splitting we have used a fitting procedure within an accurate two-band **k**·**p** model for the low energy transitions. This permitted the determination of new values for the PbSe and PbTe optical deformation potentials, which fit best the available data.

## 2.Theory

For the present purpose, the deformation potential can be simply defined with the general expression for the band-edge energy shift due to strain, i.e.:

$$\delta E_{c,\nu} = \sum_{ij} D_{ij}^{c,\nu} \varepsilon_{ij} , \qquad (1)$$

where  $D^{c,v}$  is the conduction or valence band deformation potential tensor and  $\varepsilon$  is the strain tensor. The lead-salt band edge states at each of the four equivalent L points, except for Kramers degeneracy which is not removed with strain, are non-degenerate and, in the linear regime Eq. (1) is always valid. For these states, by cubic crystal symmetry, it is known that the deformation potential tensor is determined by only two independent constants,  $D_d^{c,v}$  and  $D_u^{c,v}$ , the dilatation and uniaxial acoustic deformation potentials, respectively.

As given by Eq. (1), the strain energy shift depends on both deformation potential and strain tensors. If we consider only thin (under critical thickness) layers, i.e. pseudomorphic growth, we can assume homogeneous strain determined by the in-plane isotropic strain parameter

$$\varepsilon_{\parallel} = \frac{a_{\parallel}}{a} - 1, \qquad (2)$$

where *a* is the substrate material lattice constant and  $a_{||}$  is the common in-plane lattice constant of the epitaxial layer or MQW structure, which can be measured with good accuracy in a high resolution X-ray diffractometer. The only other strain component is the out-of-the-plane or perpendicular strain that is proportional to the in-plane strain, i.e.

$$\varepsilon_{\perp} = -2 \frac{C_{11} + 2C_{12} - 2C_{44}}{C_{11} + 2C_{12} + 4C_{44}} \varepsilon_{\parallel}, \qquad (3)$$

with the proportionality constant given by the material elastic constants  $C_{ij}$ , which are known at different temperatures.

The energy shift due to uniaxial strain in IV-VI semiconductors is different for the gap states at L points orientated differently with respect to the strain axis; and, therefore, the valley degeneracy of these materials can be lifted by uniaxial strain. In addition, the populations of different valleys may also be different. In optical experiments with uniaxially strained samples both the energy shift and the valley splitting are observable.

Let's consider in detail the typical and important examples of uniaxial strain due to lattice mismatch in epitaxial layers or MQW structures grown along the [111] or [100] crystallographic directions, as defined by common substrates for the growth of IV-VI materials. The different valleys in case of [111] direction are divided into one orientated normally to the (111) plane in reciprocal space (i.e. along the [111] growth direction) and three equivalent ones along directions forming the same angle with the growth direction, which are called oblique valleys. The interband optical transition energies probed in absorption and PL experiments depend only on the strain induced energy shift of the fundamental band gap  $E_g$  (and not on the valence and conduction band edge shifts independently). It is then convenient to define optical deformation potentials  $D_d = D_d^c - D_d^v$ and  $D_u = D_u^c - D_u^v$ , so that the valley dependent energy gap strain shift is given by [5,9]

$$\delta E_{\varphi}^{N} = D_{d} \left( 2\varepsilon_{\parallel} + \varepsilon_{\perp} \right) + D_{u} \varepsilon_{\perp} \tag{4}$$

and

$$\delta E_g^O = D_d (2\varepsilon_{\parallel} + \varepsilon_{\perp}) + D_u (8\varepsilon_{\parallel} + \varepsilon_{\perp})/9, \qquad (5)$$

for the normal and oblique valleys, respectively. In equations (4) and (5) the first term contributes to a shift in both the normal and oblique valleys by the same amount, while the second term contributes to a splitting of the two different valleys. The amount of this splitting depends only on the uniaxial deformation potential constant as follows:

$$\Delta = \delta E_g^{\ N} - \delta E_g^{\ O} = \frac{8}{9} D_u \left( \varepsilon_\perp - \varepsilon_\parallel \right). \tag{6}$$

In the case of [100]-oriented substrates all four valleys are equivalent, i.e. all the major axes of the ellipsoids make the same angle with the surface normal. The gap change is given by

$$\delta E_g^{[100]} = \frac{2(C_{11} - C_{12})}{3C_{11}} D_{iso} \varepsilon_{II} \,. \tag{7}$$

Here the isotropic (volume) deformation potential  $D_{iso}$  is expressed through the optical deformation potentials as follows

$$D_{iso} = 3D_d + D_u = -(C_{11} + 2C_{12})\frac{dE_g}{dP},$$
(8)

where  $dE_g/dP$  is the volume hydrostatic pressure gap coefficient. For PbSe and PbTe,  $D_{iso}$  has been measured with good accuracy at room and low temperatures. The  $D_{iso}$  values are presented in Table 2.

Material	PbSe			РЬТе		
Т, К	4	77	298	4	77	303
$C_{11}^{a}$ , $10^{10} \text{ N/m}^2$	14.18	13.98	12.37	12.81	12.43	10.80
$C_{12}^{a}$ , $10^{10} \text{ N/m}^2$	1.94	1.97	1.93	0.44	0.47	0.77
$C_{44}^{a)}, 10^{10} \text{ N/m}^2$	1.749	1.695	1.591	1.514	1.482	1.344
$(C_{11}+2C_{12})^{\rm a)}, \ 10^{10} {\rm N/m^2}$	18.06	17.92	16.23	13.66	13.41	12.34
$dE_{g}/dP^{b}$ , 10 <sup>-6</sup> eV/bar	-8.7±0.8	-8.6±0.2	-8.6±0.1	-7.4±0.8	-7.4±0.2	- 7.5
$D_{iso}$ , eV	15.7	15.4	14.0	10.1	9.9	9.3

Table 2. Elastic constants, hydrostatic pressure gap coefficients and  $D_{iso}$  values

<sup>a)</sup> Elastic constants were taken from Ref. 11 and Ref. 12 for PbTe and PbSe, respectively.

<sup>b)</sup> The pressure gap coefficients at 4, 77 and 300 K see in [6,8].

In MQW structures, the optical transition energies include also the addition of both electron and hole quantum size (or confinement) shifts,  $E_e$  and  $E_h$ , which besides being strongly well width dependent, can be calculated with high accuracy, especially for the lowest states, within the envelope function method based on a multi-band **k**·**p** model for the bulk (with the band gap and the electron band edge effective mass, both eventually strain shifted, as the only parameters). Therefore, if the strain is known, the optical deformation potentials remain the only two unknown parameters in the evaluation of the quantum well optical transition energies.

Due to the strong well width dependence of quantum size energies and due to the intervalley splitting sign dependence, several different energy level structures can occur. When the quantum size shift is zero or small, as in thick epitaxial layers or wide quantum well structures, the strain induced valley splitting is accurately approximated by equation (6), i.e. depends only on  $D_u$ . In PbTe/PbEuTe and PbSe/PbSrSe MQW structures, the active quantum well PbTe and PbSe layers present in-plane tensile strain, i.e.  $a_{||} > a$  and  $\varepsilon_{||}$  is positive. From Equations (3) and (6) it follows that if  $D_u < 0 \Delta$  is, in this case, positive, meaning that the lowest optical transition in such an epitaxial layer or wide quantum well is from the oblique valleys. As the well width is reduced the confinement shifts for the oblique states increase much faster than that for the normal one (due to the much smaller oblique valley electron and hole effective mass along the growth direction); and, as a result, below a certain critical (crossing) well width the lowest transition is from the normal valley. Note that for  $D_u > 0$ ,  $|\Delta|$  increases monotonically with decreasing well width, and there is no crossing.

A two-band model accounting for band nonparabolicity, many-valley, and anisotropy effects is treated within the standard envelope function approximation [13]. Since PL intensity for both MQW structures was high, comparable with one of the best thick  $(2 - 3 \ \mu m)$  epilayers grown on BaF<sub>2</sub> substrates, the heterojunction is of type-I. There is no information about band offsets for these heterojunctions. Considering the mirror like band structure of these materials and the good agreement obtained with the measured absorption spectra (including the 3 nm QW sample) [9], we have used  $\Delta E_c = \Delta E_v$  for our deep quantum wells ( $\Delta E_g \ge 0.3 \ eV$  at low temperatures), and checked that the lowest optical transition energies depend very little on deviations from such band edge discontinuities. Strain effects were also

included with the energy gap and the effective masses renormalization in accordance with previous considerations and the two-band model, respectively.

#### 3. Strain

There are two strain sources in IV-VI MQW structures grown on BaF<sub>2</sub> substrates. The first one is the lattice mismatch between structural constituents, i.e. between well and barrier. The structure growth is usually started on a relatively thick (i.e. relaxed) buffer layer and the well and barrier layers are thinner than the critical layer thickness, so in the first approximation they are elastically and uniformly strained. Since the lattice constants of PbEuTe and PbSrSe solid solutions (barriers) are larger than PbTe and PbSe (wells), respectively, the wells are under tensile in-plane strain and the barriers under compressive inplane strain. However, as the number of repetitions in our MOW samples is high (40 to 50), the MQW stack does not remain pseudomorphic (same in-plane lattice constant) to the buffer layer. It starts to relax and tends to a free-standing condition. This fact becomes especially important as the well width increases. It was demonstrated for PbTe quantum wells [14], where it was possible to fit the measured X-ray spectra of PbTe/PbEuTe MQW samples assuming a common in-plane lattice constant (different from the buffer value) for the whole MQW stack, and to determine the average strain in the PbTe wells. The fraction of the maximum parallel strain in the PbTe well decreased with the well width (by 26% at  $L_z = 20$ nm, see Figure 5 in Ref. 14).

Similar strain analysis was done here for PbSe quantum wells. The  $\omega/2\theta$  scan around the (222) Bragg diffraction peak was measured for the PbSe/PbSrSe MQW samples. In X-ray spectra there are the zero-order (most intense) plus several satellite peaks belonging to the MQW structure together with the BaF<sub>2</sub> substrate peak, which is used as a reference for the • axis. The PbSrSe buffer layer peak is overlapped by the zero-order peak for the sample with narrow PbSe well ( $L_z = 3.5$  nm) and the splitting between both peaks is already visible for the sample with larger wells ( $L_z \ge 10.6$  nm). In order to determine the strain inside the PbSe QW's, the (222)  $\omega/2\theta$  spectrum of the MQW samples was calculated in the framework of dynamical theory of X-ray diffraction, and compared to the measured ones. The perpendicular strain component  $\varepsilon_{\perp}$  is obtained by Eq. 3 using elastic constants of the bulk material (Table 2), the calculated spectra that best fit to the measured data, using the in-plane lattice constant ( $a_{\parallel}$ ) as the main fitting parameter. The parallel strain (•  $_{\parallel}$ ) in the PbSe wells of each sample was then determined using this fitting procedure. Thus, it is also necessary to take into account the well width strain dependence.

The second strain source is thermal expansion differences between the semiconductor structure and the substrate (in our case BaF<sub>2</sub>). An important question concerning IV-VI epitaxial structures grown on the BaF<sub>2</sub> substrates arises: Is there a temperature at which this thermal strain is zero? The experimental evidence (electrical and optical properties) indicates that the strain is practically zero at room temperature. The X-ray diffraction measurements show that thick epilayers are almost unstrained at 300 K (the total residual strain is lower than  $3x10^{-4}$  for a thickness of 5 µm [15] or no strain to within  $\pm 3x10^{-5}$  [16]). This result is important since our previous X-ray measurements gave only the lattice mismatch strain at room temperature.

There are two possible reasons for the negligible thermal strain near room temperature. On cooling the samples from their growth temperature a stress is generated at the interface and it is relieved by creation and movement of dislocations. In addition, although the thermal expansion coefficients ( $\alpha$ ) of IV-VI semiconductors and the BaF<sub>2</sub> substrate are similar they do

have a different temperature dependence:  $\alpha$  (IV-VI) <  $\alpha$  (BaF<sub>2</sub>) at growth temperatures of 350<sup>°</sup> C and  $\alpha$  (IV-VI) >  $\alpha$  (BaF<sub>2</sub>) at temperatures less than ~ 100<sup>°</sup> C. Thus, after sample cooling to room temperature, a partial compensation effect takes place.

On cooling the sample from room to cryogenic temperatures some residual elastic thermal strain in the sample is generated. This is based on a study [17] where this thermal strain in PbTe/BaF<sub>2</sub> films or PbTe/PbSnTe/BaF<sub>2</sub> superlattices was measured at low temperatures, and a value of  $1.4 \times 10^{-3}$  was obtained. The calculated thermal strain between PbTe and BaF<sub>2</sub> is  $1.6 \times 10^{-3}$ ,  $1.4 \times 10^{-3}$  and  $0.88 \times 10^{-3}$  at temperatures of 4 K, 30 K and 77 K, respectively. There is thus good agreement for a temperature of 30 K (the real sample temperature on the cold finger in the X-ray cryostat). These values both for PbTe and for PbSe should be added to the mismatched tensile strain values measured in the wells at room temperature.

# 4. Samples and optical measurements

The PbSe/PbSrSe [10] and PbTe/PbEuTe [9,14] MQW structures used are briefly described here. They were grown on freshly cleaved BaF<sub>2</sub> (111) substrates by MBE at temperatures of 360°C and 300°C, respectively. Before growing the MQW structure a thick (3-4  $\mu$ m) buffer layer with the same composition as the barriers was grown in order to accommodate completely the lattice mismatch of 1% and 4.4% for PbSrSe/BaF<sub>2</sub> and PbEuTe/BaF<sub>2</sub>, respectively. The barrier composition was chosen to get a barrier band gap of 0.5 eV or more at 300 K as verified from infrared absorption measurements. Therefore, the wells were deep enough at 300 K and  $\Delta E_g$  increases at low temperatures. The well width was varied from 3 to 30 nm. The barrier thickness was varied from 40 to 50 nm. The number of periods was from 40 to 50.

The samples were characterized structurally by high resolution X-ray diffraction in the triple configuration to determine the barrier and well width lattice parameters [14]. Measurements were performed at room temperature. The strain in the wells inside the MQW structure was obtained as a function of its width using the common in-plane lattice constant as the main fitting parameter. It decreased monotonically with well width. MQW structures demonstrated a good resolved satellite peak structure that indicates their high quality (thickness reproducibility, homogeneous Eu or Sr content, and low interdiffusion).

Infrared transmission spectra were obtained at sample temperatures from 5 K to 300 K in a Fourier transform infrared spectrometer [9,10]. PL spectra were measured in pulsed mode at 4 K and 77 K using a Nd: YAG laser (hv = 1.17 eV) for excitation and in CW mode at 300 K using an InGaAs laser (hv = 1.28 eV) for the excitation. A gold-doped germanium (7.5 µm cutoff wavelength) or HgCdZnTe (6 µm cutoff wavelength) detector with a detectivity of 10<sup>10</sup> cm·Hz<sup>1/2</sup>/W was used. The energy resolution was 0.5-1 meV.

As-grown samples were used for the low temperature measurements. Emission lines in PL spectra are stimulated and they arise from the high energy side of spontaneous line, therefore, they represent with high accuracy the band gap. The differential absorption spectra of PbSe/PbSrSe MQW structures are obtained by taking the difference between a transmission spectrum at one temperature and the spectrum at a slightly lower temperature [10]. This takes advantage of the temperature dependence of the PbSe band gap, so that step edges associated with different transitions in the transmission spectra become peaks in the difference spectra. Thus the temperature difference spectra are in essence energy derivative spectra. Splitting of L-valley degeneracy and remarkable peak intensity difference were observed in the spectra. The last fact reflects the different densities of states in normal and

oblique valleys, i.e. transition intensity is much higher in the three-fold degenerate oblique valleys than in the one normal valley.

# 5. Results and discussion

As discussed above, depending mainly on the well width and on the specific values of the deformation potentials, the lowest optical transition in these QW structures can be either from the normal or from the oblique valleys. The corresponding transition energies are denoted by  $E_{11}^N$  and  $E_{11}^O$ , respectively, and given by  $E_{11}^v = E_g + \delta E_g^v + E_{e,1}^v + E_{h,1}^v$ , where v = N, O and  $E_{(e,h),1}^v$  is the first electron or hole quantized state from the v valley.

If we consider the pure strain effect for the [111] direction the following relation between the normal  $(E_{11}^N)$  and oblique valley  $(E_{11}^O)$  transition energies takes place:  $E_{11}^N = E_{11}^O$  at  $D_u =$ 0;  $E_{11}^N > E_{11}^O$  at  $D_u < 0$ ; and  $E_{11}^N < E_{11}^O$  at  $D_u > 0$ . The quantum-size effect increases both energies as the well width decreases. For example for PbSe, the  $E_{11}^O$  energy is blue shifted twice as much as the  $E_{11}^N$  energy due to anisotropy effects, i.e. the transverse effective mass is almost one half the longitudinal one. The final result of both energies depends on well width, effective mass, strain and deformation potential values.

In the first PL experiments [6] the relation  $E_{11}^N < E_{11}^O$  was used for the PbTe well widths up to  $L_z = 20$  nm. Recent differential absorption spectroscopy results [10] clearly demonstrate that the following relation takes place also in PbSe:  $E_{11}^N < E_{11}^O$  at well widths up to 30 nm. The evaluations at  $L_z = 30$  nm, where the level shifts due to quantum-size and deformation effects are comparable, show that the intervalley splitting  $\Delta = E_{11}^N - E_{11}^O$  is relatively small. This means that  $D_u$  is negative and that level crossing takes place due to the quantum size effect. Using  $D_u = -0.2$  eV we were able to get the calculated intervalley splitting very close to experimental values for three well widths at 4 K: 21.1, 7.3, and 3.8 meV for  $L_z = 9.7$ , 20.6 and 29.7 nm, respectively. The well strain for each MQW structure was determined as discussed above. For the fitting we used the calculated  $\Delta$  values for the  $L_z = 20.6$  nm and 29.7 nm. The large quantum-size contribution (~ 60 meV) at  $L_z = 9.7$  nm is less accurately given by the present two-band model. Imposing the  $D_{iso}$  constraint, we thus obtain:  $D_d = 5.3$  eV and  $D_u = -0.2$  eV at 4 K.

With these deformation potentials, we have calculated the transition energies at 4 K as a function of the well width and, as shown in Figure, obtained very good agreement with the experimental data. To simplify the picture for each curve, we have used an averaged (over samples) fixed strain. In the case of 77 K, we have used the intervalley splitting  $\Delta = 5.5$  meV obtained at 66 K ( $\varepsilon_{II} = 2.18 \times 10^{-3}$ ). The best fit here leads to  $D_u = -0.5$  eV and  $D_d = 5.3$  eV. Along with the PL data at 77 K, we have plotted also the absorption data at 66 K. They are near 5 meV lower than the theoretical curves due to the PbSe temperature gap coefficient (0.4 meV/K). The second PL line corresponding to  $E_{22}^N$  transition was observed for sample  $L_z = 10.6$  nm at a high excitation level (~10<sup>5</sup> W/cm<sup>2</sup>). Finally, the results at room temperature are plotted in the same Figure. Since the intervalley splitting (~10 meV) for  $E_{11}$  transitions is small in comparison to kT at room temperature (26 meV) no differentiation between normal and oblique valleys is observed; most of the experimental points lay between the calculated curves.

Thus good agreement was obtained between the low energy state differential spectroscopy and PL data, on the one hand, and the calculations in the framework of the twoband model, which is also valid for the low energy states, on the other hand.



Figure. Calculated sub-band transition energies versus well width for PbSe/PbSrSe MQWs at 4, 77 and 295 K, and for PbTe/PbEuTe MQWs at 4 and 77 K. The solid and dashed lines correspond to transitions in normal (longitudinal) and oblique valleys, respectively. The total strain  $\varepsilon_{II}$  is averaged over samples for each curve.

It should be noted that the PbSe deformation potential values change with temperature:  $D_d$  slightly decreases and  $D_u$  by several times increases with increasing temperature (see Table 1). Taking into account that  $D_d$  and  $D_u$  are differences of big quantities we can conclude that the acoustic potential values change with temperature.

