A Look at the History of Superconductivity in Bulgaria

Elena Nazarova
Georgi Nadjakov Institute of Solid State Physics, BAS, 72 Tsarigradsko Shose Blvd., Sofia, Bulgaria
nazarova@issp.bas.bg

Abstract. The development of *low temperature physics and superconductivity* in Bulgaria began with establishment of low temperature laboratory at the former *Institute of Physics with Atomic scientific experimental base* in 1963. Three main stages exist in almost half century history of Bulgarian low temperature physics. The first ten years period is connected with elaboration of technology for production and conservation of liquid nitrogen and helium. The second (fourteen years) period (1973 – 1986) is characterized with investigations of conventional superconductors: the "*spin-glass*" state, coexistence of antiferromagnetic and superconducting phases, alternating current losses in type II superconductors ect. The third period is initiated by the discovery of non-conventional high-temperature superconductors. The good perspectives for practical application of *nitrogen* superconductors stimulated many scientific organizations to start experimental and theoretical research on this topic. Based on international collaboration Bulgaria developed its own specialists on superconductivity. Many of them worked and others still work at the authoritative centers of superconductivity all over the world.

Keywords: Superconductivity, Bulgaria, Main stages, Achievements

1. Introduction

The scientific community notes the 100th anniversary of discovery of the superconductivity in 2011. The Netherlandish physicist and Nobel laureate Heike Kamerlingh Onnes observed this remarkable phenomenon in 1911. At this time Bulgarian Learned Society (established in Braila, Romania – 1869) is transformed to Bulgarian Academy of Sciences (BAS) since 6 March 1911. G. Nadjakov, member of BAS, founded and headed the first *Institute of Physics* with Atomic scientific experimental base in the frame of BAS in 1946. Research investigations in the field of low temperature physics and superconductivity in Bulgaria started with the officially establishment of the Low temperature laboratory at the former Institute of physics with Atomic scientific experimental base (5 July 1963) [1-2]. The main initiator for that was Eugenie Leyarovski. The enthusiasm and efforts of young colleagues was supported by the deputy director of the Institute Sazdo Ivanov, who was the first head of the Laboratory.

2. First Period

Conventional superconductivity, discovered by H. K. Onnes, is a low temperature phenomenon and investigations in this field needed special equipment. In the first ten years period (until 1973), the technology of production and conservation of liquid nitrogen and helium was developed. The Institute obtained first helium liquefier and about ten nitrogen stations for production of liquid nitrogen. This initiated the research on the heat conductivity of pure superconducting metals and alloys and the influence of crystal defects on the kinetic properties of solids at low temperatures. Special attention was paid to the application of adiabatic demagnetization for production of low temperatures and cryogenic engineering problems (Fig. 1). The research work focused on studying the adsorption/desorption of inert gases at cryogenic temperatures, transport properties of metals and deformation defects behavior at low temperatures was also conducted. Heat conductivity of polycrystalline indium in superconducting state is investigated and phonon mechanism is established below $T = 0.6^{o}K$, while electron mechanism is found above this temperature [3].

In this period, the Faculty of Physics at the Sofia University also obtained helium liquefier from Czech Republic. Unfortunately, liquefier's compressor was problematic and the installation was unsuccessful. However new elective course on *Superconductivity* attracted students. Lectures were presented by the young assistant Petko Vassilev.

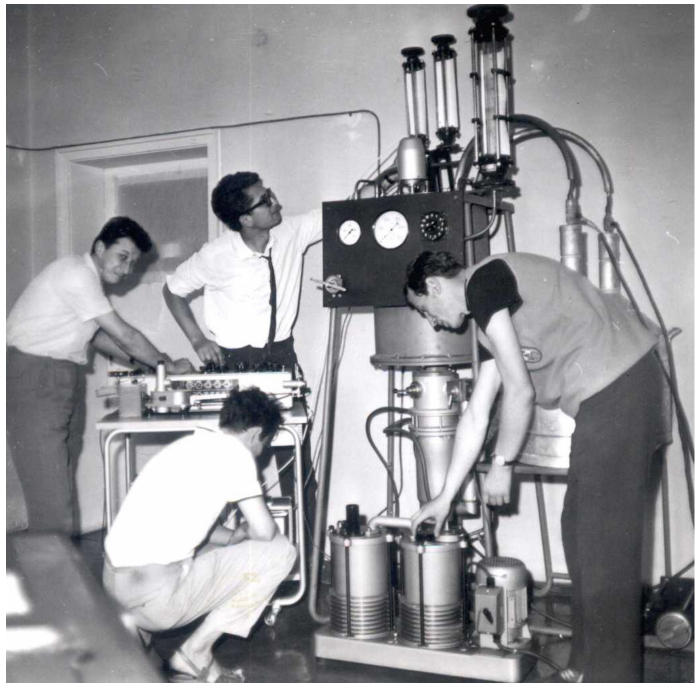


Fig. 1 *Preparation for the attendance of the International Conference in Wroclaw 24 August 1967 from left to the righ: E. Leyarovski, V. Kovachev, V. Lovchinov, down B. Nikolov*