The PbTe optical deformation potential constants were obtained (see below) from laser [18] and magneto-optical [5,19] measurements of PbTe/BaF<sub>2</sub> structures at low temperatures and they are:  $D_d = 3.53$  eV and  $D_u = -0.5$  eV. We have used these values for calculation of quantum well transition energies, which are compared with photoluminescence data for PbTe/PbEuTe MQW structures. Considering the previous evaluations of the thermal strain ( $\varepsilon_{II} = 1.6 \times 10^{-3}$  at 4 K and  $\varepsilon_{II} = 0.9 \times 10^{-3}$  at 77 K) and of the measured [14] mismatch strain (which depends on the well width and changes from  $1.9 \times 10^{-3}$  and  $2.7 \times 10^{-3}$ ), we have used an averaged total strain of  $\varepsilon_{II} = 3.9 \times 10^{-3}$  and  $3.2 \times 10^{-3}$  at 4 K and 77 K, respectively. Calculations

of the lowest (normal valley) transition energy at two temperatures are shown in the Figure where the photoluminescence data points are also presented.

As one can see in the Figure, some deviations between experimental and calculated transition energy values take place in the narrowest quantum wells ( $L_z = 2.3$  and 3.5 nm for the PbTe/PbEuTe and PbSe/PbSrSe MQW's, respectively) due to the decreasing accuracy of the two-band model with increasing energy. For these high energy transitions the six-band model should be used. It should be also noted that the obtained optical deformation potential constants for PbTe differ from most of the available data in the literature [1,6], except for the  $D_u$  value proposed in [4,5]. For more detail discussions of deformation energy shifts observed in different publications see in [20].

Summarizing, with the use of measured strain induced intervalley splitting energies, empirical isotropic deformation potentials, and a detailed analysis of the strain we were able to determine new optical deformation potential values for PbSe and PbTe. At 4 K, for example, we have found:  $D_u = -0.2$  and -0.5 eV, and  $D_d = 5.3$  and 3.5 eV for PbSe and PbTe, respectively. They result from the best fit to the photoluminescence and differential absorption spectroscopy data using an envelope function calculation based on an accurate two-band **k**·**p** model for the bulk. In general, but more specifically at low temperatures, a small uniaxial optical deformation potential constant ( $D_u$ ) is obtained for both PbSe and PbTe due probably to the mirror symmetry of the conduction and valence bands in these materials.

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# OPTICAL PROPERTIES OF CADMIUM INDIUM TELLURIDE AS A FUNCTION OF MANGANESE DOPING PERCENTAGE

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#### Abstract

The optical properties for pure and Mn doped  $CdIn_2Te_4$  thin films were studied as a function of Mn doping percentage. The estimated direct energy gap was in the range (1.06-0.96) eV for Mn concentration between (0.3-3.0) wt percent.

#### Introduction

Cadmium Indium Telluride is a semi-conducting compound with energy band gap 1.1eV and its structure is basically a chalcopyrite structure with half of one of the cations removed [1]. Some II-III<sub>2</sub>-VI<sub>4</sub> ternary compounds such as  $CdIn_2 Te_4$  have attracted attention recently both from fundamental and applied point of view. Cd-In-Te offers a system in which the optical band gap could be varied in a wide range of interest. Recently Ramirez et al. have reported a direct band gap for  $CdIn_2Te_4$  thin films prepared by close spaced vapor transport technique [2,3]. The formation of ternary semi-conductor compounds from the Cd-In-Te ternary system has been investigated by melting of different concentrations of these elements [4]. The purpose of this paper is to describe the optical properties of chemically sprayed  $CdIn_2Te_4$ : Mn films.

## **Experimental Procedure**

CdIn<sub>2</sub>Te<sub>4</sub> films were prepared by spray pyrolysis method. Solution of CdSO<sub>4</sub>, InCl<sub>3</sub> and TeO<sub>2</sub> were prepared by dissolving appropriate amounts of the high purity compounds in deionized water. Mn doped films were prepared by adding different weight percentage (0.3-3.0) wt% of Mn , by dissolving appropriate amount of MnCl<sub>2</sub> in De-ionized water and adding to the solution. The obtained solution is immediately sprayed with the help of a double nozzle sprayer onto heated substrate of glass plates. The sprayer setup and experimental details of preparation were described elsewhere [5]. The spraying rate was in the 3ml/min and the thickness of the prepared samples was in the range (0.16-0.20)  $\mu$ m. Optical absorption curves were taken on a Sp-800 pye Unicam spectrophotometer in the wave length range (300-1500) nm.

#### **Results and Discussion**

Typical absorption coefficient spectra for  $CdIn_2Te_4$  films doped with different Mn weight percent are shown in Fig. (1). It can be seen that the absorption coefficient  $\alpha$  is increasing with increasing the Mn concentration as shown in Fig (2).

The relation between  $\alpha$  and incident photon energy **hv** for direct allowed band to band transition as used by Rajaram [6] is given by the following equation :

$$(\alpha hv)^{2} = C(hv - E^{d}_{g}) \qquad hv > E^{d}_{g}$$
$$(Ahv)^{2} = 0 \qquad hv < E^{d}_{g},$$

where  $\mathbf{E}_{g}^{d}$  is the direct energy gap and **C** is nearly constant independent of photon energy [7].  $(\boldsymbol{\alpha}\mathbf{hv})^{2}$  has been plotted in Fig (3) for undoped and doped films. The extrapolation of the linear region of  $(\boldsymbol{\alpha}\mathbf{hv})^{2}=0$  gives the direct allowed band gaps. Table (1) presents the direct allowed band gaps  $\mathbf{E}_{g}^{d}$  as a function of Mn doping percentage following the previous process. For pure CdIn<sub>2</sub>Te<sub>4</sub> film the direct allowed band gap is (1.12±0.05) eV.



Fig. (1)-Absorption Coefficient a vs. Photon Energy for different Mn wt percent.

Mn.wt%	Pure	0.3%	0.6%	0.8%	1.0%	3.0%
$E^{d}_{g}$ (eV)	1.12	1.06	1.025	0.98	0.97	0.96

Table (1)-The direct band gaps for different Mn doping percentage.



Fig. (2)-Absorption Coefficient  $\alpha$  vs. Mn doping percentage for different photon energy.



Fig. (3)-  $(\alpha hv)^2$  vs. Photon Energy for different Mn doping wt percentage.

# **Conclusion Remarks**

- The optical properties of CdIn<sub>2</sub>Te<sub>4</sub>: Mn films were investigated for doping concentration varied between (0-3) wt percent.
- The direct energy gaps were calculated as a function of doping concentration. It was found that the direct energy gaps decreased with increasing doping concentration.

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# KINETIC COEFFICIENTS IN Bi<sub>0.88</sub>Sb<sub>0.12</sub> ALLOY: INFLUENCE OF ANISOTROPIC DEFORMATION

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The change of kinetic coefficients in  $Bi_{0.88}Sb_{0.12}$  alloy under influence of anisotropic deformation at temperature 80 K was studied. The diagrams of the magneto resistance rotation were considered. The anisotropic deformation was applied along the trigonal axis  $C_3$  of the crystal.

The obtained results were interpreted in framework of the Lax ellipsoidal-non parabolic (ENP) model. The modifications of the energy band gap width  $(E_g)$  and charge carriers effective masses were examined.

It was shown that the changes of properties of electrons and holes under pressure may differ. The possible causes of this difference were discussed.

#### Introduction

Bismuth and bismuth antimony (Bi-Sb) alloys have some extraordinary physical properties. The charge carriers in Bi-Sb have relatively small concentrations but very high strongly anisotropic mobility. The main galvanomagnetic effects, dimensional oscillations in magnetic field, the microwaves without relaxation and other effects were discovered and studied in bismuth. The properties and applications of Bi-Sb are discussed in [1-4]. Owing to crystallographic symmetry of Bi-Sb the only hydrostatic pressure and anisotropic pressure along the axis  $C_3$  cause equivalent changes of all electron quasiellipsoid properties. If anisotropic pressure is applied in other directions these changes are non-equivalent [5,6].

In [7] there were studied the changes of electron and hole concentrations and mobilities in semiconducting alloy  $Bi_{0.88}Sb_{0.12}$  (further – BS12) at temperature (*T*) 80 K and compression along axis C<sub>3</sub>. This composition is very interesting both for scientific researches (the isoenergetical surfaces of electrons and holes are similar) and for practical applications, because the charge carriers have high mobilities. The obtained results are analyzed in the present article.

# **Results and discussion**

# 1. Kinetic coefficients

In [7] there were calculated kinetic coefficients in BS12. The data [8, 9] were taken into account. The results of calculation are in a good agreement with experimental data. Table shows the results of numerical analysis [7]. Here N=n=p, where *n* and *p* are electron and hole concentrations respectively (according to [7] they are equal), *P* is an applied pressure,  $\mu_i$  and  $\nu_i$  (i = 1,2,3) are components of the mobility tensors for electrons and holes correspondingly. They were determined in the coordinate system connected with inverted effective mass tensor ellipsoids.

According to [7] the charge carrier concentrations decrease if the pressure is applied. Two possible reasons can cause this effect.

(I) Bismuth and its isoelectronic analogues (antimony and arsenic) have the crystallographic lattices, which belong to  $D_{3d}^5$  class [1-4]. When we pass from arsenic to antimony and from antimony to bismuth, then both rhombohedric distortion of the crystallographic lattice and free charge carrier concentrations become less.

Table
The calculated kinetic coefficients in BS12 at temperature 80 K [7].

P,	Mobility, m <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup>						
KG/cm	$\mu_l$	$\mu_2$	$\mu_3$	$v_l$	<i>v</i> <sub>2</sub>	<i>V</i> 3	
0	109.4	1.87	54.7	5.7	0.06	2.85	7.54*10 <sup>16</sup>
60	98.7	1.68	49.4	5.44	0.057	2.72	7.22*10 <sup>16</sup>

The latter effect may be explained by interaction of p- and d-states waves functions (p-d hybridization [3]). We believe this phenomenon may arise when the mechanical compression along the trigonal axis is applied, because in that case the rhombohedric distortion is reduced too.

Taking into account the band structure of bismuth and BS12 [3,4] it is possible to expect the rhombohedric distortion reduction evokes the similar changes both for bismuth and BS12.

(II) Since the atoms of antimony have less atomic radius than the ones of bismuth, it was advanced a theory that in Bi-Sb alloys the compression is equivalent to small antimony adding [3]. According to [3] adding of a small antimony concentration rises a band gap width (BGW) in BS12. Also the compression may rise this value and reduce the electron and hole concentrations (EHC). This EHC reduction was ascertained in [7].

# 2. The change of the band gap width under pressure

The Lax ENP model is often used to approximate an energetic spectrum of charge carriers in bismuth and Bi-Sb alloys, because it describes well the kinetic phenomena in these materials. This model had generalized the Kane model [10,11] for ellipsoidal isoenergetic surfaces.

For the ENP model the dispersion relation for one isoenergetic surface is:

$$E\left(1+\frac{E}{E_g}\right) = \frac{h^2}{2m_0} \sum_{i,j} \alpha_{ij} k_i k_j \tag{1}$$

Here E is energy of the free charge carriers. For electrons this energy is counted up off the conduction band bottom. For holes it is counted down off the valence band top. h is

Planck's constant,  $m_0$  is the free electron mass,  $\alpha_{ij}$  (i,j = 1,2,3) are components of the reversal effective mass tensor,  $k_i$ ,  $k_j$  are components of the wave vector.

In BS12 both for electrons and holes the Fermi surface consists of three non-bonded ellipsoids located in L-points of the Brillouin zone.

Taking into account the data [12-15] we have made the control calculations, which confirmed the Lax model validity in BS12. According to [12-16] in this alloy  $E_g \approx 17$  meV at  $T \leq 4.2$  K. On the other hand it is difficult to realize the precise BGW measure at higher temperatures.

Different authors [17-19] obtained the various values of BGW in BS12 at temperature 80 K.

Taking into account these data it was considered the possible BGW change from 12 meV to 22 meV. This consideration allows examining the influence of this parameter on the final results.

Further two main assumptions were used.

(I) The electron and hole concentrations were equal. This result was obtained in [7]. Also in [20] the similar result was show. According to [20] in  $Bi_{0.90}Sb_{0.10}$  alloy it was found  $n = p = 9 * 10^{16}$  cm<sup>-3</sup> at T = 77 K. We have not found any refutation of this result in following publications. In BS12 BGW is somewhat more than in  $Bi_{0.90}Sb_{0.10}$  alloy [3,4], therefore the results [7] (see table) seem to be reasonable.

(II) The electrons and holes states densities effective masses in BS12 are practically equal [12].

According to these assumptions the Fermi level in BS12 at temperature 80 K was proposed to be in the middle of the band gap [10, 11]. On the other hand in ENP model effective mass is proportional to BGW [10, 11]. These assumptions lead to formula:

$$n_{s}/n = (I + \Delta E_{g}/E_{g})^{3/2} * I^{0}_{3/2,0} (\eta_{s}, \beta_{s})/I^{0}_{3/2,0} (\eta, \beta)$$
<sup>(2)</sup>

Here index "s" (suppression) shows the pressure is applied,  $\Delta E_g$  is increasing of BGW under pressure,  $\eta = E_f / kT$ ,  $E_f$  is the Fermi energy counted up of the conduction band bottom, k is Boltzmann constant,  $\beta$  is a no parabolic factor ( $\beta = kT/E_g$  [10,11]).

$$I_{3/2,0}^{0}(\eta,\beta) = \int_{0}^{\infty} (-\frac{\partial f}{\partial x})(x+\beta x^{2})^{3/2} dx$$
(3) [11]

Here x = E / kT, *f* is Fermi-Dirac distribution function [10, 11]. Further we determined  $\eta$ ,  $\beta$ ,  $I_{3/2,0}^0$  ( $\eta$ ,  $\beta$ ) for different possible BGW. The ratio  $n_s/n$  was obliged to coincide with one from the table. The method of proportional parts [21] was used. On the other hand it was determined the change of BGW for non-degenerated semiconductor, when ellipsoidal-parabolic (EP) model is valid [10].

In this case it is possible to write:  $n_s/n = exp (-\Delta E_g/2kT)$  (3a).

Then  $\Delta E_g = 2kT \ln (n/n_s) \approx 0.59 \text{ meV}$ . The obtained results are shown in fig. 1.

If EP model is valid, the change of BGW under pressure does not depend on the initial BGW, because effective masses and density of states remain constant.

In ENP model there is another situation: when BGW becomes more the effective mass rises too [10, 11]. Also the density of states increases. In this situation two main factors determine the change of the free electron concentration (FEC).



Fig. 1. The calculated change of the band gap width under pressure 60 kG/cm<sup>2</sup> in dependence on the initial band gap width: 1 – for ENP model, 2 – for EP model.

(I) The fall of the Fermi level, which is in the middle of the band gap. This factor diminishes FEC [10, 11].

(II) The increase of the density of states, which increases FEC.

Certainly, the first factor is stronger and FEC becomes less both in EP and ENP models. But in ENP model this reduction is less. Therefore if it is necessary to obtain the certain FEC reducing, in ENP model it requires more BGW increasing than in EP model.

If initial BGW is higher this effect becomes weaker, because the relative change of the effective mass becomes less. Therefore when initial BGW rises, curve 1 (fig. 1) falls and approaches curve 2.

For L-holes the same situation is realized. According to [10, 11] it is possible to write for Kane model:  $m(E) = m_0 * (1 + 2 E/E_g)$  (4), where m(E) is the effective mass of electrons with energy E, and  $m_0$  is the one at the conduction band bottom (E = 0). Relation (4) was obtained for isotropic effective mass, but it is valid also for ENP model if m (E) and  $m_0$  are effective masses in any direction. If the pressure is applied, the actual formula is:  $m_s$  (E) =  $m_{0s}$ \*  $[1 + 2 E / (E_g + \Delta E_g)]$  (4a). Here the direction indexes are omitted, because this formula is valid in all directions. From (4) and (4a) it is possible to obtain the ratio:

$$\frac{m_s(E)}{m(E)} = \frac{m_{0s} \frac{1+2E}{(E_g + \Delta E_g)}}{m_0 1+2E/E_g}$$
(5)

All values in (5) are positive and 
$$\frac{m_s(E)}{m(E)} \le \frac{m_{0s}}{m_0}$$
 (5a)

The inequality (5a) becomes stronger when BGW is being decreased, because the no parabolic factor becomes larger. This effect relaxes the increase of both density of states and FEC when BGW rises under pressure. This effect restricts the factor (II) mentioned above. It is seen from fig.1:  $\Delta E_g$  rises when BGW is being decreased, but this rising becomes slower if BGW becomes less than 16 meV.

On the other hand if BGW is more than 20 meV the no parabolic factor becomes less, and the further fall of  $\Delta E_g$  (with rising of BGW) becomes slower. The situation for ENP model approaches the one in EP case.

# 3. The changes of effective masses and charge carrier concentrations under pressure

According to [12-15] in  $Bi_{1-x}$  Sb<sub>x</sub> near x=0.12 the electrons effective masses at the conduction band bottom are practically proportional to BGW. Then we obtain from (5):

$$\frac{m_s(E)}{m(E)} = 1 + \frac{\Delta E_g}{E_g + 2E}$$
(6), or 
$$\frac{\Delta m(E)}{m(E)} = \frac{\Delta E_g}{E_g + 2E}$$
(7).

Here  $\Delta m$  (*E*)  $\equiv m_s$  (*E*)-*m* (*E*). Fig. 2 shows the relative change of effective masses (in all directions) under pressure in dependence on initial BGW.

According to fig.2, when initial BGW is being decreased the relative change of effective masses becomes less because  $\Delta E_g$  becomes less (see fig. 1, curve 1).

If electron energy rises, the relative change of its effective mass under pressure becomes less (see the above formulae (5), (5a) and discussion of them). Also the change of mobility under pressure was analyzed. The common formula for mobility is shown in [4].

The corresponding analysis in our case when scattering on acoustic phonons is actual [10, 11, 16] leads to formula

$$\overline{\mu}_{i} = \frac{e\tau_{0}}{m_{i0}(kT)^{3/2}} * \frac{\int_{0}^{\infty} (1+\beta x)^{1/2} f(x)dx}{\int_{0}^{\infty} x^{1/2} (1+\beta x)^{1/2} (1+2\beta x) f(x)dx}$$
(8)

Here  $\overline{\mu}_i$  is the middle value of mobility in i-direction (it is an averaged value in actual energy

region),  $\tau_0$  is a constant and  $m_{i0}$  is an effective mass in i-direction on the conduction band bottom.

The corresponding calculations in our case (non-degenerated semiconductor and  $0.3 \le \beta \le 0.6$ ) lead to result:

$$\overline{\mu}_{i} \approx \frac{2}{\sqrt{\pi}} \frac{e\tau_{0}}{m_{i0} (kT)^{3/2}} \frac{1 + \beta/2}{(1 + 3\beta/2)^{3/2}}$$
(9)

Then the ratio between mobility under pressure and the one without pressure may be written as

$$\frac{\overline{\mu_{is}}}{\overline{\mu_{i}}} \approx \frac{m_{i0}}{m_{i0s}} \frac{(1+\beta_{s}/2)(1+3\beta/2)^{3/2}}{(1+\beta/2)(1+3\beta_{s}/2)^{3/2}} = \frac{E_{g}}{E_{g}+\Delta E_{g}} \frac{2+\beta_{s}}{2+\beta} \frac{(2+3\beta)^{3/2}}{(2+3\beta_{s})^{3/2}}$$
(10)

The results of calculations are shown in fig.3.



Fig. 2. Relative change of effective mass at different energy levels in dependence on the initial band gap width. 1 –at the conduction band bottom, E=0, 2 – at the level E=kT (this energy corresponds to the most probable speed of electrons [10, 11, 22]), 3 –at the level E=3kT/2 (there is a middle energy of non-degenerated electron gas [10]).

Comparing results of figures 2, 3 we see that mobility decreases when effective mass increases. Analysis of curves 1,2,4 shows that average mobility is larger than partial mobility at the conduction band bottom (curves 1,4), but less than the partial one for electrons with most probable speed or middle energy (see curves 2,3,4).

It is clear, because when the scattering on the acoustical phonons is being realized the relaxation time falls if electrons energy rises, and contribution of electrons with little energies is more sufficient.

The obtained data for change of average mobility were compared with those from [7]. The results are shown in fig. 4.

In actual energy range the change of mobility strongly depends on the initial BGW. Its average value in actual interval ( $E_g = 17 \text{ meV}$ ) is close to the one at helium temperatures, where it was determined exactly [12-16]. The corresponding result (curve 2 in fig. 4) describes better the hole mobility change than electrons one (compare curves 2 and 4, 2 and 5 in fig. 4).

The pressure evokes deformation of the crystal lattice in BS12. This deformation creates the defects. The scattering on these defects may sufficiently reduce the electron mobility. The common reduction is more than it is possible to expect if the only effective mass change occurs.



Fig 3. The relative change of mobility under pressure: 1, 2, 3 – partial mobility (numeration coincides with the one in fig. 2), 4 – average mobility.



Fig. 4. The change of mobility under pressure: 1,2,3 – the data of this article for  $E_g = 12,17,22$  meV, 4 – holes [7], 5 – electrons [7].

For holes there is another situation. The hole mobility in BS12 is sufficiently less than the one of electrons. This effect may be bound with the interband scattering, when holes from L-band pass to  $\Sigma$ -band of heavy holes [23]. Namely this scattering mechanism severely restricts the hole mobility, the other mechanisms are less important.

In this situation the change of hole mobility under pressure may be well explained by the change of their effective masses.

## Conclusion

According to the obtained results the study of Bi-Sb alloy properties under pressure gives important information about kinetic coefficients and energy spectra of charge carriers in these materials. The scattering mechanisms of electrons and holes may be defined more precisely.

These data have both scientific and practical importance (e.g. for creation of stress sensors).

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## THERMOELECTRIC POWER OF TI-DOPED PbTe MONOCRYSTAL

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#### Abstract

Results of the measurements of thermoelectric properties of thin monocrystal wires of  $Pb_{1-x}Tl_xTe$  (x=0.001 ÷ 0.02, d = 5 ÷ 100 µm) in the temperature region 4,2 ÷ 300 K, which were obtained from solution melt by the filling of quartz capillary with the following crystallization of material are presented. For the samples corresponding to chemical composition with concentration of thallium 0,0025 < x <0,005 double change of the sign of thermoelectric power is observed. In pure samples and samples with thallium concentration more than 1 at.% thermoelectric power is positive in the whole temperature range. Various mechanisms which can lead to observable anomalies, including Kondo-like behavior of a non-magnetic degenerate two-level system are discussed. Obtained experimental results let suppose that the observed anomalies can be interpreted on the basis of model of an impurity with mixed valences.

#### 1. Introduction.

Doping of semiconductor compounds of type  $A_4B_6$  by elements of III group leads to a number of features in their electro physical and optical properties [1-2]. By that is explained the interest to such materials and, in particular, to semiconductor compound  $Pb_{1-x}Tl_xTe$  as to the most striking example in which a lot of unique properties have been observed. Specific action of thallium consists in the following: the thallium impurity generates on the range of the permitted band states of a valence band an impurity band that leads to essential change of density of band states. It leads to essential change of transport coefficients, which are determined by density of states, by the form of the impurity band and by the relative position of the Fermi level [1,2]. On the other hand, thallium is an impurity element of III group in the compounds  $A_4B_6$ , which show a mixed valence [3]. It means that thallium can have the valence from 1 up to 3, and the most unstable is the state with a bivalent impurity. In such case they should dissociate as [4]:

$$2\mathrm{Tl}^{2+} \rightarrow \mathrm{Tl}^{1+} + \mathrm{Tl}^{3+}$$

Theoretical description of that assumes existence of the centers with negative correlation energy U:

$$U_n = (E_{n+1} - E_n) - (E_n - E_{n-1}) < 0,$$

where valence number n takes the values 1, 2, 3.

Theoretically it has been predicted, that the presence of the U-centers can lead to those features in electro physical properties which were observed in the system  $Pb_{1-x}Tl_xTe$  [4]. Such a behavior of an impurity of thallium in PbTe is similar to Kondo effect in metals and should be manifested in particular on the thermoelectric properties of this compound. From this point of view in the presented work an attempt of interpretation of experimental data of the research of thermoelectric properties of Pb<sub>1-x</sub>Tl<sub>x</sub>Te monocrystal wires is undertaken.

#### 2. Experimental results and discussion.

Monocrystal microwires of  $Pb_{1-x}Tl_xTe$  (diameter  $d = 5 \div 100 \ \mu m$ , length  $1 \sim 20 \ sm$ ) with thallium average concentration  $x = 0.001 \div 0.02$  were grown in the following way [5]. In the quartz tube (diameter - 15 mm) initial material with corresponding chemical composition was placed. The bulk material was prepared in the following way. Since pure Tl oxidizes in the air quickly and greatly, it is necessary for a preparation of initial mixtures to use compounds of thallium - in our case TITe. Syntheses of polycrystalline materials (PbTe)<sub>1-x</sub>(TITe)<sub>x</sub> of corresponding compounds were made in the quartz tube in the hydrogen atmosphere. Over the material the bunch of quartz capillaries is situated. The choice of quartz as the material for capillaries is limited by the high temperature of its softening, what must be higher than the melting temperature of material. The tube was evacuated up to residual pressure  $10^{-2} \div 10^{-3}$  Pa and placed in vertical zone furnace, in which the temperature on the whole length of the capillary is the same and higher than the melt temperature of material ( $T_{melt} < T < T_{soft}$ ). After melting of material the capillaries with open lower ends were put down in the melt material. Afterwards in the tube pressure rose under which capillaries were filled by the melting material. Crystallization of melting material was realized directly beginning from soldered ends to open one at the expense of move of furnace (rate of move may be changed and make up several centimeters per hour). The given method of obtaining of monocrystal microwires allows to produce samples with different diameters under the same growth conditions with high structural perfection. The structural quality was tested by X-ray diffraction and Laser Microprobe Mass Analyzer (LAMMA).

The samples for the measurements were prepared in the following mode. The sample of the corresponding diameter was chosen from the set of crystals obtained in that way for carrying out of measurements. As the initial sample has glass isolation, it was preliminary subjected to selective etching in a solution of acid HF. Reliable electrical contact was made using eutectic In-Ga. Measurements have been executed both on samples with different diameters, and on samples of the same diameters. Measurements of temperature were carried out by means of thermocouple Cu - (Cu + 0.04 at % Fe). Such thermocouple makes it possible to carry out experiments with high precision in low temperature region.

In Fig.1, 2 temperature dependences of thermoelectric power of monocrystal microwires of  $Pb_{1-x}Tl_xTe$  are shown. The analysis of temperature dependences of thermoelectric power shows, that in the doped samples thermoelectric power manifested anomalous character - at low temperatures this dependence becomes essentially non monotonic. For  $Pb_{1-x}Tl_xTe$  (x=0,0025; 0,005) thermoelectric power changes the sign twice, and for other compounds on temperature dependence the curve without change of the sign is shown. At higher temperatures (T > 100K) dependence of thermoelectric power vs temperature shows usual behavior, characteristic of

strongly doped lead telluride, and numerical values of thermoelectric power in this region are comparable with the data resulted in [6].

The change of the sign of thermoelectric power in the dependence of concentration of thallium impurity at temperatures above the temperature of liquid nitrogen in lead telluride was observed earlier [7] and was interpreted within the model of features of resonant scattering of carriers. On dependence of thermoelectric power from concentration of thallium the deep minimum downing up to change of its sign [2] is observed. It is known, that in strong degenerated samples the values of the coefficient of thermoelectric power are determined by parameter of dispersion r. For such behavior of thermoelectric power the expression for the parameter of scattering in the conditions of resonant scattering describing domination was proposed in the form:

$$r = \frac{2\mu(\mu - \varepsilon_i)}{(\mu - \varepsilon_i)^2 + (\Gamma/2)^2},$$

where  $\mu$  is chemical potential,  $\varepsilon_i$  is the mid position of the impurity band and  $\Gamma$  its width. The analysis of this formula allows to describe features observed on dependence of thermopower on concentration of an impurity in system Pb<sub>1-x</sub>Tl<sub>x</sub>Te.



Fig.1. Temperature dependences of thermoelectric power of monocrystal wires of  $Pb_{1-x}Tl_xTe$ .



Fig.2. Temperature dependences of thermoelectric power of monocrystal wires of  $Pb_{1-x}Tl_xTe$ .

Theoretical calculations are done and they agreed with experimental results for a lot of  $A_4B_6$  compounds doped with Tl. However as follows from obtained experimental data the change of the sign of thermoelectric power is observed both at high and low temperatures. Furthermore the resonant scattering of carriers is not a process of activation type. It means, that at  $k_0T << \Gamma$  relaxation time does not depend on temperature. Therefore the anomaly behavior of thermoelectric power at low temperatures cannot be explained with features of resonant scattering.

The reason of low temperature changes of the sign of thermoelectric power can be electronphonon drag. It was observed earlier for pure lead telluride at T <20K ( $p = 10^{18} \text{ sm}^{-3}$ ) [8]. However in monocrystal microwires of Pb<sub>1-x</sub>Tl<sub>x</sub>Te where concentration of carriers is more than by the order larger than in samples investigated in [8] electron-phonon drag cannot lead to low temperature change of thermoelectric power sign.

The assumption of the mixed mechanism of scattering of carriers either does not allow explaining the non-monotonic temperature dependence of thermoelectric power.

Another mechanism, enabling an adequate explanation of observed anomalies of temperature dependences of thermoelectric power, is based on the theory of the transport phenomena in large scale non-uniform medium. Large scale non-uniform is possible to count a medium, in which the size of heterogeneity is much greater than the free path lengths in each of phases. In our case it is necessary to understand areas with various values of local kinetic factors.

Qualitative results for effective thermoelectric power for quasi-two-dimensional two-phase thin monocrystal micro wires are obtained:

$$\alpha = \frac{\alpha_1 \sqrt{\sigma_1 \kappa_1} + \alpha_2 \sqrt{\sigma_2 \kappa_2}}{\sqrt{\sigma_1 \kappa_2} + \sqrt{\sigma_2 \kappa_1}},$$

where  $\kappa_1$ ,  $\kappa_2$  are the thermal conductivities of the phases;  $\sigma_1$ ,  $\sigma_1$  are the conductivities of the phases,  $\alpha_1$ ,  $\alpha_2$  are their thermoelectric powers. At thallium concentration in lead telluride corresponding to the beginning of overlapping of Fermi level with Tl-impurity band, small fluctuations in distribution of the impurities should lead to the occurrence of the areas with sharply distinguished transport parameters due to threshold character of resonant scattering. Thus having attributed index 1 for the areas with low impurity concentration (Fermi level outside of Tl-impurity band), and index 2 for the areas with Fermi level in Tl-impurity band we can describe qualitatively abovementioned kinds of temperature dependence of thermoelectric power. Since at low temperatures thermal conductivity has mainly lattice character small fluctuations of the impurity concentration will not considerably affect their values, that is  $\kappa_1 = \kappa_2$  and

$$\alpha = \alpha_1 \left[ 1 + \frac{4}{3} \frac{\mu \Delta}{\Delta^2 + \left(\Gamma/2\right)^2} \left( 1 + \sqrt{\frac{\sigma_1(0)}{\sigma_2(1 + AT)}} \right) \right],$$

where A is an fitting parameter determined from temperature dependences of  $\sigma(T)$  for nonstoichiometry of thin monocrystal wires of PbTe. It is established, that settlement curves

qualitatively reproduce observed kind of temperature dependences of thermoelectric power in the range of low temperatures that testifies for the argumentation of the assumptions made above.

It is necessary to note, that the assumption about large-scale non-uniform medium is based on the experimental results obtained earlier for monocrystals wires of  $Pb_{1-x}Tl_xTe$  [10].

In spite of this it is necessary to mention, that the set of results obtained on massive crystals indicates that the observed anomalies in electrophysical and thermoelectrical properties cannot be explained only by non-uniform distribution of an impurity. The identified anomalies have their intrinsic distinctive features of the given material - lead telluride doped with thallium. Non-uniform distribution of an impurity, which is most obviously shown in the low dimensional systems, can increase (or reduce) only the manifestation of the effects having origin that can to be connected with features of impurity Tl in PbTe, its influence being similar to influence of magnetic impurity in metals.

The analysis of temperature dependences of thermoelectric power of monocrystal wires of  $Pb_{1-x}Tl_xTe$  in the whole range of concentration of a doping impurity at low temperatures shows, that the appearance of the maximum is characteristic. It is known [9], that in systems with magnetic impurity the appearance of low temperature maximum of thermoelectric power is provided by the interaction of the carriers with the magnetic moments of impurities. Isolated Kondo-impurity gives a negative contribution to thermoelectric power and as a first approximation does not depend neither on temperature, nor on concentration of the Kondo-centers. Only the temperature at which thermoelectric power starts to deviate from the behavior characteristic of metals depends on concentration of the impurities. Such picture is observed until the temperature goes down to Kondo temperature where thermoelectric power starts to decrease quickly on the module, tending to zero value at  $T \rightarrow 0K$ .

It is necessary to add, that in investigated monocrystal microwires of  $Pb_{1-x}Tl_xTe$  all the electrophysical properties characteristic of bulk crystals [11] are observed:

- superconductivity with  $T_c > 0.4 \text{ K x} > 0.01$ ;
- starting with  $T = 30 \div 40$  K samples exhibited negative temperature coefficients of resistance down to T = 0.4 K;
- all samples demonstrated negative magnetoresistance at helium temperature.

#### 3. Conclusions.

In the present work the results on research of thermoelectric properties of monocrystal wires of  $Pb_{1-x}Tl_xTe$  (x=0.001  $\div$  0.02, d = 5  $\div$  100 µm) in a wide range of temperatures are presented. The principal task of research was the analysis of the experimentally established features of thermoelectric properties of these systems in the range of low temperature. For all investigated samples at low temperatures anomalies on the temperature dependence of thermoelectric power are observed. Considering features of behavior of thallium impurity in lead telluride and comparing the obtained results with similar for metals with magnetic impurity it is possible to conclude, that the reason for the observed anomalies is charge Kondo effect associated with mixed valence of Tl impurity states, which is manifested in the PbTe.

Similar conclusions about features of doping action of thallium in monocrystals of  $Pb_{1,x}Tl_xTe$  (Tl concentrations up to 1,5 at. %) were made in work [12] on the basis of the executed measurements of thermodynamic and transport properties in low-temperature region. Moreover,
Kondo-type behavior of impurity of thallium in PbTe is the mechanism that allows to explain the anomalous high temperature of superconducting transition in Tl-doped PbTe.

It is necessary to note, that the question on a charging state of thallium in lead telluride remains open in comparison with other impurities of elements of III group [3]. Set of available experimental data on thallium impurity in PbTe is explained on the basis of model of occurrence on the background of the permitted band states of a valence band of a resonant impurity level with high density of states near the valence band [1,2]. It is possible to expect that in connection with growth of interests to compounds  $A_4B_6$  doped with elements of III group in the near future it will be possible by direct experimental methods to establish character of behavior of Tl impurity in PbTe.

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## OPTICAL BIAS EFFECT ON TRANSIENT PHOTOCURRENT IN AMORPHOUS As<sub>2</sub>Se<sub>3</sub>: Sn FILMS

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## Abstract

Optical bias effect on transient photocurrent of  $As_2Se_3$ :  $Sn_x$  (x=0÷1.0 at.%) amorphous films, excited by a monochromatic light pulse with long-wavelength of 0.63 µm was investigated. The relaxation of the photocurrent has been recorded in the wide time interval (from 0.05 up to 25 s) and was determined by capture on the deep acceptor-like traps. In a non-doped sample of  $\alpha$ -As<sub>2</sub>Se<sub>3</sub> the relaxation of the photocurrent weakly depends on a level of optical bias. For the samples with tin impurity, even the low levels of optical bias result in sharp reduction of the photocurrent. The experimental results are discussed in frame of the model of recombination controlled by capture on deep states.

### 1. Introduction

It is known, that in a large time-domain (from 10<sup>-3</sup> up to 10 s) the photocurrent relaxation in amorphous semiconductors is essentially determined by the capture of non-equilibrium carriers on defect and/or impurity deep states, and then due to recombination [1-4]. Results of other studies, based on measurements of the photocurrent in conditions not far from the equilibrium (time-of-light measurements [5-7], modulated photocurrents [8-10]), also indicate these processes and are interpreted in frame of the multiple-trapping model. Nevertheless, these measurements do not specify the well-determined process of deep capture and thus not assume the structured form of the density-of-states distribution with distinct levels of defects [11].

In this paper the studies of transient photocurrent in  $As_2Se_3$ :  $Sn_x$  samples: pure (x=0) and with tin impurity (x~1 ar. %), and various levels of optical bias, are presented. These studies are continuation of our previous work in which the detection of persistent photoconductivity in a- $As_2Se_3$ : Sn, samples associated with the deep states was reported, and also have the aim to clear up this phenomenon by experiments with the optical bias. It is supposed, that owing to quasi-Fermi-level movement, optical bias changes population of these centers and can result in suppression of deep capture and/or increase in the recombination rate [2,12]. Based on the photocurrent relaxation curve analysis obtained for various levels of optical bias it was shown, that the origin of the long-term of photocurrent decay in  $As_2Se_3$ : Sn samples is associated with the special nature of acceptor-like centers induced by tin. These states are characterized by a small value of hole capture cross-section and their density is sufficiently higher.

#### 2. Samples and experimental method

The optical bias effect was measured in amorphous films a-As<sub>2</sub>Se<sub>3</sub>: Sn<sub>x</sub> (x=0÷1.0 at. %), prepared by thermal flash evaporation in vacuum on the glass substrate heated up to 120  $^{0}$ C.

The thin film of a thickness about L~2  $\mu$ m were placed between two sprayed aluminum electrodes, one of which (top) was semi-transparent (the electrode area A~0.56 sm<sup>2</sup>).

The transient photocurrent was excited by a monochromatic light pulse from SPM-2 spectrometer (wavelength  $\lambda$ =0.63 µm, intensity F = (1÷2)•10<sup>13</sup> photon/(cm<sup>2</sup> s), with the spectral resolution  $\Delta\lambda < 20$  nm), and was formed by the electromechanical shutter (time of operation of about 0.02 s). The wavelength of the additional illumination corresponded to the a-As<sub>2</sub>Se<sub>3</sub> optical absorption edge provided homogeneous generation of photo-carriers in bulk of the sample. The light intensity was adjusted by the spectrometer slip width, and controlled by the Ge-photo diode.

The applied level of optical bias was created by an usual incandescent lamp illumination passed through the red filter. The level of optical bias was set by a current in a circuit of the lamp and determined by the value of steady-state photocurrent.

The positive polarity of constant voltage bias of about 2 V was applied to the top electrode (anode). Transient photocurrent was amplified by an electrometer and then recorded by the two-coordinate (X-Y) potentiometer; its operation was synchronized with a pulse of exciting light. The relaxation of the photocurrent was measured at room temperature in the time interval 0.05 - 25 s.

# 3. Experimental results 3.1 Non-doped sample

Fig. 1 illustrates results of measurement of a transient photocurrent in non-doped sample of  $As_2Se_3$  without optical bias (curve 1) and for four consistently increased levels of optical bias (curves 2-5). The appropriate levels of optical bias (in values of steady-state photocurrent  $I_{OB}$ ) are given in explanations of figure 1. Curve 1 in the figure obtained without optical bias, is similar to those obtained earlier for samples  $As_2Se_3$  [13,14]. It is seen that after the light is switched on the photocurrent sharply increases and then at t~1 s achieves saturation. It is usually supposed that in this region of saturation the current is determined by electron-hole pair generation rate and their recombination.

The relaxation of a photocurrent at the moment when the light is switched off and without optical bias also is characterized by fast decay (curve 1 in Fig. 1). The decay time constant  $\tau \sim 0.05$ , 0.15 is close to the reported values obtained in multi-trapping model for a-As<sub>2</sub>Se<sub>3</sub> films [15]. The following curves 2, 3, 4 and 5, situated below, were obtained at the presence of optical bias (I<sub>OB</sub>~2·10<sup>-10</sup>, 4.3·10<sup>-10</sup>, 8·10<sup>-10</sup> and 8·10<sup>-9</sup> A, respectively). They are similar to a curve 1 however the saturating value of photocurrent (near 1 s) is lower. This is in the consent with reduction of the decay of time constant  $\tau$  at illumination and specifies correlation between the photocurrent decay and recombination [4,16,17].

Let's note related to optical bias effect the weak change of a relaxation rate and the form of decay curves on long time (t > 1 s) shown in Fig. 2, when processes of carrier capture and release from deep traps are essential. Curves of photocurrent decay are normalized to it's value at the moment t=0 s, appropriate to termination of the exciting light pulse. For the lowermost curve 5 obtained at the largest intensity of illumination, the relaxation is observed in a time interval limited by noise of measuring installation.