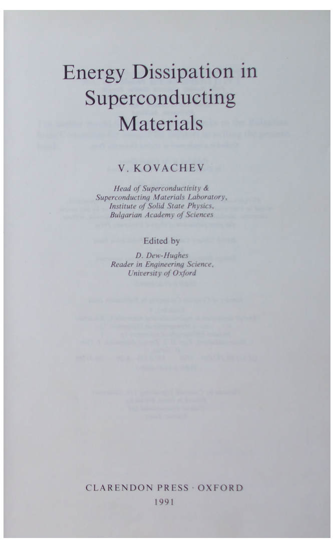
The initial steps of a new *Low temperatures laboratory* are extraordinary not only in the frame of our country, but they also had international significance. Two important projects between *Low temperature laboratory* and *National committee for science and technical progress* were accomplished: (a) the contract for research and development of small helium turboexpander, and (b) the application of multiple adsorption/desorption method for attaining pure gases of He and Ne from wasted gases in nitrogen/oxygen production in industrial plants. These projects gave the financial support for new equipment supply, enlargement of staff and validated the *Low temperature laboratory* as the only group in Bulgaria dealing with research and development in the area of low temperature physics and engineering [1]. The scientific results from one of the project brought the first international recognition for the *Low temperature laboratory*. The presented "*New method for attaining pure gases of He and Ne from wasted gases*" by E. Leyarovski won two gold medals awards from the World patents exhibition in Geneva (1973) and Brussels (1975) [2]. The other important event was the agreement signed in 1968 between the Academies of Sciences of Poland, Bulgaria, the former East Germany and USSR on the foundation of *International laboratory of high magnetic fields and low temperatures* in Wroclaw, Poland. The introduction of the agreement best described the purpose of the Laboratory *to conduct theoretical and experimental research in the area of high magnetic fields and low temperatures*.

The International laboratory in Wroclaw had big influence on the development of low temperature and superconductivity investigations in Bulgaria in the second (fourteen years) period (1973 – 1986). Many researchers from the Bulgarian Academy of Sciences and from the Sofia University visited Wroclaw to use the experimental equipment and share their knowledge. It is a great honour for the Bulgarian low temperature science that E. Leyarovski was elected as deputy director of the International Laboratory in the period of 1974 – 1977.

3. Second Period

In the beginning of second period some administrative changes take place in Bulgarian Academy of Sciences. The former Institute of physics with Atomic scientific experimental base was split into Institute of Solid State Physics (ISSP) and Institute of Nuclear Research and Nuclear Energy by a Decree of the Bulgarian Ministry Council from 16 October 1972. However the real existence of these scientific institutions dates since 1 January 1973. Institute of Solid State Physics was directed to specialize in fundamental and applied research in the field of condensed matter physics, optics, spectroscopy and laser physics. A new department of *Magnetism and low temperatures* at ISSP incorporated three groups: *Magnetism* from the Faculty of Physics in Sofia University (headed by A. Apostolov), *Low temperature physics* (headed by E. Leyarovski) and *Applied superconductivity and cryogenics* (headed by V. Kovachev).

At this period special attention is paid to the development of experimental techniques for obtaining of low temperatures (below 1°K). Nanokelvin range (300°nK) was reached (Fig 2). From today's point of view especially important was the search for superconductivity below 1K in transition metal borides (in 1979). A lot of compounds with the formula MeB_2 (Me=Ti, Zr, Hf, V, Nb, Ta, Cr, Mo) were examined. Superconductivity was observed only in NbB_2 with T_c=0.62°K [4]. Unfortunately MgB_2 was not among the investigated compounds and superconducting transition with 39°K was observed in it as late as 2001. The other important results are the discovery of new superconductors in the system Nb-Al [5], and the coexistence of antiferromagnetic and superconducting phases [6].



New specific direction of investigations was the alternating current losses in type II superconductors: A-15 (Nb_3Sn, Nb_3Ge) [7], C-15 (V_2Hf and other ternary Lave's phases compounds) [8] and B-1 (NbN) [9]. Loss values were obtained by an electronic wattmeter multiplying two signals: one proportional to the voltage induced in the sample and second proportional to the alternating current component of the magnetic field. For the first time in the literature a minimum of alternating current loss in Nb_3Sn under alternating current and direct current magnetic fields was reported, analyzed and modeled in details [10-12]. All results of the group in this topic are presented and discussed in the monograph of V. Kovachev [13] (see the picture in left).