## **3.2 Doped sample**

Results of optical bias effect on transient photocurrent in samples doped with tin impurity (x=1.0 at. %) are presented in Fig. 3 and Fig. 4. At low intensities of additional

illumination and in darkness (curves 1, 2 and 3 in Fig. 3) the impurity influence is opposed to optical bias effect. Really, after the light is switched on the delayed character of transient photocurrent from time and absence of saturation is seen at long times (comparable with an excitation pulse duration t~5 c). Thus, the absolute value of photocurrent is higher than in a non-doped sample.

After light is switched off the decay curves weakly vary in time and, at t>0.05-0.1 s, are characterized by an extended plateau with a very small decay rate (the time constant  $\tau$  is about 1.0-3.0 c). It is persistent photoconductivity effect, which was revealed and described by us in the previous works [14,18].

Photocurrent on this slow portion of a relaxation appreciably decreases at illumination and, already at a small level of optical bias ( $I_{OB}$ ~4.5 x 10<sup>-9</sup> A), the full suppression of effect takes place. Simultaneously to reduction of photocurrent on this portion, there is a reduction of a decay time constant. The fast portion of decay curves (t<0.5 s) as well as in a non-doped sample weakly varies at illumination.

**Fig. 1**. Photocurrent transient recorded in darkness and for four consistently increased levels of optical bias for a non-doped sample of a-As<sub>2</sub>Se<sub>3</sub>. A current of constant bias at a voltage of 2 V in A:  $1 - 8.0 \times 10^{-11}$  (in darkness),  $2 - 2.0 \times 10^{-10}$ ,  $3 - 4.3 \times 10^{-10}$ ,  $4 - 8.0 \times 10^{-10}$ ,  $5 - 8.0 \times 10^{-9}$ .





Fig. 2. Normalized photocurrent decay (after light is switched off), deduced from curves in Fig. 1 numbering by the same manner. Solid lines are result of the best adjustment with stretched exponent. Coincidence of curves 1-4 is observed in the overall time interval.

Thus, distinction between curve Fig. 2 and Fig. 4 is shown in the range of large times (0.1-10 s) and is associated to a portion of a slow relaxation in a sample of a-As<sub>2</sub>Se<sub>3</sub>: Sn. Optical bias dramatically influences the form and decay rate of curves, reduces photocurrent. Only at the initial stage of a relaxation and/or the high optical bias the behavior of transient photocurrent well coincides with the curves in Fig. 2 obtained for a non-doped sample. Limiting value of photocurrent and decay time constant (curve 5) becomes same, as well as in a non-doped sample.



Fig. 4. Normalized photocurrent decay (after light is switched off), deduced from curves in Fig. 3 numbering by the same manner. Solid lines are result of the best adjustment with stretched exponent. Concurrence of curves is observed only at small times t < 0.05 s.

## 4. Relaxation of photocurrent controlled by deep capture

Systematical studies of the optical bias effect on transient photocurrent in amorphous semiconductors have begun from known paper by R. Pandya and E. A. Schiff [20]; it was shown, that for interpretation of the effect, it is necessary to take into account the final population of traps, which changes under optical bias and influences the issue of relaxation. In

papers [21,22] transient photocurrent was measured in thick (up to 10  $\mu$ m) As<sub>2</sub>Se<sub>3</sub> and As<sub>2</sub>Se<sub>3</sub>: Sn layers in the time-of-flight mode and at the higher levels of optical bias. It was shown that under these conditions the drift mobility essentially increases but, vice-versa, the recombination time decreases. These studies were limited by small times (from 10<sup>-5</sup> up to 10<sup>-1</sup>s) in which only the fundamental band tail has been revealed in experiment.

The results presented in our paper were obtained in the wide time interval (up to 20 s) and mainly related to processes of capture and recombination on deep states of defects. Hence, the model which would examine photocurrent relaxation on large times and which would take into account these states is necessary for the analysis of the obtained results. Recently such model was proposed by V. I. Arkhipov [23]. It was used for analysis of the slow photocurrent decay in amorphous  $As_2S_3$  chalcogenide films doped with ions of praseodymium [23].

It was assumed that due to a high density of gap states in amorphous semiconductors the majority of non-equilibrium charge carriers are localized already at the first time of relaxation. Therefore, decay of photocurrent on large times is determined by the dynamics change of captured hole density within the quasi-continuously distributed localized states. For bimolecular mode of recombination (typical for  $As_2Se_3$  at room temperature [7,24]) the kinetic equation takes the form

$$\frac{dp(t)}{dt} = -Rp_c(t)p(t), \qquad (1)$$

where  $p_c$  is the free holes concentration, R is the recombination's constant, p is the full hole concentration. Then it was assumed that in the experimental time interval t >1 s the slow relaxation of a photocurrent is completely controlled by carrier release from the localized states above the quasi-Fermi-level and described by expression [25]:

$$p(t) = \int_{0}^{\infty} dE \exp\left(-\frac{t}{\tau_{e}}\right) g(E) \approx \int_{kT \ln(vt)}^{\infty} dE g(E) .$$
(2)

Here E is the energy of the localized state,  $\tau = v^{-1} \exp(E/kT)$  is the time constant of thermal release processes, g(E) is the density-of-states distribution (DOS-function), k is Boltzmann's constant, T is the temperature and v is the typical phonon frequency.

Substitution (2) in (1) results in expression for time dependence of photocurrent decay I(t):

$$I(t) = Ae\left(\frac{\mu_c}{R}\right)F\frac{kT}{t}\left[\int_{kT\ln(vt)}^{\infty} dEg(E)\right]^{-1}g(kT\ln(vt)), \qquad (3)$$

(*e* is the elementary charge,  $\mu_c$  is the mobility of charge carriers in the band of conducting states). As well as in the model describing measurements of phase shift [8,9], it is supposed that the emission rate of captured carriers from deep traps exponentially decreases with increase of energy and restricts to rate of the relaxation process. Nevertheless it is seen that as against result, which is turning out at measurement of modulated photocurrents, this dependence is not related directly to DOS-function.

In Fig. 5 the I(t) x t vs. kTln(vt) diagrams for non-doped (a) and doped (b) samples, along with model curves predicted by equation (3) (solid lines), are presented. In calculations the ratio ( $\mu_C/R$ ) was used as adjusting parameter and DOS-function was chosen as quasi-continuously distributed traps of exponential tail and Gauss-form band of deep traps:

$$g(E) = \frac{N_t}{E_0} \exp\left(-\frac{E}{E_0}\right) + \frac{N_d}{\sqrt{2\pi\sigma}} \exp\left[-\frac{(E - E_d)^2}{2\sigma^2}\right].$$
 (4)



Fig. 5. I (t) x t diagrams obtained for sample  $As_2Se_3$  (a) and  $As_2Se_3$ : Sn (b) samples from the curves presented in Fig. 2 and 4, accordingly. Numbering of curves corresponds to Fig. 1 and 3. Solid lines are calculations based on equations (3) and (4) (see text for details).

with the  $N_t$ ,  $E_0$  parameters of an exponentially band tail and  $N_d$ ,  $E_d$ ,  $\sigma$ , are parameters of a band of deep trap distributions listed in Table 1.

Without optical bias and for a non-doped sample product I (t) x t characterizes the effective density-of-states (curve 1) and has a bump features with a maximum at  $E_d \sim 0.65$  eV, which corresponds to characteristic time constant  $\tau \sim 0.1$  s obtained for this sample.

Measurements of the modulated currents [26] and transient photoconductivity [3] also result in similar peak near 0.7 eV. It seems obvious that under optical bias the effective concentration of traps is suppressed. It is in accordance with the conclusion based on analysis of a transient photocurrent. Curves for higher levels of optical bias show similar dependence.

<u>Table 1</u>. The parameters of the deep centers obtained by modeling of experimental data I (t) x t in Fig. 5 with the DOS-function described by formula (4) T=289 K, F= $10^4$  V/cm. The steady-state photocurrent for curves 2-5 characterizes a level of optical bias.

[Sn],	crv.	I <sub>dark</sub> , A	I <sub>OB</sub> , A	$\mu_{C}/R \cdot 10^{8}$ ,	$N_t$ , cm <sup>-3</sup>	N <sub>d</sub> , cm <sup>-3</sup>	E <sub>d</sub> , eV	$\sigma$ , eV
at. %	numb			$cm^{-1}V^{-1}$				
	er							
0.0	1	8e-11		0.0065	5e19	6e15	0.639	0.038
	2		2e-10	0.005	5e19	5e15	0.636	0.036
	3		4.3e-10	0.0068	10e20	1e16	0.648	0.035
	4		8e-10	0.003	1.5e19	1.5e15	0.632	0.034
	5		8e-9	0.0008	2e20	1e16	0.623	0.03
1.0	1	1.76e-9		1.35	4e19	1.2e18	0.875	0.079
	2		2.5e-9	1.35	4e19	1.2e18	0.924	0.09
	3		3e-9	1.1	3.5e19	1.2e18	0.954	0.1
	4		4e-9	1.0	5e19	1.2e18	0.968	0.102
	5		4.5e-9	0.5	1e19	1e17	1.06	0.134

In samples with tin impurity the form of curves specifies a band of traps, their concentration increases towards mid-gap according to the exponential law and also falls with increase of the optical bias level.

## 6. Discussion

The observed features of a transient photocurrent in As<sub>2</sub>Se<sub>3</sub> amorphous films, that are associated with doping, have the general enough character and are not restricted to material of a chalcogenide film and/or impurity type (Sn), chosen in our experiment. For example, in As<sub>2</sub>S<sub>3</sub> amorphous films doped with rare earth ions (Pr) [23] the shift of DOS peak to large energies and substantial increase of characteristic decay time constant of the photocurrent relaxation were also revealed. Besides the shift of deep traps distribution into mid-gap was observed in amorphous silicon too [27]. Results obtained in the present work at additional illuminations allow us to look after the occurrence of features in a photocurrent transient and to tie them with a form of DOS-distribution. So the suppression of a maximum on I(t) x t diagrams in a non-doped sample and removal of a plateau accompanying it in curves of Fig. 5a towards the smaller energy (curves 2-5) can be related to increase in the number of recombination centers due to capture of non-equilibrium electrons on gap states [16,17]. The evaluated concentration  $N_d \sim 10^{16}$  cm<sup>-3</sup>, energy position of DOS peak  $E_d \sim 0.62$ -0.64 eV and the width of this peak  $\sigma \sim 0.034$  eV seem typical for the deep centers in a-As<sub>2</sub>Se<sub>3</sub>, - the same as also bimolecular character of recombination. It is proved by coincidence of modeling curves with the experimental points.

Situation is different in samples with tin impurity: the trend of curve I (t) x t in Fig. 5b is monotonic and does not reveal a maximum, as in a case shown in Fig. 5a. At the same

concentration of the tail traps  $N_t \sim 10^{19}$  cm<sup>-3</sup> the concentration of deep centers  $N_d \sim 10^{18}$  cm<sup>-3</sup> is essentially larger; significantly deeply and widely a band of the deep states (see Table 1). Along with the enhancement of optical bias level the energy position of the defect band is displaced deep into the gap, which is directly opposite to the considered for As<sub>2</sub>Se<sub>3</sub> sample; the value of this shift (~0.13 eV) is also large. Despite significant reduction in recombination constants we think that in this case the mechanism of photocurrent relaxation is controlled by deep capture too as experimental points well coincide with modeling curves. Based on estimations of density-of-states distribution in Fig. 5 and the parameters listed in Table 1 it is possible to assume that in doped samples despite a higher concentration of deep states the suppression of deep capture takes place. Really the effective density of states can be presented as

$$g(E)_{eff} = g(E)[1 - f(E)] = g(E) \left[ 1 - \frac{\tau_e}{\tau_e + \tau_c} \right] = g(E) \frac{\tau_c}{\tau_e + \tau_c},$$
(5)

where  $\tau_c$  is a capture time constant, f(E) characterizes a population of deep trap. It is seen that in a case  $\tau_c <<\tau_e$  the optical bias can suppress effective density of states. It seems this case is realized in a non-doped sample. On the contrary, for a doped sample it is possible to assume that  $\tau_c >>\tau_e$  and effective density-of-states g(E)<sub>eff</sub> =g(E) doesn't depend at all on a degree of the deep state filling.

The large capture time  $\tau_c$  can be associated with a special nature of the centers induced by tin impurity, for example, such as pairs (Sn<sup>2+</sup>-Se<sub>2</sub>); these centers can be positively charged to have repulsive Coulomb potential for holes and therefore, - the small value of capture cross-section. This conclusion inferred from X-rays diffraction [28] and the Measbauer's spectra studies [29]. The central result of these studies is that in the samples with tin impurity Se atoms form tetrahedral coordinated structural units such as Sn (Se<sub>1/2</sub>)<sub>4</sub> and can promote occurrence of the new acceptor-like deep centers.

Certainly, the mechanism of shift of deep state band under optical bias is not so obvious. We believe that for its explanation the theoretical representations advanced in [30] can be used. According to these representations introduction of compensating impurity should result in formation in the band gap of semiconductor of some additional allowed states caused by increase of amplitude of an impurity potential fluctuations. These states are near the band edges and can result in shift of effective activation energy  $E_a$  to mobility edge:

$$E_a \approx E_t - \Delta E \quad . \tag{6}$$

Here  $\Delta E \sim Ke^2 (NR^3)^{1/2} / (\epsilon R)$  is the depth of potential well formed by root-mean-square fluctuation of an impurity concentration with characteristic size R (N is the average concentration, K is a constant and  $\epsilon$  is the dielectric permeability of the semiconductor).

It is obvious, that the amplitude of fluctuations and the largest depth of potential wells are limited by size of screening radius:  $R \le R_s$ . As the amplitude of fluctuations decreases with increase of the concentration of charge carriers, there will be a progressing reduction of effective density-of-states and shift of activation energy deep into the gap, that is seen from Fig. 5b. In strongly compensated semiconductors reduction of radius  $R_s$  ( $\sim N^{1/3}/p^{2/3}$ ) occurs by far faster, than at screening by free carriers. Estimations show that at typical values of N~10<sup>18</sup> cm<sup>-3</sup> and concentration of the photo-excited carriers p (= $G\tau_R \sim 10^{15}$  cm<sup>-3</sup>,  $R_s$  can be about of 100 nm; appropriate values  $\Delta E$  make 0.1 eV, that coincides with the found shift of DOS distribution for a doped sample. Besides, modulation of band edges by an impurity potential fluctuations in a doped sample results in a strong reductions of recombination's constant

 $R_{eff}$ =Rexp(- $\Delta E$ ) [31]; the appreciated values of  $\mu_C/R$  in samples As<sub>2</sub>Se<sub>3</sub>: Sn<sub>1.0</sub> more than 100 times exceed these values in As<sub>2</sub>Se<sub>3</sub> sample and also decrease at additional illumination (see Table 1). As a result in a doped sample the trend of curve I (t) x t curves is monotonic and does not reveal a maximum as in a case shown in Fig. 5a for a non-doped sample. The calculations reported in [23] show, that a plateau corresponding to hyperbolic law of a photocurrent decay, and seen in this figure, can not be observed at all even if upper limit of a relaxation recording times is indefinitely large.

Thus, the examined model allows us to explain the slow term of a photocurrent decay observed in a doped sample, to tie shift of a maximum of density-of-states distribution at additional illumination by reduction of amplitude of a potential fluctuations. It essentially differs from the model of quasi-Fermi-level movement, which is usually used at interpretation of experiments with optical bias. Estimations show, that the maximal displacement  $\Delta E_{Fp}$ =kTln ( $I_{OB}/I_{dark}$ ) at the maximal illumination in our experiment ( $I_{OB}\sim10^{-9}$  A) makes only 0.03 eV whereas for an explanation of the observed DOS shifts the steady-state photocurrent must be larger ( $\sim10^{-8}$  A). The found out the dependences of a photocurrent relaxation rate on intensity of additional illuminations and the energy shift of DOS-distribution in doped samples As<sub>2</sub>Se<sub>3</sub>: Sn make this model in many respects similar to model of an activation barriers, offered for an explanation of a lot of phenomena as persistent photoconductivity [30,32], relaxation of the energy levels of deep states [33,34] and recently, - the low-frequency 1/f noise in amorphous a-Si: H films [35,36].

## 7. Conclusions

Experimental data obtained in the present work show that the characteristic time constant of carrier capture on deep traps is increased at doping of sample and determines the rate of recombination. Finally it results in occurrence of slow components in photocurrent relaxation related to phenomenon of persistent photoconductivity.

Trend of curves I (t) x t shows that position of a maximum of DOS-distribution changes at doping of samples with tin impurity and is determined by screening processes of potential fluctuations by excess charge carriers appearing at additional illumination. In non-doped sample optical bias only insignificantly shifts these distributions to the band edge.

The analysis of the photocurrent relaxation curve carried out within the model of recombination, which is controlled by deep capture allows us to estimate a number of the important characteristics of a material and to tie them with parameters of DOS distribution.

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## METHOD OF KRAMERS-KRONIG: ANALYSIS OF OPTICAL FUNCTIONS OF HIGH-TEMPERATURE SUPERCONDUCTOR La<sub>2</sub>CuO<sub>4</sub>

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## Abstract

The full complex of fundamental optical functions parallel and perpendicular to the **c** axis of single crystals LaCuO<sub>4</sub> is determined at 293 K (0.1 - 16 eV) and 80 K (1-5 eV) from Kramers-Kronig analysis of reflectivity data. Strong anisotropy of spectra obtained is observed.

## Introduction

One of primary objectives of superconductivity research has been to raise the transition temperature  $T_c$ . It was established [1] that in the range 20-40 K  $T_c$  occurs for system  $La_{2-x}M_xCuO_{4-y}$  with M=Ba, Ca, Sr. A schematic representation of the phase diagram has been presented in [2].

At high temperature these materials are in the body-centered I4/mm K<sub>2</sub>NiF<sub>4</sub> structure [3]. When the temperature is lowered below 500 K LaCuO<sub>4</sub> transforms to a single-face-centered orthorhombic  $D_{2h}^{I8}$  structure [4]. But its structure is only a slight distortion ( $\approx 1\%$  difference between a and b) of the K<sub>2</sub>NiF<sub>4</sub> tetragonal structure. Existence of a lower-symmetry structure at low temperature is also possible [5].

The parameters of the lattice are determined in [4-5]. LaCuO<sub>4</sub> exhibits strong anisotropy behavior. In this material Cu-O<sub>2</sub> layers are present, which form the a-b planes. A series of electronic structure calculations have been carried out [6-9]. The results of these calculations are compared in [10] with the experimental data.

## **Optical measurements**

The results of numerous optical experiments have been reported previously (see review [10]). Photoemission was investigated in [11]. Mid- infrared absorption (0.1-1.2 eV, 10 K) is described in [12]. The Raman spectra were obtained in [13-14]. The analysis of ellipsometric data was executed in [15] at room temperature from 0.7 to 4.9 eV

The big number of articles are devoted to investigation of reflectivity spectra of LaCuO<sub>4</sub> crystals. However most of the earlier optical studies on high-T<sub>c</sub> cuprate La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> materials have been carried out on ceramic polycrystallin samples, as in [16,19] and other papers (see references in [20]).

Sometimes the flat surface was obtained by polishing with Al<sub>2</sub>O<sub>3</sub> powder which was sufficient for optical measurements in the wavelength range  $\lambda \ge 300$  Ű. The growing of large

qualitative monocrystals allows to carry out measurements in polarized light ( $\mathbf{E} \parallel \mathbf{c}$  and  $\mathbf{E} \perp \mathbf{c}$ ).

Optical reflectivity spectra of  $LaCuO_4$  have been measured over a wide spectral range (0.1-40 eV [21], 0.004-35 eV [22]), as well as in visible region (0.3-6 eV [20]) however only at room temperature.

The difference between the two polarizations is significant except in the very highenergy region. The most intensive structures were observed in LaCuO<sub>4</sub> in region 6-9 eV. A very weak peak at approximately 2 eV was discovered in the  $E \perp c$  spectrum in [19,21]. Strong anisotropy is observed in [15]. For  $E \parallel c$  the optical spectra are nearly featureless, while for  $E \perp c$  there is a sharp peak in  $Im(\varepsilon)$ .

The reflectivity spectra of LaCuO<sub>4</sub> at liquid nitrogen temperature ( $\sim 6^{\circ}$  incident) over an energy range 1 to 5 eV were obtained using DFS-12 monochromator and a Glan-Thomson polarizing prism, with high resolution (1nm/mm) and accuracy (about 0.03%) [24]. The light source was a 200 W xenon lamp and a 100 W galogen lamp. Samples were cooled by liquid nitrogen through a copper block.

The spectra *R* have been measured at 293 K and 80 K in detail. Reflectivity spectra of the sample similar in composite to LaCuO<sub>4</sub> have nonpolarized step at 1.7 eV, principal maximum at 2.08 eV ( $E\perp c$ ), step at ~2.98 eV and minimum at 3.6 eV ( $E\perp c$ ) and also a broad step at 2.4 eV ( $E\parallel c$ ). Increasing of temperature from 293 to 80 K transforms the step at 2.4 eV into clear-cut maximum at 2.36 eV.

## **Calculations of optical functions**

Kramers-Kronig relationships [25,26] were used in [15] with the aim of calculations of reflectivity *R* from experimental  $\varepsilon_{l}$ ,  $\varepsilon_{2}$ . On the contrary in [21] Kramers-Kronig transformations allowed to calculate from known *R* the effective electron density and the imaginary part of the dielecrtic constant, which indicates that the damage on the sample surface suffered by polishing is not serious. The value of optical conductivity  $\sigma$  was calculated in this work. The comparison between results obtained experimentally and those calculated from band theory [8] was carried out.

Our problem was to obtain the set of majority of known optical functions for polarized light ( $\mathbf{E} \| \mathbf{c}$  and  $\mathbf{E} \perp \mathbf{c}$ ). Using Kramers-Kronig analysis, basing on our experimental results [24] and taking into account the data of article [22] the full complex, containing fourteen optical functions was calculated over an energy interval 0.1- 16 eV at 293 K.

In this work we examine the following functions: reflection coefficient *R*, absorption coefficient  $\mu$ , real ( $\varepsilon_1$ ) and imaginary ( $\varepsilon_2$ ) parts of permittivity, refractive index *n*, absorption index *k*, functions of bulk ( $-Im \varepsilon^{-1}$ ) and surface ( $-Im (\varepsilon+1)^{-1}$ ) plasmons, effective number of valence electron  $n_{\rm ef}$ , effective permittivity  $\varepsilon_{ef}$  and differential functions  $\alpha$ ,  $\beta$ . All these functions are represented in Figs 1-6.

The peculiarities of function *R* are discribed earlier in [24]. The spectra of  $\mu$  are very similar to *R*. The maximal value of  $\mu$  is observed at 6-9 eV. The functions *n*,  $\varepsilon_1$  are correlate with the spectrum of *R* in interval 0.1- 3 eV and fall off steaply at hv > 3 eV. The spectra of *k*,  $\varepsilon_2$  have a marked difference from *R* at hv > 5 eV.

The functions of bulk and surface plasmons have noticeable structures at energies 7-9 eV and 11-13 eV respectively. The functions  $n_{ef}$ ,  $\varepsilon_{ef}$  are monotone and effective permittivity attained saturation at 16 eV. The differential function  $\alpha$  descends monotonically and has very





Fig. 1-6. Optical functions  $R, \mu; \varepsilon_l, \varepsilon_2; n, k; -Im\varepsilon^{-l}, -Im(\varepsilon+1)^{-l}; n_{ef}, \varepsilon_{ef}; \alpha, \beta$  at temperature 293 K for polarization  $\mathbf{E} \parallel \mathbf{c}$  (full line) and polarization  $\mathbf{E} \perp \mathbf{c}$  (dashed line).



Fig. 7-10. Optical functions *R*, *n*,  $\varepsilon_1$  and *k*,  $\mu$ ,  $\varepsilon_2$  at temperature 80 K for polarization  $\mathbf{E} \parallel \mathbf{c}$  (top) and polarization  $\mathbf{E} \perp \mathbf{c}$  (bottom).

Fig.7-10 illustrate the results obtained at 80 K. We examined functions R, n,  $\varepsilon_1$  and k,  $\mu$ ,  $\varepsilon_2$  in the range 1-5 eV. The functions n and  $\varepsilon_1$  are similar to those of R only in case of **E** $\perp$ **c**. All functions have noticeble structures at energies  $\approx 2$  eV, however maxima of n,  $\varepsilon_1$  are shifted in the region of smaller energies.

In case of  $\mathbf{E} \| \mathbf{c}$  we observe very weak structures at  $hv \cong 2-2,5$  eV, the half of enumerated functions have not clear maxima. So, strong anisotropy is observed for optical spectra of superconductor LaCuO<sub>4</sub>. The results obtained in this work may be useful in practical aims and for determination of the origin of optical transition in LaCuO<sub>4</sub> in the light of the theoretical predictions.

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## LUMINESCENCE MECHANISM OF HIGHLY EFFICIENT YAG AND TAG PHOSPHORS

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## Abstract

The highly efficient yttrium aluminum garnet ( $Y_3Al_5O_{12}$  or YAG) and terbium aluminum garnet ( $Tb_3Al_5O_{12}$  or TAG) were prepared by solid state reaction (SSR). Particle distribution was very narrow and homogenous by using multilevel sieve after chemical route. Luminescence properties were improved and optimized by co-doping TAG with 2 activators:  $Ce^{3+}$  and  $Eu^{3+}$ . Introducing  $Eu^{3+}$  in the host lattice of TAG: Ce is more effective than in YAG:Ce. Luminescence mechanism and the role of Tb in the host lattice as a sensitizer are discussed.

#### Introduction

The idea of a white light emitting diode (LED) seems not to be inherently unusual or surprising. It was not until the recent successful creation of high frequency light LEDs in the blue/ultraviolet region when the white LED made its debut. With the perspective of a highly efficient, cold light source, the LED market will have an enormous growth and the white LED will be a likely candidate for the replacement of the light bulb once production costs fall as the technology advances. The first commercially available white LED based on phosphors was produced by Nichia Co., which was also first to manage to make the blue LED. Nichia used a blue light emitting Gallium Indium Nitride and coated the chip with yellow fluorescent phosphor Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>: Ce, well known now as (YAG: Ce). A little later another yellow phosphor Tb<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>: Ce (TAG: Ce) was also used by OSRAM Co with GaInN chip for white light production. YAG and TAG, activated with trivalent cerium, have been found to be efficient phosphors for converting the blue LED radiation into a very broad yellow emission band. The yellow emission from YAG: Ce and TAG: Ce are intense enough to complement the residual blue light which escapes through the phosphor in order to produce a white light. By far, YAG: Ce and TAG: Ce have been the most excellent phosphors satisfactorily applied in white phosphor-based LED commercial market. Therefore, any

improvement in the luminescence of YAG: Ce and TAG: Ce is extremely valuable to raise the light efficiency for different applications.

Usually these TAG: Ce and YAG:Ce phosphors are synthesized by solid state reaction (SSR) method and they have the similar properties. We also used this SSR method, because the phosphors with large-size particles from SSR show a more intense luminescence than those with small-size particles from other methods.

The aim of this study is to modify the sample preparation, to investigate the phosphors properties and luminescence mechanism of highly efficient YAG and TAG samples and to improve and optimize the luminescence parameters.

## **Experimental details**

The samples TAG: Ce and YAG: Ce as well as (Y, Tb) AG: Ce phosphors were synthesized by SSR in Korea Advanced Institute of Technology (KAIST) [1]. In order to synthesize TAG: Ce and YAG:Ce phosphor, high purity yttrium oxide ( $Y_2O_3$ ), aluminum oxide ( $Al_2O_3$ ), terbium oxide ( $Tb_4O_7$ ), and cerium oxide (CeO<sub>2</sub>) were used as raw materials. They were mixed thoroughly by using ethanol as a solvent for mixing. Generally, sintering temperature and reaction time are two important factors that affect the crystallization and luminescence intensity. In our case raw materials were fired at 1500° C for 5 hours. After these procedures, the phosphors were yellow in color, due to presence of the Ce<sup>3+</sup> ion in the garnet structure.

*X-ray diffraction measurement* – The crystal structures of the prepared samples were determined by X-ray diffraction measurement using goniometer (Rigaku, D/max- C(3kw) with Cu- K $\alpha$  ( $\lambda$  = 1.5418 Å) at 40 kV and 45 mA. The scan rate was 3 °/min and covered the range between 10° and 80°.

**Photoluminescence (PL) measurement** – In order to investigate the optical properties, PL was measured by using xenon lamp (500 W) and DARSA system. Measurement was done at  $\lambda_{exc} = 450$  nm.

*Morphology and size measurement* – For observation of the particle size and morphology, SEM micrographs of phosphor powders were taken by using SEM (Philips, XLFSEG). In order to control the particles size of the phosphor the laser diffraction was carried out using HELOS particle size analysis system.

## **Results and discussion**

Some fragments of SEM images of TAG: Ce, (Y,Tb)AG:Ce, and YAG:Ce phosphor powders are presented in fig.1. Qualitatively the particle sizes of TAG: Ce phosphor are larger



than those of the YAG:Ce phosphor prepared in the same conditions.

Fig.1. SEM images of (a) TAG: Ce, (b) (Y,Tb)AG:Ce and (c) YAG:Ce

For quantitative analysis of particle dimensions, the special method of the laser diffraction was carried out using HELOS particle size analysis system. The comparative results are shown in fig.2.



Fig.2. Real particle distribution in solid state reaction for YAG (a) and TAG (b) phosphors

For both YAG and TAG phosphors, the particle distribution is relatively large with maximum at 6 and 8 micrometers, respectively. Moreover, the PL emission intensity of TAG: Ce phosphor is stronger than that of YAG:Ce phosphor. These two results are consistent with the well known fact that as phosphor powder size becomes larger, PL emission property becomes better [2].



Fig.3. Influence of particle size on luminescence intensity

Unfortunately, the large and non-homogenous particle distribution has some disadvantages in the LED application. First of all, the particles with large size dispersion have different quantum efficiency and different luminescence. Secondly, different particles have non-homogenous distribution in LED packaging that makes worse the packaging process and decrease the device luminescence. It is demonstrated in the following model (fig.4)



Fig.4. Schematic presentation the LED device with non-homogenous particle distribution.

For obtaining of the phosphors with homogenous narrow particle distribution we separated phosphors by particle sizes using the multilevel sieves after chemical route. The basic principle of this construction is presented in fig.5. The distinctive feature is that upper sieve has a 2  $\mu$ m more grid than lower one.



Fig.5 Separation of phosphors with multilevel sieves

Due to this process, the homogenous phosphors with optimized particle size introduce in LED, and the final device efficiency increases by about 15-20%.

Fig. 6 shows X-ray diffraction patterns of synthesized phosphors. These results indicate that other intermediate phases such as YAP and YAM were entirely transformed at  $1500^{\circ}$ C into YAG. YAG:Ce and TAG: Ce have the same crystal structure which is garnet with a different lattice parameter: lattice parameter of Tb<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> is 12.074 Å and that of Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> is 12.01 Å [3].



**Fig.6**. X-ray diffraction patterns of YAG:Ce and TAG: Ce phosphors



The unit cell of garnet structure is shown in fig.7.

In garnet structure, there are 24 dodecahedral sites, 16 octahedral sites, and 24 tetrahedral sites.  $Tb^{3+}$  ions and  $Y^{3+}$  ions are located in dodecahedral sites [3]. W.W. Holloway et al. [4] reported that substitution by larger ions in the  $Y^{3+}$  sites shifted the emission peak to a longer wavelength while larger ions in the  $Al^{3+}$  sites shifted the emission peak to a shorter wavelength. Substitution by larger ion of Y sites increases the deviation of cubic component of the crystal field. Then excitation occurs at lower energy and emission band shifts to a longer wavelength region [5]. We can verify this emission band shifts in Fig. 8. Theoretically, compared with YAG:Ce, the spectrum of the TAG: Ce is slightly shifted to the red, because of reduced local symmetry. The ionic radius of  $Tb^{3+}$  (1.18 Å) is a little bigger than  $Y^{3+}$  (1.16 Å). However, this shift is not sufficient to compensate for lack of a red component.





**Fig.8.** PL emission spectra of (a) TAG: Ce, (b) (Y,Tb)AG:Ce and (c) YAG:Ce phosphors

**Fig. 9**. PL excitation spectra of (a) TAG: Ce, (b), (Y, Tb)AG:Ce and (c) YAG:Ce phosphors

Figures 8 and 9 show the PL emission and excitation spectra of TAG: Ce, (Y,Tb)AG:Ce, and YAG:Ce phosphor. Emission spectra are under 450 nm excitation. The maximum emission peaks of TAG: Ce, (Y,Tb)AG:Ce, and YAG:Ce phosphor are at 552.5 nm, 545.5 nm, and 538nm, respectively. A broad yellow emission of YAG:Ce phosphor is due to  $5d\rightarrow4f$  transition of Ce<sup>3+</sup> ion. Usually the emission consists of a broad band with two peaks in the long-wavelength region of ultraviolet. Since the ground state of the Ce<sup>3+</sup> ion is a doublet ( ${}^{2}F_{5/2}$  and  ${}^{2}F_{7/2}$ , fig. 10) with a separation of about 2000 cm<sup>-1</sup>, Ce<sup>3+</sup> emission band is expected to show two peaks. This doublet character of the emission band depends on temperature and Ce<sup>3+</sup> concentration and is not always observed [5]. In this fig. 8, we can verify only one emission band in visible range.



Spin-orbital coupling

**Fig.10**. A simplified energy level scheme of the  $Ce^{3+}$  ion  $(4f^{1})$  [5]

Fig.10 shows a simplified 5d energy level scheme of  $Ce^{3+}$  ion in the garnet structure. Since excitation band of  $Ce^{3+}$  ion in YAG host material is at around 450 nm, we used 450 nm blue light excitation source, and then we measured PL spectra in 480 nm ~ 780 nm region. In garnet structure crystal field splitting of <sup>2</sup>D level of  $Ce^{3+}$  ion is large [5]. 4f  $\rightarrow$ 5d band difference corresponds to the blue light. From fig.8 TAG: Ce as well as YAG:Ce shows a broad band emission. In this case, the emission is also due to the 5d $\rightarrow$ 4f transition of Ce<sup>3+</sup> ion. This Ce<sup>3+</sup> emission in the two yellow phosphors is in the green and red region due to the crystal field effect [6].

Fig. 9 shows the difference between PL excitation spectrum of TAG: Ce and that of YAG:Ce phosphor. The difference is remarkable in the ultraviolet region. Fortunately, in blue spectral region, two phosphors have the same excitation spectra, so that we can apply both these two phosphors to the white emitting light source using blue emitting LEDs. However, any improvement in the luminescence of these phosphors is extremely valuable to raise the light efficiency for different applications. In order to obtain white LED with high color rendering index (CRI), a separated red light source with secondary phosphor emitting at red region will work. Therefore, it is like to achieve the objective by co-doping Ce<sup>3+</sup> and other

rare earth ions into YAG and TAG phosphors. Red emission is found from a number of rare earth ion activators, such as trivalent Eu (at 590 and 610 nm), Sm (at 616 nm), or Pr (at 611 nm). All of them originate from f–f transitions. Search is underway in finding suitable ions for co-doping with Ce to increase the red component to improve the CRI of white light. Using double Eu-Ce or Sm-Ce activation in YAG phosphor does not seem very fruitful, because it only diminishes the Ce luminescence, but using them in TAG could increase essentially the luminescence and improve CRI. In combination Eu-Tb-Ce terbium plays the role of sensitizer, it absorbs the exciting radiation from the LED and subsequently transfers this energy to Eu and Ce. Moreover, one additional way of transfer energy is possible: the radiation transitions in Tb may excite directly the neighboring Eu and Ce atoms. In such case, Tb<sup>3+</sup> in TAG does not serve as a doping element but becomes a part of the host structure. After migration in the Tb sublattice the activation energy is transferred from Tb<sup>3+</sup> ( ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ ) to a Eu<sup>3+</sup> activator ( ${}^{7}F_{J} \rightarrow {}^{5}D_{J}$ ). This part of the process was demonstrated for the single-doped case of TAG:Eu in [7]. The luminescence mechanism could be understood from energy level diagram (Fig.11) and quantitatively is confirmed by 3-level model for energy transfer [8,9]



Fig.11. Luminescence mechanism in TAG:Eu,Ce

The common way to improve the emission spectra of lighting devices is co-activation of the conversion phosphors, for example with  $Eu^{3+}$ , which shows an intense line emission in the

red. A codoping with  $\text{Sm}^{3+}$ ,  $\text{Pr}^{3+}$  or  $\text{Eu}^{3+}$  looks very fruitful for improvement of luminescence properties of YAG:Ce and TAG: Ce. The luminescence is more intense when the gap between the excited state and the more energetic component of the ground state multiplet, is larger. This explains the prominent role played by  $\text{Eu}^{3+}$  as co-activator. Introducing  $\text{Eu}^{3+}$  in the host lattice of TAG: Ce is more effective than in YAG:Ce. When  $\text{Eu}^{3+}$  is introduced in YAG, the part of exciting LED energy will excite the  $\text{Eu}^{3+}$  ions and reduce the  $\text{Ce}^{3+}$  excitation, that decrease the luminescence intensity. In the case of TAG, Tb<sup>3</sup> transfers its energy to Ce<sup>3+</sup> and  $\text{Eu}^{3+}$  and can be used as a sensitizer. In addition, one new luminescent mechanism can exist when Tb luminescence excites direct Ce<sup>3+</sup> and Eu<sup>3+</sup>. The total luminescence increases and red shift appears, that improves CRI and CIE. It is very important to optimize the concentrations of activators and co-activator to improve the properties. TAG seems to be more perspective than YAG in the white light devices

## Conclusions

In this study, we have investigated the PL properties and luminescent mechanism of TAG: Ce and YAG: Ce phosphors. They have similar structure, and the properties are expected to be similar and determined by Ce doping. In TAG: Ce and YAG:Ce phosphors, there are excitation bands in blue spectral region and it means that the yellow TAG: Ce and YAG:Ce phosphors can be good candidate materials for the application of white emitting light source using blue emitting LEDs.

Since  $Tb^{3+}$  ion is larger than  $Y^{3+}$  ion, crystal field splitting of 5d energy level of  $Ce^{3+}$  ion is larger in TAG: Ce phosphor. Therefore emission band shifts to a longer wavelength, so white emitting light source using blue emitting LEDs and TAG: Ce phosphor can overcome weak red emission intensity of that using blue emitting LEDs and YAG:Ce phosphor. In the case of using TAG: Ce phosphor to fabricate white emitting light source, we can expect better white emitting light source for illumination.

However, this shift in red region is not sufficient to compensate the lack of a red component. A codoping with  $\text{Sm}^{3+}$ ,  $\text{Pr}^{3+}$  or  $\text{Eu}^{3+}$  looks very fruitful. The luminescence is more intense when the gap between the excited state and the more energetic component of the ground state multiplet, is larger. This explains the prominent role played by  $\text{Eu}^{3+}$  as co-activator.

Introducing  $Eu^{3+}$  in the host lattice of TAG: Ce is more effective than in YAG:Ce. When  $Eu^{3+}$  is introduced in YAG, the part of exciting LED energy will excite the  $Eu^{3+}$  ions and reduce the Ce<sup>3+</sup> excitation, that decrease the luminescence intensity. In the case of TAG, Tb<sup>3</sup> transfers its energy to Ce<sup>3+</sup> and Eu<sup>3+</sup> and can be used as a sensitizer. In addition, one new luminescent mechanism can exist when Tb luminescence excites direct Ce<sup>3+</sup> and Eu<sup>3+</sup>. The total luminescence increases and red shift appears, that improves CRI and CIE. It is very important to optimize the concentrations of activators and co-activator to improve the properties.

TAG seems to be more perspective than YAG in the white light devices

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## METHOD OF STUDY GALLIUM AND ARSENIC LOSSES IN TECHNOLOGY OF GALLIUM ARSENATE OBTAINED FROM WASTES

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## Abstract

Having the goal to recover gallium (Ga) and arsenic (As) from technological wastes derived from the process of growing epitaxial gallium arsenide structures, it is proposed to extract gallium arsenate (GaAsO<sub>4</sub>) by precipitation and filtration of the sediment. In this paper it is proposed to measure the concentrations of Ga and As by means of the atomic absorption spectrometer AAnalyst 800 directly in the filtrate solution. We compare the results obtained by two methods of elemental Ga and As atomization: flame and thermal atomization. The values of Ga and As concentrations in filtrate are function of pH for solutions containing 1-680 mg/1 of Ga and 55-880 mg/1 of As. The developed method can be used to study and further optimize the technological process.