The group of *Applied superconductivity and cryogenics* headed by V. Kovachev participated in the Cryogenics program of countries from former Council for Mutual Economic Assistance. As a leading group of alternating current loss measurements in superconducting materials it organized the workshop where scientists from Moscow, Kiev, Wroclaw and Bratislava were introduced in the measurement technique. In 1982 in the frame of this program a conference "*Electro-conductance in electro-energetic and electro-technique*" take place in Varna, Bulgaria with 60 specialists from Russia, Poland, Czechoslovakia and Bulgaria. Among the Russian participants was Alexey Abrikosov. He was awarded the 2003 Nobel Prize in Physics for his research in superconductivity.

In 1971 and 1983 Bulgaria hosted the 10th and 21st International conferences on *Low temperature physics and techniques* of countries from the Council for Mutual Economic Assistance.

Fig. 2 *Cryostat for investigations at liquid helium temperatures*

4. Third Period

The next period in superconductivity research in Bulgaria is connected with the high-temperature superconductivity discovered in 1986 by G. Bednorz and K. Müller. On the 20 April 1987 specialists from the Institute of Solid State Physics registered superconducting transition at T_c $(0.5R_n) = 86.5^oK$ in Y-Ba-Cu-Pt-O system [14-15]. Thus, the era of *nitrogen* superconductors started in Bulgaria too. The big enthusiasm in the beginning was connected with the more realistic perspectives for practical applications. On the other hand, the difficulties in the experimental investigations of conventional superconductors were overcome. Many new scientific institutions were included in the preparation and investigations of new high-temperature superconducting materials in different form: single- and poly-crystals, thin and thick films, multi-structures, tapes and wires. Very often, the investigations have been carried out on collaboration between the researchers from different scientific institutions. Some of them started his investigations in superconductivity with the discovery of high-temperature superconductivity: Institute of Electronics – Bulgarian Academy of Sciences (BAS), Institute of General and Inorganic Chemistry (BAS), University of Chemical Technology and Metallurgy, Chemistry Department of Sofia University. More experienced colleagues are from the Institute of Solid State Physics (Superconductivity and superconducting materials laboratory; Low temperature and magnetic phenomena laboratory) and from the Physics Department of the Sofia University. However, every scientific institution has its own aspect in high-temperature superconducting investigations.

For example in the Institute of General and Inorganic Chemistry (BAS) synthesis of different superconducting materials have been performed [16-18], but particular emphasis was on X-ray diffraction methods including qualitative and quantitative phase analysis, diffraction line-broadening analysis (crystallite size distribution and micro-strains), as well as structure refinement by the Rietveld method on different superconducting materials.

In fact, the superconductivity investigations started at the Institute of Electronics (BAS) a few years before discovering the high-temperature superconductivity [19]. The earliest articles on superconductivity are connected with calculations of 1/f noise power spectrum for thin film devices (bolometers, Josephson junctions and SQUIDs) [20], analysis of the radio frequency (RF) SQUID in regime, where the bias frequency (ω) is comparable to the natural frequency of the SQUID ring [21] and modeling the very high-frequency phenomena in current driven Josephson junction [22]. In the beginning of high-T_c superconductivity metal additions and substitutions in polycrystalline samples have been investigated [23-24], as well technological aspects for thin films preparation by laser ablation [25] and radio frequency magnetron sputtering [26], optical emission of laser induced plasma plume [27] and development of different methods for samples investigations [28]. In spite of all, the Institute of Electronics has his specific field of research connected with development of cryoelectronics-especially in investigations of high-T_c Josephson Junctions and SQUIDs [29].

University of Chemical Technology and Metallurgy, Sofia was included in high –T_c superconducting materials preparation and investigation almost in the beginning of this research [30]. The influence of different additives (Ag, Te, Sn) on the microstructure and phase formation in 1-2-3 and Bi-based superconducting systems is investigated systematically [31-32]. Samples were prepared by standard solid state reaction method and by melt-quenching method as well [33]. Spectrophotometric method for determination of oxygen content was developed in cooperation of specialists from the chair of Analytical Chemistry and the Institute of Solid State Physics (BAS) [34].