## Introduction

It is known [1] that using epitaxial technologies for production of semiconductor devices the most part of the initial materials consumed during the process are deposited on the surface of the technological equipment inside the reactor, generating solid wastes. For instance, during the process of gallium arsenide layer growing by a gaseous transport chemical reaction [2] about 70% initial Ga and As are deposited in the cold part of the reactor. The sediment is then chemically treated by an acidic solution to prepare the next technological cycle, being transformed in this way into liquid wastes. One of the developed technological processes of wastewater treatment at the place of their formation [2] consists of the recovery of gallium and arsenic as solid gallium arsenate (GaAsO<sub>4</sub>). Gallium and arsenic concentrations in these liquid wastes achieve values of 30-120 g/l and can be determined by the spectrophotometrical method [3]. The determination of these elements in the sediment is problematic due to diverse factors. The errors of the gravimetric method to determine the weight of the sediment are considerable and can be also caused by co-precipitation of the other elements, present in initial acidic solution. In this paper it has been proposed and described a solution of the problem by direct measurement of gallium and arsenic concentrations in the filtrate solution after removal of GaAsO<sub>4</sub>, using the Atomic Absorption Spectrophotometer Aanalyst-800. This method has found exhaustive use for determination of small concentrations of arsenic [4] and gallium [5] for determination of trace amounts of gallium by tungsten metal furnace.

Gallium ion concentrations  $(Ga^{3+})$  are determinant for gallium arsenate sedimentation process from the waste solutions under investigation. For this reason the measurements of

gallium as well as arsenic concentrations in the filtrate solution after removal of gallium arsenate are important and can be used to study and further optimize the technological process of wastewater treatment.

## 1. Materials and Sample Preparation

#### **1.1. Sedimentation of the gallium arsenate.**

For the presented study we considered the model waste solutions obtained by dissolution of stoichiometric gallium arsenide GaAs in aqua regia, the acidic solution being used for chemical etching of the technological equipment [2]. The gallium and arsenic concentrations in the model waste solution were proved to be higher than the corresponding values in real wastewaters, 108 g/l for Ga and 101 g/l for As. The concentration of these elements in the real wastewaters is within 30-60 g/l. The process of gallium arsenate sedimentation has been controlled by the variation of the pH of the solution. The weight of the sediment obtained after filtration was determined by using a gravimetric method. The filtrate solution after the removal of the gallium arsenate represents the object under investigation. This solution contains gallium in the form of Ga<sup>3+</sup> and arsenic in the form of AsO4<sup>3-</sup>, whose concentrations characterize the losses of gallium and arsenic during the technological process, or in other words, the quality of the process of gallium arsenate removal.

## **1.2.** Preparation of the samples

The samples for the investigation have been prepared from the solution rested at once after filtering process of the precipitation. The concentrations of Ga and As in the filtrate varied in the diapason of 1-680 mg/l for Ga and 55-880 mg/l for As depending on value of pH. The filtrate was limpid when visually investigating and didn't contain any solid particles. Before measurement the samples were well mixed by shaking up and they were diluted with micropipette in a measuring vessel for a necessary time (K). The ones with higher concentrations were deluted twice.

## 2. Spectrophotometer

For the determination of Ga and as losses in the process of gallium arsenate synthesis the atomic-absorption spectroscopy method was used. Measures have been done by an atomic-absorption spectrophotometer AAnalyst-800 (Perkin-Elmer, USA), supplied with a flame atomizer with pneumatic nebulizer and interchangeable burner heads, the thermoelectric atomizer transversely-heated graphite furnace THGA incorporating an electromagnet for longitudinal Zeeman-effect background correction and flow injection system FIAS-400. As line radiation source we have used the hollow cathode HCL lamp for determination of Ga and the electrode less discharge EDL lamp for determination of arsenic. A P-E firm AA Win Lab 4.1 program with utilization of Pentium III computer controlled the machine work and the analysis process. The instrumental parameters for both elements are shown in table 1.

	Flame		THGA		FI-MHS	
	As	Ga	As	Ga	As	
Wavelength (nm)	193,7	287,4	193,7	287,4	193,7	
Lamp	EDL	HCL	EDL	HCL	EDL	
Lamp current (mA)	380	20	380	20	380	
Background correct.	Deuterium	Lamp	Zeeman corre	ector		
Atomizer	Air-acetylene		Electrother. Atomizer		Quartz cell	
	flame					
	Time Average					
Signal Processing	Time Av	erage	Peak Area	a	Peak Height	
Signal Processing Sample Volume, µl	Time Av 500	erage	Peak Area 20	a	Peak Height 500	
Signal Processing Sample Volume, µl Atom. Temperat. <sup>0</sup> C	Time Av 500 2000-2	erage 300	Peak Area 20 2000	a 2300	Peak Height 500 900	
Signal Processing Sample Volume, µl Atom. Temperat. <sup>0</sup> C Reagents, modifiers	Time Av 500 2000-2	erage 300	Peak Ares 20 2000 Pd + Mg (NO	a 2300 D <sub>3</sub> ) <sub>2</sub>	Peak Height 500 900 NaBH <sub>4</sub>	
Signal Processing Sample Volume, µl Atom. Temperat. <sup>0</sup> C Reagents, modifiers Gas	Time Av 500 2000-2 - Air-C <sub>2</sub>	erage 300 H <sub>2</sub>	Peak Ares 20 2000 Pd + Mg (NO Ar	a 2300 D <sub>3</sub> ) <sub>2</sub>	Peak Height 500 900 NaBH <sub>4</sub> Ar	
Signal Processing Sample Volume, µl Atom. Temperat. <sup>0</sup> C Reagents, modifiers Gas Analyses Time, sec	Time Av 500 2000-2 - Air-C <sub>2</sub> 6	erage 300 H <sub>2</sub>	Peak Ares 20 2000 Pd + Mg (NO Ar 180	a 2300 D <sub>3</sub> ) <sub>2</sub>	Peak Height 500 900 NaBH <sub>4</sub> Ar 30	
Signal Processing Sample Volume, µl Atom. Temperat. <sup>0</sup> C Reagents, modifiers Gas Analyses Time, sec Sampling	Time Av 500 2000-2 - Air-C <sub>2</sub> 6 Manu	erage 300 H <sub>2</sub> al	Peak Area 20 2000 Pd + Mg (NO Ar 180 Automat AS	a 2300 D <sub>3</sub> ) <sub>2</sub> -800	Peak Height           500           900           NaBH4           Ar           30           Aut. AS-90	

Table 1. Instrumental Parameter	Table 1.	<ol> <li>Instrumental Param</li> </ol>	ieters
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## 3. Methods of technological solution analysis

Depending on the investigation technology selection the samples were brought in an atomizing source (flame, cuvette, hydride system) and they were analyzed in automatic rate at the Aanalyst-800. By means of calibration graph preliminary built, the machine gives out in automatic rate for every sample on the display screen the following parameters:  $C_i$  – the concentration of determine element in the analyzing dilute solution (g/l); SD – the standard deviate of concentration (g/l); RSD – the relatively standard deviate (%). After every ten samples the stability of calibration graph is verified and if it is necessary, the last samples are recurred. The obtained data are used to calculate the concentrations taking into account the dilution coefficient  $C_m = C_i * K$ .

By choosing the optimal conditions of Ga analyzing advantages and shortcomings of two atomization possibilities – flame and thermal have been appreciated. Possibilities of hydride technique have been supplementary estimated. Characteristic Mass and Linear of caliber diagrams for study variant are shown in table 2.

		Flame, mg/l	THGA,µg/l	FI-MHS, µg/l
As	Char. Mass	1,4	1,5	0,1
	Linear	100	150	20
Ga	Char. Mass	3,0	2,5	-
	Linear	100	200	-

Table 2. Characteristic Mass and Linear.

As follows from tab. 2 the hydrid method is characterized by the highest relative sensibility but the flame atomization method – by the least one. Selection of the method for technological solution analyses depends on the reproduction and precision obtained at the measuring results. In this investigation there is excess of Ga and As in large pitch

concentrations, therefore it would be interesting to carry out some parallel experiments of the same samples with diverse methods and to estimate the advantage of them.

## 4. Results and Discussion

Table 3 shows the results obtained by different technologies and certainly different dilution of initial samples.

			Flame			THGA			
Element	Sample	K dill	C mg/l	C <sub>mg/l</sub> K	K dill	C µg/l	C <sub>mg/l</sub>		
Ga	142	1	73,43	73,43	1000	76,0	76,0		
		20	3,803	76,06	500	127,3	63,65		
		10	7,521	75,21					
	143	20	35,22	704,0	10000	59,3	593,0		
		10	68,68	686,8	5000	97,4	485,0		
	146	20	<2	<2	20	54,0	1,08		
		10	<2	<2	10	99,2	0,99		

Table 3. Concentration of Ga and As in the solution by different dilution degree

		Flame			FI-MHS			
Element	Sample	K dill	C mg/l	C <sub>mg/l</sub> K	K dill	C µg/l	C <sub>mg/l</sub>	
	173	10	5,416	54,16	1000	54,81	54,81	
		5	11,04	55,20	2000	28,61	57,22	
	167	10	65,66	656,6	10000	52,0	520,0	
As		5	136,9	684,5	5000	99,8	499,0	
	179	20	11,55	231,0	500	54,36	271,8	
		10	24,28	242,8	200	132,5	265,0	
		5	52,35	261,75				

As follows from tab.3 the results for Ga in flame analysis with 10-20 time dilution are in a good agreement with the results obtained in thermal atomization with 500-1000 time dilution and they are very different at K=5,000-10,000 (sample 143). If the initial sample contains less than 2 mg/l of Ga the analysis in flame isn't carried out, a more sensitive method of thermal atomization with 10-50 time dilution is used. The results for As are well agreed with both methods at the 5-20 time dilution for flame one and the 200-2000 time delusion for hydride technique. The FI-MHS method also gives lower results for higher dilute time (5,000-10,000 sample 167). The experimental errors represent 12 % and are more significant when the dilution factor is over 5000-10000.

In the figure the measured gallium and arsenic concentrations in the filtrate solutions depending on the value of pH are shown. The concentration value represents the mean quantity of two measurements by different methods. As it is clear from the figure the least of gallium losses at the precipitating gallium arsenate from oxide solution with stoichiometric GaAs is obtained in space 3.2-4.2 of pH value.



Gallium and arsenic losses in the filtrate of the model waste

## 5. Conclusions.

In this paper it was shown the opportunity of using the atomic absorption spectrometer AAnalyst 800 to investigate the gallium and arsenic losses in technological process of precipitation and filtration the gallium arsenate. The filtrate in this process contains 1-680 mg/l of gallium and 55-880 mg/l of arsenic, depending on the value of pH. For this reason it is necessary to dilute the investigated solutions for using those measuring methods. So the dilution of solutions only of 5-20 times for atomization method in flame, of 100-1,000 times for thermal method and up to 10,000 times for hydride technique is necessary. The investigated method can be used to study and further optimize the technological process.

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## POLYTYPISM OF CRYSTALS OF Cu (D-Ser) (D-But) MIXED COMPOUND

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## Abstract

The faculty of mixed copper (II) compound with optically active forms of serine (Ser) and butyrin (But) Cu(D-Ser)(D-But) to crystallize in polytypic modifications was traced on the basis of obtained crystallographic structure data by electron diffraction technique. The unit cell parameters, the space groups of symmetry and the numbers of formula units per unit cell of two obtained polytypic modifications are: I – a=10.17(2) Å, b=9.60(1) Å, c=5.07(1) Å,  $\gamma=92.3(2)^0$ ,  $P2_1$ , Z=2; II – a=20.35(2)Å, b=9.59(1) Å, c=5.08(1) Å,  $\gamma=92.3(2)^0$ ,  $C2_1$ , Z=4;

## Introduction

Earlier, we determined crystal structure of mixed copper (II) compound with optically active forms of serine (Ser) and butyrin (But) modification I Cu(D-Ser)(D-But) [1].

It was distinguished one more modification of the Cu(D-Ser)(D-But) compound in the process of sample preparation of crystals for electron diffraction technique by their crystallization from aqueous solution of ethyl alcohol. The analysis of obtained diffraction images of crystal of both modifications permitted to reveal preliminarily the resemblances and differences traits of these modifications by visual observation in conformity with the geometry arrangement peculiarity of three-dimensional set of reflections and appropriateness arrangement of its intensity [2,3].

In the diffraction images type oblique textures the similarity of both modifications are expressed by common totality of ellipses, along which the reflections are arranged. This signifies that their crystal lattices have a common basal plane and, as a result, have two metric and two similar angular parameters of unit-cells of both modifications.

It was also discovered that the splitting quantities of corresponding reflections in the oblique textures are identical, and the reflection alternation periods are different. The equality of the splitting quantity of the reflections means that the third angular unit cell parameters are identical too. The difference trait of these modifications was evidenced rather clear in the geometrical reflections arrangement of the oblique textures and its intensity distribution.

These diffraction distinctions indicate, that the third linear unit cell parameters of crystals of both modifications are different and also there are essential distinctions in the order of the structural units being in their structure.

## Determination of Crystal Structure Cu(D-Ser)(D-But) modification II

The diffraction image identification indicated, that the crystals Cu(D-Ser)(D-But) of modification II of mixed compound belong to monoclinic singony with the following crystallographic parameters: a=20.35(2) Å, b=9.59(1) Å, c=5.08(1) Å,  $\gamma=92.3(2)^{0}$ . The number of formula unity per unit cell Z=4. In the crystal diffraction images the 00l reflections with l=2n+1 and hkl reflections with h+k=2n+1 are absent. Such intensity arrangement corresponds to base-centered space group of symmetry  $C2_1$  and C2/m. However, the C2/m space group of symmetry realization in the crystals Cu(D-Ser)(D-But) is impossible, because in this case the compound should include the serine and butyrin residues in racemic form, whereas in reality it contains only the optically active forms of serine and butyrin.

The coordinates of non-hydrogen atoms of the structure were determined using a threedimensional set of 257 reflections. The value of discrepancy factor is R=10.35%. The coordinates of base atoms of the structure are listed in Table 1 and the fragment of structure is shown in Fig.1. The structure is built of mixed complexes, in which the serine and butyrin residues appear as bidentate ligands that form five-member chelate cycles with copper atoms. The symmetry of the complex is almost near to the centrosymmetrical motif without the group of atoms C5H<sub>2</sub> and C6H<sub>2</sub> and the complex conformation without lateral radical C5H<sub>2</sub>O5H and C6H<sub>2</sub>C7H<sub>3</sub> serine and butyrin residues is plane.

Atom	x/a	y/b	z/c				
Cu	000	250	250				
O1	-20(6)	422(6)	59(7)				
O2	20(6)	78(6)	443(7)				
O3	-90(6)	599(6)	42(7)				
O4	90(6)	-98(6)	463(7)				
O5	-211(6)	312(6)	483(7)				
N1	70(6)	185(6)	-6(7)				
N2	-70(6)	315(6)	506(8)				
C1	-110(7)	425(8)	380(8)				
C2	110(7)	75(8)	122(8)				
C3	69(7)	12(8)	362(8)				
C4	-70(7)	492(8)	144(8)				
C5	-170(7)	358(8)	282(8)				
C6	180(7)	25(8)	60(8)				
C7	225(7)	145(8)	223(8)				

Table 1. Coordinates of non-hydrogen atoms  $(x10^3)$  in the crystal structure  $Cu(D_2Ser)(D_2Surf)$  modification II



Fig. 1 The principle of crystal construction of Cu(D-Ser)(D-But) compounds

The coordination polyhedron of the copper atom appears as an almost regular octahedron, which is formed by two amino-group nitrogen atoms N1 and N2 and four carboxyl oxygen atoms O1, O2, O6 and O7 of serine and butyrin residues. The calculated interatomic distances and bond angles in the structure are listed in Table 2. The structure is built by two-dimensional structural units (layers), formed by Cu(D-Ser)(D-But) mixed complexes. The period of the layer alternation is a/2. The complexes in the layers are involved in two-dimensional hydrogen bond network, that forms amino-groups with oxygen atoms of carboxyl groups of the adjacent complexes. The N...O contacts are in the limits of 3.08-3.12 Å. Besides, in the layers, the complexes are involved by the forces of the interaction of the copper ions with the oxygen atoms of the carboxyl groups of the adjacent complexes [Cu---O(6) and Cu---OO(7) 2.73 Å]. These bonds arrange the complexes in the layer limits in such a way, that methyl 1 (C7H<sub>3</sub> C8H<sub>3</sub>) and hydroxyl (O10H, O11H) groups are concentrated on the surface of the layers on both its sides. In the period of structure formation the layers are distributed one to another in a such way, that the methyl and hydroxyl groups of one of the layers adjoin correspondingly to methyl and carboxyl groups of the other layer and the interactions C7-H<sub>3</sub>...C8-H<sub>3</sub> (3.39 Å), O10-H...O11-H (3.22Å) appear between them. Perhaps, a significant role in the increasing of bond angles N1-C2-C6 and C3-C2-C6 and shortening of distance C1–C5 and C6–C7 is played by the steric factors, conditioned by these interlayer contacts. However, it is possible that some distortions of these distances and bond angles are caused by inaccurate determination of periphery atom coordinates.

Atoms	Distance	Atoms	Angle
Cu-O1	1 97(1)	O1-Cu-N1	96.3
$C_{\rm u} O_{\rm c}$	1.97(1) 1.07(1)	O1 Cu N2	83 7
Cu-02	1.97(1) 2.04(1)	O2 Cu N2	06.2
	2.04(1)	02-Cu-N2	90.3
Cu-N2	2.04(1)	O2-Cu-N1	83.7
C4-O1	1.29(1)	O1-C4-O3	125.6
C4-O3	1.26(1)	O1-C4-C1	116.4
C4-C1	1.59(1)	O3-C4-C1	118.0
C1-N2	1.50(1)	N2-C1-C4	108.9
C1-C5	1.45(1)	C5-C1-C4	108.2
C5-O5	1.38(1)	C5-C1-N2	108.4
C3-O2	1.29(1)	C1-C5-O5	111.6
C3-O4	1.26(1)	O2-C3-O4	125.6
C3-C2	1.59(1)	O2-C3-C2	116.4
C2-N1	1.49(1)	O4-C3-C2	118.0
C2-C6	1.58(1)	C3-C2-N1	108.9
C6-C7	1.46(1)	C3-C2-C6	123.8
		N1-C2-C6	127.3
		C2-C6-C7	108.6

Table 2. Interatomic distance (Å) and bond angles (deg.) in the structure Cu(D-Ser)(D-But) modification II

## Comparative Structural Particularities of Crystal Cu(D-Ser)(D-But) Modifications

It is interesting to compare the crystals characteristics of modification II of the Cu(D-Ser)(D-But) crystals determined in this work with results of the similar data of modification I obtained earlier in [1]. As seen from Table 3, the unit cell dimensions of the crystals of both modifications are characterized by close value of their parameters b, c and by similar monoclinic angles, that was preliminary confirmed during the analysis of the geometrical

arrangement of reflections in the diffraction images of these modifications. The unit cell of crystal modification I differs from the unit cell of crystal modification II only on the account of double shortening of the *a*-parameter, along which the layers alternate in the structure. In the structures the space groups of symmetry  $P2_1$  and  $C2_1$  are realized correspondingly. Both structures are built from octahedron mixed complexes. The comparison of bonds and bond angles of the complexes of modification II with corresponding value of crystals of modification I shows the precise conformity of the latter.

			(	,		
Compound	<i>a</i> (Å)	b(Å)	$c(\text{\AA})$	γ (deg)	Ζ	Space
						gr.
Cu(D-Ser)(D-But) modification I	10.17	9.60	5.07	92.3	2	$P2_1$
Cu(D-Ser)(D-But) modification II	20.35	9.59	5.08	92.3	4	$C2_1$

Table 3. The crystallography characteristics of the compounds Cu(D-Ser)(D-But) modification I and II

The analysis of structure characteristics shows, that common for both modifications are the complex conformation and stratified structure. The principle of layer building is identical too. However, the layer succession in the crystals of both modifications is different. Both structure modifications are different by the displacement of the adjacent layers along the *b*axes. In the case of modification I the displacement along the *b*-axes is zero, for the modification II the displacement is 1/2b. As a result, the modification I has the *a* period in one layer and the modification II has the *a* period in two layers. Also the differences are in the geometry of mutual arrangement of methyl and hydroxyl groups of serine and butyrin residues in the interlayer space. These are the essential structural differences, that characterize the crystals of both modifications. Thus, both structures are built of the same identical layers and are different only by the mode of layer alternation in the space, that's why the both structures are polytypic modifications of mixed complexes Cu(D-Ser)(D-But).

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# KINEMATICS OF WAVES INTERACTIONS IN UNDULAR FRAMES

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### Abstract

In this paper the concept of undular frame is defined as a system of tools consisting of waves, having the same nature as observed waves. Such definition of used tools set is equivalent to the problem about behavior and self-organizing of waves in absence of heterogeneous objects. The theorem has proved that the velocity of signal propagation in medium does not depend on undular frame selected. The location of undular frames cannot be determined relatively to the medium-carrier of waves. Between undular frames the principle of relativity is completely observed, is not possible to distinguish any undular frame. If the waves interactions are considered in undular frames, then there are gained not only trivial solutions corresponding to a principle of superposition, but also solutions, which describe interactions between waves as between mechanical particles. At the interaction of stable standing wave with the traveling wave the quantization of the latter takes place.

### 1. Introduction

The undular processes are applied as the etalons of time and length as it is known. For example, as the time etalon, the period of oscillations of caesium atoms is chosen, and the wave length of krypton atoms radiation serve as length etalon. In other words, the measuring of time and lengths represents operations of comparison with the waves parameters: with the period *T* and wave length  $\lambda$ .

Usually it is considered, the etalons do not vary during measuring and they are heterogeneous in relation to investigated processes. In practice, any tool is exposed to action during measuring. The changes in tools are taken into account through errors. However there are cases, when the tools of measuring are the participants of processes. Hence, the changes, which happen to tools, cannot be taken into account with the help of errors. This situation takes place, when all objects, which participate during the measuring process, have an undular nature.

The subject of the present work is the study of wave interaction provided that as tools of time and length measuring serve waves, which exist in same medium, as investigated waves. Or else, we want to describe, how the waves "perceive" each other. Such statement, in fact, is equivalent to a problem about behaviour and self-organizing of waves in unbounded medium, without heterogeneous insertions. We have published separate results on examination of this problem in works [1-7]. In offered paper we systematized results on the kinematics of waves, described in undular frames.

## 2. The metric of undular frames

## 2.1. The definition of undular frames

The result of interaction of free physical object is its transition from one reference system in other. Therefore, first of all, we shall spot concept of the undular reference system, or frame, and the rules of transition from one system in another. The reference system should contain scales for measuring the time and the length. Such scales consist of repeated intervals of time and length. The standing wave possesses the property of periodicity in space and in time, it can be described by expression:

$$a = A\cos(-kx)\cos(\omega t).$$

(1)

By setting such wave, we thus set the metrics, namely:

- the direction of an axis x - coincides with a direction of the wave propagation;

- the spatial gauge - is determined by the wave length  $\lambda = \frac{2\pi}{k}$ ;

- the time gauge - is determined by the wave period  $T = \frac{2\pi}{\omega}$ . Or else, the standing wave (1)

execute a role of the ruler and chronometer simultaneously.

If in medium there is a certain wave-object, described by expression:

$$a_0 = A\cos(-k_0 x)\cos(\omega_0 t), \qquad (2)$$

the measuring of its length in a frame (1) consists in definition of the number equal to ratio of wave-object and wave-gauge lengths:

$$n = \frac{\lambda_0}{\lambda} \,. \tag{3}$$

Similarly, the measurement of wave-object period consists in determination of ratio of wave-object and wave-gauge periods:

$$n = \frac{T_0}{T} \tag{4}$$

The wave-object (2) can be decomposed into two travelling waves, which run in opposite directions, of a kind:

$$a_{01} = \frac{A}{2}\cos(\omega_0 t - k_0 x)$$
(5)

$$a_{02} = \frac{A}{2}\cos(\omega_0 t + k_0 x).$$
 (6)

Generally, in expressions (5) and (6) the frequencies and the wave numbers can differ, that is, these expressions take view:

$$a_{01} = \frac{A}{2}\cos(\omega_{01}t - k_{01}x)$$
 And  $a_{02} = \frac{A}{2}\cos(\omega_{0}t + k_{0}x)$ ,

at that  $\omega_{01} \neq \omega_0$  and  $k_{01} \neq k_0$ . Then the wave-object will be described by the formula:

$$a_0 = a_{01} + a_{02} = A_0 \cos\left(\frac{\omega_{01} - \omega_0}{2}t - \frac{k_0 + k_{01}}{2}x\right) \cos\left(\frac{\omega_{01} + \omega_0}{2}t - \frac{k_0 - k_{01}}{2}x\right).$$
(7)

Formula (7) describes so-called beats, or standing wave, the maximums of which are moving in the course of time. We shall term such wave - quasi-standing wave. At that, the value

$$\omega' = \frac{\omega_{01} + \omega_0}{2} \tag{8}$$

and

$$k' = \frac{k_{01} + k_0}{2} \tag{9}$$

are perceived as frequency and wave number of moving wave-object (7), and its velocity is determined by expression

$$v_0 = \frac{\Delta x}{\Delta t} = \frac{\omega_{01} - \omega_0}{k_0 + k_{01}}.$$
 (10)

If the observer goes with velocity defined by expression (10), from his point of view the wave (7) will be standing, or fixed, and it will be described by expression having view (2), or, at n=1, by expression of view (1). Hence, in system of the moving observer this wave can be used as a wave, which sets a frame. Thus, we come to the conclusion, that within the framework of the accepted model, there can be many reference systems, which are moving one, relatively another with various velocities, and all of them are equivalent.

*Definition*: the undular reference system, or undular frame is a frame, in which as time etalon there serves the period of standing or quasi-standing wave in a fixed point, and the length etalon is equal to distance between two points having same phase.

### 2.2. Theorem on invariance of velocity of traveling wave relatively to undular frames.

As it is marked above, a preferred frame cannot exist. Or else, for undular frames the principle of relativity is realized. However there is one circumstance, which can put under doubt last statement. The velocity of traveling waves c, described by expressions (5) and (6) is determined by properties of medium. Naturally there can be the idea: to use a standing wave as the tool for determining velocity of traveling waves c. Then, knowing velocity c, to determine velocity of undular frame concerning the medium. In fact, such experience is similar to a known experiment of Michelson and Morley, with help of which the attempt was undertaken to spot velocity of the motion concerning the ether in 1887. In our case, if such experience will give positive result, then it will be possible to choose one "true undular frame", in which the velocity of the motion concerning the medium - carrier is equal to zero. Such system will be privileged in relation to other undular frames. In this case, for undular systems the principle of relativity will not be realized. Let's prove, that it not true.

*Theorem*: the velocity of traveling waves *c* has the same value in all undular frames.

We suppose there are two undular frames, which are described by expressions:

$$a = A\cos(-kx)\cos(\omega t), \tag{11}$$

and

$$a' = A\cos\left(\frac{\omega_1 - \omega}{2}t - \frac{k + k_1}{2}x\right)\cos\left(\frac{\omega_1 + \omega}{2}t - \frac{k - k_1}{2}x\right).$$
(12)

The relative motion velocity of these systems is determined by expression:

$$v = \frac{\omega_1 - \omega}{k + k_1} = c^2 \frac{T - T_1}{\lambda_1 + \lambda}.$$
(13)

Let admit that, some wave-object rest in system (12) and in this system it is described by the formula:

$$F_0' = A_0 \cos(-k_0' x') \cos(\omega_0' t').$$
(14)

The same wave-object, in system (11) will be described by expression

$$a_0 = A_0 \cos\left(\frac{\omega_{01} - \omega_0}{2}t - \frac{k_0 + k_{01}}{2}x\right) \times \cos\left(\frac{\omega_{01} + \omega_0}{2}t - \frac{k_0 - k_{01}}{2}x\right).$$
(15)

Let's copy (15) taking into account (13):

$$a_0 = A_0 \cos\left(\frac{k_0 + k_{01}}{2}(vt - x)\right) \cos\left(\frac{\omega_0 + \omega_{01}}{2}(t - \frac{v}{c^2}x)\right).$$
(16)

Expressions (16) and (14) describe the same wave-object. In expression (16) the value (vt - x) represents instantaneous coordinate of wave-object, as well as x' in expression (14). The transformation of segment length along coordinate should take place under the same law as transformation of this coordinate. Hence, the length of moving wave-object (16) will be

 $\lambda_0' = \lambda_0 - \nu T_0$ 

and its wave number:

$$k_0' = \frac{2\pi}{\lambda_0 - vT_0}.$$
 (17)

Following a similar reasoning for frequency, we shall obtain:

$$\omega_0' = \frac{2\pi}{T_0 - \frac{\nu}{c^2} \lambda_0}.$$
(18)

The ratio of circular frequency  $\omega$  to a wave number k is equal to velocity of traveling wave c. Thus, the proof of the theorem formulated above is reduced to the demonstration of relation

$$c = \frac{\omega_0}{k_0} = \frac{\omega_0}{k_0} = c'.$$

By using (17) and (18) we shall obtain:

$$c' = \frac{\omega_0'}{k_0'} = c^2 \frac{\lambda_0 - vT_0}{c^2 T_0 - v\lambda_0}$$

In view of expressions (3), (4) and (13) we can write:

$$c' = \frac{\lambda - Tc^2 \left(\frac{T - T_1}{\lambda + \lambda_1}\right)}{T - \lambda \left(\frac{T - T_1}{\lambda + \lambda_1}\right)} = \frac{\lambda (\lambda + \lambda_1) - Tc^2 (T - T_1)}{T (\lambda + \lambda_1) - \lambda (T - T_1)} = \frac{\lambda}{T} = c .$$

We have proved: in undular frames, the velocity of traveling wave c does not depend on choice of frame. Hence, the velocity of traveling wave cannot be used for definition of velocity concerning the medium-carrier, and all undular reference frames are equivalent.

# 2.3. Transformation of the length and time scales at transition from one undular system in another

We will found the transformation rules for segments of length and time intervals at transition from one undular system in another. Let's choose two undular frames. For distinguishing them, one of them we shall mark by an accent. We assume, that, the marked frame moves relatively not marked system with velocity v.

The measuring of the length segment and time interval in a undular frame consists in its comparison with the respective gauges, as which serve: the wave length  $\lambda$  and period *T*. Hence, for the segment of length *x* and time interval *t* in not marked system it is possible to note:

 $x = n\lambda$ , t = nT,

and for marked system:

$$x' = n\lambda', \quad t' = nT'. \tag{19}$$

The wave-object, situated in marked system, will be described by expression:

$$a_0' = A_0 \cos(-k_0' x') \cos(\omega_0' t'). \tag{20}$$

The same wave in not marked system will look like:

$$a_0 = A_0 \cos\left(\frac{\omega_{01} - \omega_0}{2}t - \frac{k_0 + k_{01}}{2}x\right) \times \cos\left(\frac{\omega_{01} + \omega_0}{2}t - \frac{k_0 - k_{01}}{2}x\right).$$
(21)

We shall term *proper frame* the reference frame, in which wave-object is situated. Comparing expressions (2) and (7), we can define a proper frame and as system, in which  $\omega_1 = \omega_2$  and  $k_1 = k_2$ . According to expression (13), the velocity of proper system relatively to laboratory frame can be expressed as

$$v = \frac{c(\omega_{01} - \omega_0)}{\omega_{01} + \omega_0} = \frac{c(k_{01} - k_0)}{k_0 + k_{01}}.$$
(22)

Relations from here follow:

$$k_{01} = k_0 \frac{c+v}{c-v}$$
(23)

and

$$\omega_{01} = \omega_0 \frac{c+v}{c-v} \qquad . \tag{24}$$

By inserting (23) and (24) in (21) we shall obtain:

$$a_0 = A_0 \cos\left[\frac{k_0 c}{c - v}(vt - x)\right] \cos\left[\frac{\omega_0 c}{c - v}\left(t - \frac{v}{c^2}x\right)\right].$$
(25)

Let's compare (20) and (25). These expressions describe the same wave-object. In both expressions, the arguments of first *cos* represent the same ratio of length segment to gauge i.e. to wave-object length, in respective reference frame. This is a dimensionless value, or simply a number, which does not depend on a reference frame. Therefore we can equate the arguments of *cos* from (20) and (25), and obtain:

$$x' = \frac{k_0}{k'_0} \frac{c}{c - v} (x - vt).$$
(26)

In correspondence with expression (17) and (19)

$$k_0' = \frac{2\pi}{\lambda_0 - vT_0} = \frac{2\pi n}{x - vt},$$
 (27)

here *n* is number of waves lengths  $\lambda$ , located on a considered segment *x*.

Inasmuch all undular frames are equivalent, similarly, by transferring from marked system in the not marked system, it is possible to obtain the expression:

$$k_0 = \frac{2\pi}{\lambda_0' - v' T_0'} = \frac{2\pi n}{x' - v' t'} \,. \tag{28}$$

In this expression v'- represent the velocity, with which not marked frame move from "point of view" of marked system. Hence:

v' = -v,

and (28) will be copied:

$$k_0 = \frac{2\pi n}{x' + vt'}.$$
 (29)

2

$$x' = \frac{\frac{2\pi n}{x' + vt'}}{\frac{2\pi n}{x - vt}} \frac{c}{c - v} (x - vt) = \frac{c}{(c - v)(x' + vt')} (x - vt)^2.$$

In correspondence with (19)

$$x'/t' = n\lambda'/nT' = c$$

Hence:

$$x' = \frac{1}{t'} \frac{c}{(c-v)(c+v)} (x-vt)^2 \, .$$

That is equivalent to:

$$x' = \frac{x - vt}{\sqrt{1 - \frac{v^2}{c^2}}} = \frac{x - vt}{\sqrt{1 - \beta^2}} = \gamma(x - vt),$$
(30)

where  $\beta = \frac{v}{c}$  - is- normalized velocity,

and

$$\gamma = \frac{1}{\sqrt{1 - \beta^2}} \qquad (31)$$

We remind, in our example the proper system is the marked system. Let the length of segment in the proper system be equal to:

$$\Delta x' = x_2' - x_1'$$

We designate as  $\Delta x$  the length of segment in system, relatively which it moves. Then, in correspondence with (30), we shall obtain:

$$\Delta x' = x'_2 - x'_1 = \gamma (x_2 - x_1) = \gamma \Delta x .$$
(32)

Having done a similar transformations with argument of second cos in (25), we shall obtain the expression for proper time, corresponding to (26):

$$t' = \frac{\omega_0}{\omega_0} \frac{c}{c - v} \left( t - \frac{v}{c^2} x \right).$$
(33)

Similarly to formulas (27) and (28), for frequencies it is possible to write the expressions:

$$\omega_{0}' = \frac{2\pi}{T - \frac{v}{r^{2}}\lambda} = \frac{n2\pi}{t - \frac{v}{r^{2}}x},$$
(34)

$$\omega_0 = \frac{2\pi}{T' - \frac{v'}{c^2}\lambda'} = \frac{n2\pi}{t' + \frac{v}{c^2}x'}.$$
(35)

Here, *n* is the number of wave-object periods *T*, elapsed from the beginning of readout up to a considered instant. We insert (34) and (35) in (33) and obtain:  $n^{2\pi}$ 

$$t' = \frac{\frac{n2\pi}{t' + \frac{v}{c^2}x'}}{\frac{n2\pi}{t - \frac{v}{c^2}x}} \frac{c}{c - v} (t - \frac{v}{c^2}x) = \frac{c}{(t' + \frac{v}{c^2}x')(c - v)} (t - \frac{v}{c^2}x)^2.$$

Let's solve this expression relative to t' taking into account that:

$$t'=nT', x'=nl', \lambda'/_{T'}=c.$$

We obtain:

$$t' = \frac{t - \frac{v}{c^2}x}{\sqrt{1 - \frac{v^2}{c^2}}} = \gamma \left(t - \frac{v}{c^2}x\right).$$
 (36)

Hence, the relation between measurement results of time interval in two reference frames will be the following:

$$\Delta t' = t_2' - t'_1 = \gamma (t_2 - t_1) = \gamma \Delta t .$$
(37)

Here  $\Delta t$  represents the time interval between two events happening in the same point x, in proper system;  $\Delta t$  is the same interval measured in system, relatively which the wave-object moves.

Expressions (30) and (37) represent the Lorentz transformations. From the proofs above mentioned, it is possible to make the following conclusions:

- the Lorentz transformations are not linked to presence or absence of any waves mediumcarrier, in other words, presence of the waves medium-carrier does not contradict Lorentz transformations;
- the Lorentz transformations can be presented as algebra (group), defined on the set of functions of view (5) and (6).

Last statement was discussed by us in more detail in works [7, 8].

## 2.4. The transformation of parameters of traveling waves at frame changing.

For the analysis of interactions between waves, it is necessary to find else the transformation rules for frequency and wave number of traveling wave at transition from one undular frame in another. Let's consider a traveling wave described by expression:

$$a = A\cos(\omega t - kx), \tag{38}$$

in two states, with different values of phases:

$$\varphi_0 = \omega t_0 - k x_0 \tag{39}$$

and

$$\varphi_1 = \omega t_1 - k x_1. \tag{40}$$

If

$$-\omega_1 - \omega_1$$
.

$$\varphi_1 - \varphi_0 = 2\pi n$$

where n - integer, the difference

$$\frac{\varphi_1}{2\pi} - \frac{\varphi_0}{2\pi} = n \tag{41}$$

describes the number of periods between states with phases  $\varphi_1$  and  $\varphi_0$ . Taking into account (39) and (40), it is possible to copy expression (41):

$$(\omega t_1 - k x_1) - (\omega t_0 - k x_0) = 2\pi n$$

or:

$$\omega \left( t_1 - t_0 - \frac{x_1 - x_0}{c} \right) = 2\pi n .$$
(42)

As *n* is simply a number, it should not depend on reference system. Hence, for any other frame (marked by an accent) the same expression will be valid:

$$\omega'\left(t_{1}'-t_{0}'-\frac{x_{1}'-x_{0}'}{c}\right)=2\pi n.$$
(43)

Equating the left-hand parts of expressions (42) and (43), we shall obtain:

$$\omega \left( t_1 - t_0 - \frac{x_1 - x_0}{c} \right) = \omega' \left( t_1' - t_0' - \frac{x_1' - x_0'}{c} \right).$$
(44)

Taking into account relations (30), (36), and also (31) we shall copy (44):

$$\omega\left(t_{1}-t_{0}-\frac{x_{1}-x_{0}}{c}\right)=\omega'\gamma\left(t_{1}-t_{0}-\frac{v}{c^{2}}(x_{1}-x_{0})-\frac{x_{1}-x_{0}-v(t_{1}-t_{0})}{c}\right)$$

We consider the change of a phase from  $\varphi_1$  up to  $\varphi_2$  in a fixed point  $x_1=x_0$ . This corresponds to passage of a wave packet in interval of time  $t_1$ - $t_0$ . Expression (44) will take the view:

$$\omega = \omega' \gamma (1 + \beta),$$

or:

$$\omega = \omega' \sqrt{\frac{1+\beta}{1-\beta}} \; .$$

This expression allows to obtain the expressions for frequencies of travelling components of moving wave-object:

$$\omega_1 = \omega \sqrt{\frac{1-\beta}{1+\beta}} \qquad \qquad \omega_2 = \omega \sqrt{\frac{1+\beta}{1-\beta}}, \qquad (45)$$

where  $\omega$  is the frequency of wave-object in the proper reference frame.

Taking into account, that  $\omega = ck$ , we shall obtain similar expressions for wave numbers:

$$k_2 = k \sqrt{\frac{1+\beta}{1-\beta}} \qquad \qquad k_1 = k \sqrt{\frac{1-\beta}{1+\beta}}$$
(46)

Thus, the formulas, which relate the values of frequencies and wave numbers of a traveling wave in different undular systems, coincide with the relativistic formulas for a longitudinal Doppler effect.

If to insert expressions (45) in (8), we shall obtain the relation between the oscillation frequency of wave-object in proper system  $\omega$  and oscillation frequency of wave-object  $\omega'$ , measured in marked system:

$$\omega' = \frac{\omega}{2} \left( \sqrt{\frac{1-\beta}{1+\beta}} + \sqrt{\frac{1+\beta}{1-\beta}} \right) = \frac{\omega}{\sqrt{1-\beta^2}} \,. \tag{47}$$

### 3. Kinematics of interaction of stables waves-objects.

It is accepted to consider, that in linear media the principle of superposition is observed, and the waves practically do not interact among themselves. When talking about interactions between waves, it is meant usually that the medium is either nonlinear, or nonuniform. We shall demonstrate, that, if to describe process in undular frames, along with the solution, which corresponds to the superposition principle, it is possible to obtain the solution, in correspondence with which, the waves can interact among themselves in linear, homogeneous medium.

It is known, that at interaction of waves, the spatially-time resonance of waves takes place, the conditions of which have the view:

$$\sum \Delta \omega_i = 0 \sum \Delta k_i = 0;, \qquad (48)$$

Where  $\Delta \omega_i$  and  $\Delta k_i$  are the changes of frequencies and wave numbers of interacting waves. That is, at interaction of two waves, the changes of their frequencies will be identical in value, but will have opposite signs:

$$\Delta \omega_1 = -\Delta \omega_2 \,. \tag{49}$$

Expressions (48), (49) are the consequence that, time intervals of interaction for the both waves are identical. For wave numbers of two interacting waves also it is possible to note:

$$\Delta k_1 = -\Delta k_2 \,. \tag{50}$$

However in case of wave numbers it is necessary to mean, that they are vectors. The vectors of wave numbers of traveling waves-component are directed to the opposite parties and have equal modulo in the proper frame of standing wave-object.

$$k_1 = -k_2 = k$$
.

Therefore resulting wave number of a wave (2):

$$k_r = k_1 + k_2 \,$$

that is wave-object in a quiescence, is equal to zero. The wave-object, which moves, is described by expression:

$$a' = A' \sin\left(\frac{k_1 + k_2}{2}r' - \frac{\omega_1 - \omega_2}{2}t'\right) \sin\left(\frac{\omega_1 + \omega_2}{2}t' + \frac{k_1 - k_2}{2}r'\right) \qquad .$$
(51)

Here wave numbers of traveling waves-component  $k_1$  and  $k_2$  do not have equal modulo. The resulting wave number of wave-object  $k_r$  is equal to half from difference of wave numbers of waves-components. From here, in view of expressions (46), for a resulting wave number of moving wave-object it is possible to note:

$$k_r = \frac{k}{2} \left( \sqrt{\frac{1+\beta}{1-\beta}} - \sqrt{\frac{1-\beta}{1+\beta}} \right) = \frac{\beta k}{\sqrt{1-\beta^2}} \,. \tag{52}$$

Thus, expression (50) for resulting wave numbers of two waves-objects, will gain the form:

$$\Delta k_{r1} = -\Delta k_{r2} \tag{53}$$

In the above-mentioned deductions we did not impose any restrictions on amplitude. In particular, the amplitude can be some spherically symmetric function from radius r. Then instead of expression (2) will be the wave-object, described by the formula

$$a = A(r)\sin kr\sin\omega t, \qquad (54)$$

and representing the superposition of two waves, convergent and divergent, without a singular point in center.

Let's assume, that there exists a stable spherical wave of the view (54). It means this wave maintains the shape in the proper frame at interactions with another wave. We will solve a problem about interaction of two such waves, using undular frames.

In laboratory system, we shall designate:  $\beta_1$  and  $\beta_2$  - the normalized velocities of centers of waves-object along the axis x before interaction, and  $\beta_1$ ',  $\beta_2$ ' - the same velocities after interaction.

Let the frequencies of interacting waves be equal accordingly to  $\omega_{01}$  and  $\omega_{02}$  in proper frames. Then, according to formula (47), the frequencies of waves-objects measured in laboratory system up to interaction of waves, will be:

$$\omega_1 = \omega_{01} \frac{1}{\sqrt{1 - \beta_1^2}}$$
 and  $\omega_2 = \omega_{02} \frac{1}{\sqrt{1 - \beta_2^2}}$ , (55)

and after interaction:

$$\omega_1' = \omega_{01} \frac{1}{\sqrt{1 - (\beta_1')^2}} \text{ and } \omega_2' = \omega_{02} \frac{1}{\sqrt{1 - (\beta_2')^2}}.$$
 (56)

In this case expression (49) is possible to write as

$$\omega_1 - \omega_1' = \omega_2' - \omega_2. \tag{57}$$

By inserting (55) and (56) in (57), we shall obtain the equation for frequencies:

$$\frac{\omega_{01}}{\sqrt{1-\beta_1^2}} - \frac{\omega_{01}}{\sqrt{1-(\beta_1')^2}} = \frac{\omega_{02}}{\sqrt{1-(\beta_2')^2}} - \frac{\omega_{02}}{\sqrt{1-\beta_2^2}}$$
(58)

Similarly, following expression (52), for resulting wave numbers of waves-objects, before interaction, it is possible to note:

$$k_{r1} = \frac{\beta_1 k_{01}}{\sqrt{1 - \beta_1^2}}, \ k_{r2} = \frac{\beta_2 k_{02}}{\sqrt{1 - \beta_2^2}},$$
(59)

and after interaction:

$$k_{r1}' = \frac{\beta_1' k_{01}}{\sqrt{1 - (\beta_1')^2}}, \quad k_{r2}' = \frac{\beta_2' k_{02}}{\sqrt{1 - (\beta_2')^2}}.$$
(60)

We shall copy equation (53) for wave numbers as

$$k_1 - k_1' = k_2' - k_2$$

now we shall insert (59) and (60):

$$\frac{\beta_1 k_{01}}{\sqrt{1 - \beta_1^2}} - \frac{\beta_1' k_{01}}{\sqrt{1 - (\beta_1')^2}} = \frac{\beta_2' k_{02}}{\sqrt{1 - (\beta_2')^2}} - \frac{\beta_2 k_{02}}{\sqrt{1 - \beta_2^2}}$$
(61)

Thus, we have obtained a system from two equations, (58) and (61), characterizing the process of interaction between two quasi-standing waves-objects. Taking into account that  $k = \omega/c$ , this system is possible to rewrite as:

$$\frac{\omega_{01}}{\sqrt{1-\beta_1^2}} + \frac{\omega_{02}}{\sqrt{1-\beta_2^2}} = \frac{\omega_{01}}{\sqrt{1-(\beta_1')^2}} + \frac{\omega_{02}}{\sqrt{1-(\beta_2')^2}}$$
(62)

$$\frac{\omega_{01}\beta_1}{\sqrt{1-\beta_1^2}} + \frac{\omega_{02}\beta_2}{\sqrt{1-\beta_2^2}} = \frac{\omega_{01}\beta_1'}{\sqrt{1-(\beta_1')^2}} + \frac{\omega_{02}\beta_2'}{\sqrt{1-(\beta_2')^2}}.$$
(63)

In this system from two equations, we shall consider as unknowns the normalized velocities of waves-objects after interaction.

The combined equations (62) and (63) have two pairs of the solutions. The first pair is trivial solution:

$$\beta_1' = \beta_1; \ \beta_2' = \beta_2 \ . \tag{64}$$

In correspondence with these solutions, the waves pass one through another, without any changes. It means expressions (64) describes the wave superposition. As usual these solutions are considered single possible for ideal medium.

The nontrivial solutions of combined equations (62) and (63) will be the expressions:

$$\beta_1' = \frac{A}{BD} \tag{65}$$

$$\beta_2' = \frac{E}{FD} \tag{66}$$

Here we used the following designation:

$$4 = \left[\beta_{2}\omega_{02}\left(1-\beta_{1}^{2}\right)\sqrt{1-\beta_{2}^{2}}\right]\left[3\beta_{1}\omega_{01}^{2}\left(1-\beta_{2}^{2}\right)-\omega_{02}^{2}\left(\beta_{1}+\beta_{1}\beta_{2}^{2}-2\beta_{2}\right)\right]+ +2\beta_{2}\omega_{01}\omega_{02}^{2}\sqrt{1-\beta_{1}^{2}}\left(\beta_{1}+\beta_{2}-\beta_{1}\beta_{2}^{2}-\beta_{1}^{2}\beta_{2}-\beta_{2}^{3}\right)+ +\beta_{1}^{2}\omega_{01}\sqrt{1-\beta_{1}^{2}}\left[\omega_{01}^{2}\left(1-2\beta_{2}^{2}+\beta_{2}^{4}\right)+\omega_{02}^{2}\left(3\beta_{2}^{4}-1\right)\right]$$
(67)

$$B = 2\beta_1\beta_2\omega_{02}^2 + \beta_2^2(\omega_{01}^2 - \omega_{02}^2) - 2\omega_{01}\omega_{02}\sqrt{1 - \beta_1^2}\sqrt{1 - \beta_2^2} - \omega_{01}^2 - \omega_{02}^2$$
(68)

$$D = \beta_1 \omega_{01} \sqrt{1 - \beta_1^2} \left( \beta_2^2 - 1 \right) + \beta_2 \omega_{02} \sqrt{1 - \beta_2^2} \left( \beta_1^2 - 1 \right)$$
(69)

$$E = \left[\beta_{1}\omega_{01}\left(1-\beta_{2}^{2}\right)\sqrt{1-\beta_{1}^{2}}\right]\left[3\beta_{2}\omega_{01}^{2}\left(1-\beta_{1}^{2}\right)-\omega_{01}^{2}\left(\beta_{2}+\beta_{1}^{2}\beta_{2}-2\beta_{1}\right)\right]++2\beta_{1}\omega_{01}^{2}\omega_{02}\sqrt{1-\beta_{2}^{2}}\left(\beta_{1}+\beta_{2}-\beta_{1}^{2}\beta_{2}-\beta_{1}\beta_{2}^{2}-\beta_{1}^{3}\right)++\beta_{2}^{2}\omega_{02}\sqrt{1-\beta_{2}^{2}}\left[\omega_{02}^{2}\left(1-2\beta_{1}^{2}+\beta_{1}^{4}\right)+\omega_{01}^{2}\left(3\beta_{1}^{4}-1\right)\right]$$
(70)

$$F = 2\beta_1\beta_2\omega_{01}^2 - \beta_1^2(\omega_{01}^2 - \omega_{02}^2) - 2\omega_{01}\omega_{02}\sqrt{1 - \beta_1^2}\sqrt{1 - \beta_2^2} - \omega_{01}^2 - \omega_{02}^2$$
(71)

We shall show that at

$$\beta = \frac{v}{c} << 1$$

from expressions (65) and (66) the formulas follow which coincide with the formulas describing the collision of two bodies in classical mechanics. For this purpose, in formulas (65) - (71) there is taken into account only terms having the least power of  $\beta$ , and  $\beta$  is neglected in comparison with unity. In this case expression (65) is conversed in the formula:

$$\beta_{1}' = \frac{\beta_{2}\omega_{02} \left(3\beta_{1}\omega_{01}^{2} - \beta_{1}\omega_{02}^{2} + 2\beta_{2}\omega_{02}^{2}\right)}{\left(2\omega_{01}\omega_{02} + \omega_{01}^{2} + \omega_{02}^{2}\right)\left(\beta_{1}\omega_{01} + \beta_{2}\omega_{02}\right)} + \frac{2\beta_{2}\omega_{01}\omega_{02}^{2}\left(\beta_{1} + \beta_{2}\right) + \beta_{1}^{2}\omega_{01}\left(\omega_{01}^{2} - \omega_{02}^{2}\right)}{\left(2\omega_{01}\omega_{02} + \omega_{01}^{2} + \omega_{02}^{2}\right)\left(\beta_{1}\omega_{01} + \beta_{2}\omega_{02}\right)}$$
(72)

After a series of transformations expression (72) can be reduced to the form:

$$\beta_1' = \frac{\beta_1(\omega_{01} - \omega_{02}) + 2\beta_2\omega_{02}}{(\omega_{01} + \omega_{02})}.$$
(73)

In a similar manner, from solution (66) we shall obtain the expression

$$\beta_{2}' = \frac{\beta_{2}(\omega_{02} - \omega_{01}) + 2\beta_{1}\omega_{01}}{(\omega_{01} + \omega_{02})}.$$
(74)

By multiplying formulas (73) and (74) on  $c^2$  and we shall obtain the expressions

$$v_{1}' = \frac{v_{1}(\omega_{01} - \omega_{02}) + 2v_{2}\omega_{02}}{(\omega_{01} + \omega_{02})}$$
(75)

$$v_{2}' = \frac{v_{2}(\omega_{02} - \omega_{01}) + 2v_{1}\omega_{01}}{(\omega_{01} + \omega_{02})} \qquad (76)$$

If we change the frequencies by masses in expressions (75) and (76), the formulas will be transformed in formulas, which describe the elastic collision of two mechanical bodies. Thus, description of process in undular frames, leads us to the conclusion, that the stable standing waves can interact as mechanical particles.

## 4. Interaction between standing and traveling wave

Let's suppose that the stable wave-object is situated in laboratory system and is described before interaction by expression (54). Its projection to the axis x is:

$$a = A(x)\sin kx\sin \omega t . \tag{77}$$

We remind, that the stable wave-object always remains invariant in a proper frame. That is, in proper frame it will be described by expression (77) or (54) always.

Incident traveling wave of the form

$$a_i = A\cos(\omega_i t - k_i x) \tag{78}$$

will try to deform wave-object (77), but this is not compatible with stability of the latter. Therefore wave-object (77) cannot remain immovable in laboratory system and will begin to move. Hence, in laboratory system it will be described already by expression for moving wave-object:

$$a' = A'(x)\sin\left(\frac{k_1 + k_2}{2}x' - \frac{\omega_1 - \omega_2}{2}t'\right)\sin\left(\frac{\omega_1 + \omega_2}{2}t' + \frac{k_1 - k_2}{2}x'\right).$$
(79)

Thus, after interaction with a traveling wave, the wave-object will be described by expression (77) in proper system, and expression (79) in laboratory system.

We will found the wave-object velocity after interaction. We mark the frequency of wave-object before interaction  $\omega$ , after interaction -  $\omega'$ , and frequencies of incident wave -  $\omega_i$  and  $\omega_i'$  respectively. Let's insert it in (49):

$$\omega_i - \omega_i' = \omega' - \omega$$
.

At total absorption of traveling wave, its frequency after interaction  $\omega_i' = 0$ . Hence

$$\omega_i = \omega' - \omega$$

In view of expression (47):

$$\omega_i = \omega \left( \frac{1}{\sqrt{1 - \beta^2}} - 1 \right).$$

By solving this equation, we shall obtain velocity, gained by wave-object as a result of interaction with the incident wave.

$$\beta = \pm \frac{\sqrt{2\omega\omega_i + \omega_i^2}}{\omega + \omega_i}$$

We note, that the similar formula describes the interaction of a light quantum with an elementary particle.

Let's consider now the case, when the front of incident wave is non-uniform. It means, in expression (78)  $A = A_i(y)$ . In this case the incident wave acts asymmetrically in relation to center of wave-object, and after interaction the wave-object will move under some angle  $\psi$  relatively to axis x. As the wave numbers of interacting waves vary by the same value, the wave vector of the incident wave also will deviate by some angle  $\varphi$  (fig. 2).



Figure 2. The wave-object (54), under action of a non-uniform travelling wave in two-dimensional representation

Let us suppose, the wave-object is situated in laboratory system before interaction, and is described by expression (54) (figure 1), its frequency is  $\omega$ , and resulting wave number -  $k_r$ . The frequency of incident wave (78) before interaction is  $\omega_i$ , and its wave number is  $k_i$ . The same values after interaction we shall mark by an accent.

As a result of interaction the frequency of wave-object will vary by value  $\Delta \omega = \omega' - \omega$ , or, taking into account (47):

$$\Delta \omega = \omega \left( \frac{1}{\sqrt{1 - \beta^2}} - 1 \right). \tag{80}$$

As was marked above, in the proper frame of wave-object, the wave numbers vectors of traveling waves-components are directed to opposite parties and have equal modulo. Therefore, in a quiescence, the resulting wave number of wave-object

$$k_{\rm r} = 0.$$

After interaction the wave-object will gain some velocity v, and will be described by expression (79), in which the wave numbers of components now do not have equal modulo. Therefore the resulting wave number of wave-object  $k_r$  will be determined in correspondence with expression (52):

$$k_r' = \frac{\beta k_r}{\sqrt{1 - \beta^2}} \, .$$

Thus, the wave number of wave-object will change in result of interaction on:

$$\Delta k_r = k_r' - k_r = \frac{\beta k_r}{\sqrt{1 - \beta^2}}$$

As  $k = \omega/c$ , with  $\Delta k_r$  it is possible to link some frequency  $\Delta \omega_r$ ,

$$\Delta \omega_r = \frac{\omega_1 - \omega_2}{2} = \frac{\beta \omega}{\sqrt{1 - \beta^2}},$$

taking into account (47):

$$\Delta \omega_r = \omega' \beta$$
.

Then the difference:

$$(\omega')^2 - \omega^2 = (\omega')^2 - (\omega')^2 (1 - \beta^2) = (\omega')^2 \beta^2,$$

or

$$(\omega')^2 - \omega^2 = (\Delta \omega_r)^2.$$
(81)

As was marked above, the frequencies of interacting waves vary by the same value  $\Delta \omega = -\Delta \omega_i$ 

or

$$\omega' - \omega = \omega_i - \omega_i' \,. \tag{82}$$

As the wave number is a vector, the principle of identical change of wave numbers for interacting waves should be noted separately for projections on each axis:

$$\Delta k_r \cos \varphi = k_i - k_i' \cos \varphi , \qquad (83)$$

$$\Delta k_r \sin \varphi = k_i' \sin \varphi . \tag{84}$$

Let's raise to the second power expression (83) and (84) and sum it:

$$(\Delta k_r)^2 = k_i^2 + (k_i')^2 - 2k_i k_i' \cos \varphi .$$

By dividing this expression by  $c^2$ , we shall obtain

$$(\Delta \omega_r)^2 = \omega_i^2 + (\omega_i')^2 - 2\omega_i \omega_i' \cos \varphi .$$
(85)

We shall copy expression (82) as:

$$(\omega')^2 = (\omega_i - \omega_i' + \omega)^2 = \omega_i^2 + (\omega_i')^2 - 2\omega_i\omega_i' + 2\omega(\omega_i - \omega_i') + \omega^2,$$
(86)  
tract (85) from (86):

now we shall subtract (85) from (86):

$$(\omega')^2 - (\Delta \omega_r)^2 - \omega^2 = -2\omega_i \omega_i' (1 - \cos\varphi) + 2\omega (\omega_i - \omega_i').$$
(87)

In correspondence with expression (81), the left-hand part of (87) is equal to zero, so:  $\omega \cdot \omega' (1 - \cos \omega) = \omega(\omega \cdot - \omega')$ 

$$\omega_i \omega_i' (1 - \cos \varphi) = \omega (\omega_i - \omega_i')$$

or:

$$\frac{1-\cos\varphi}{\omega} = \frac{\omega_i - \omega_i'}{\omega_i \omega_i'}$$

That is equivalent to expression:

$$\frac{1-\cos\varphi}{\omega} = \frac{1}{\omega_i} - \frac{1}{\omega_i},\tag{88}$$

Taking into account, that  $\omega = \frac{2\pi c}{\lambda}$ , expression (88) will be copied as:  $\lambda_i - \lambda_i' = \lambda(1 - \cos\varphi)$ 

Where:  $\lambda_i$  and  $\lambda_i$ ' are wave length of incident and dispersed traveling waves, and  $\lambda$  is wave length of wave-object "reposing" in laboratory system. If we designate the change of length for the traveling wave, resulted from its interaction with the standing wave as  $\Delta \lambda_i = \lambda_i' - \lambda_i$ , we shall obtain:

$$\Delta\lambda_i = 2\lambda\sin^2\frac{\varphi}{2}.$$
(89)

This is the Compton's formula, which describes the interaction between electron and light quantum. We have obtained it without use of the concepts of mass, impulse or energy. Thus, the Compton effect can be presented as kinematic effect of interaction between the standing stable wave and traveling wave.

### 5. Conclusions

- 1. In the deductions presented above, any medium-carrier properties of waves do not appear, thus these deductions are valid for all wave types irrespective of medium. It signifies, that the Lorentz transformations are not interlinked on the presence or absence of the wave medium-carrier and can be considered as rules of some algebra (or group), which is defined on set of wave functions.
- 2. The application of undular frames allows us to obtain not only a trivial solutions relevant to a principle of superposition, but also solutions, which describe the interactions between waves as between mechanical particles.
- 3. At wave interaction their frequency varies. At interaction between the stable standing wave and the traveling wave, the quantization of traveling wave takes place.

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