Fig. 3 *First generation monofilamentary* $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_x$ *superconducting tape with Silver sheath*

After the successful start in high-T_c superconductivity specialist from the Institute of Solid State Physics (BAS) continue their work. Single-phase polycrystalline samples were obtained by "*wet*" nitrate and solid state reaction methods. The coexistence of Meissner domains and mixed state phase was established below the Earth's field in YBCO system [35]. The role of 4f electrons in the formation and coexistence of superconductivity and magnetism, thermodynamic fluctuations of the superconducting order parameter in 1-2-3 superconducting system were studied. The influence of different substitutions and additives on the magnetic properties of 1-2-3 and Bi-based superconducting systems was investigated systematically [33, 36]. Different new superconducting systems: (Pb, M)Sr_2(Y, Ca)Cu_2O_z with M=Sn; Ag ($Hg_{1-x}Sn_xBa_2Ca_3O_y$; cadmium analog of the mercury system; (Pb,M)Sr2YCu2Oz; Sn – doped Ru-1222 were synthesized (Fig. 3) and investigated [37-39]. Systematic investigations of the overdoped state in 1-2-3 superconducting system were carried out [40]. First generation superconducting tapes with Bi-based and Y(Ca)BCO superconducting core were produced and investigated [41-42]. All this works were carried out in the frame of many project with National Scientific Fund and international projects with NATO and Europen Euratom program.

The work on high-T_c superconductivity in Physics Department in Sofia University started immediately after the publication of J. G. Bednorz and K. A. Müller in Zeitschrift für Physik B [43]. The first efforts are connected with obtaining the La-Ba-Cu-O superconducting system. It was late understood that as a result of possible replacement of La and Ba atoms this system is not so easy to be obtained. For that reason La based compound with 1-2-3 stoichiometry was the last obtained with critical temperature in the range of 90^{o}K. In spite of this initial disappointment the colleagues from the Physics Department have their great contribution to the development of high-T_c superconductivity in Bulgaria.

The important theoretical articles appeared, where possible mechanisms of high-temperature superconductivity were discussed [44-46]. A lot of experimental works were done in the field of Raman spectroscopy of new materials [47-49]. Bulgarian group became one of the leading in the world. The head of the group, Professor Milko Iliev, was invited by Paul Ching-Wu Chu to establish the Raman Spectroscopy Laboratory at the Superconductivity center in Houston, USA.

Bulgaria developed its own school of specialists on superconductivity. Many of them worked or still work at the authoritative centers of superconductivity all over the world: in USA – Texas Center for Superconductivity (M. Iliev), Superconducting Super Collider Laboratory, Dallas (V. Kovachev), University of California, Riverside (E. Leyarovski), Ohio State University (I. Kostadinov), Ilinois Institute of Technology (N. Leyarovska); High Energy Accelerator Research Organization (KEK) in Japan (V. Kovachev), University of Wollongoug, Australia (K. Konstantinov), University of Gothenburg, Sweden (Z. Ivanov), in UK – University of Cambridge (R. Tomov, V. Tzaneva), University of Birmingham (R. Chakalov), in Germany – Technical University of Braunschweig and KfA Juelich (S. Tinchev), Leibniz Institute for Solid State and Materials Research – Dresden (K. Nenkov), Karlsruhe Institute of Technology (S. Terzieva), in Spain – University of Barcelona (K. Zalamova), Catalan Institution for Research and Advanced Studies (V. Skumriev) etc.

5. Conclusion

In fact, a Bulgarian low temperature and superconductivity research has approximately half century history. For this short historical period significant experimental and theoretical results have been obtained. More frequently, this is a result of successful international collaboration between our leading scientific organizations in this field and prestigious laboratories and institutes in different countries. Especially important result is a creation of qualified specialists working at home and abroad.

Fig. 4 *Physical Properties Measurements System (USA) for matherials characterization at the ISSP-BAS. The apparatus is delivered in 2009.*

More difficult is the implementation of superconductivity in different fields of activity in the country. The first scientific apparatus consisting of superconducting magnet were supplied to the Institute of Organic Chemistry with Centre of Phyto-chemistry (Bruker nuclear magnetic resonance spectrometer with 14 T magnet) and the Institute of Solid State Physics at the BAS (Physical properties measurements system with 9 T magnet) (see Fig. 4). In the past 10 – 15 years many apparatuses for Nuclear Magnetic Resonance for medical investigations have been bought (in Tokuda hospital, Losenetz hospital, Military hospital in Sofia and some hospitals in the country). Bulgarian Institute of Metrology plans to provide the voltage etalon based on the Josephson effect. Introducing the high-temperature superconductors in different apparatus and machines will increase the applicability of superconductivity in various areas of human activity.

Acknowledgments. *The author is grateful to the colleagues for a critical reading of manuscript.*

References

1. V. **Kovachev**, E. **Nazarova**, V. **Lovchinov**, E. **Vlakhov**, B. **Terzijska**, D. **Dimitrov**, N. **Balchev**, Superconductivity and Superconducting Materials Laboratory, *Jubilee Collection 30-th Anniversary of the Institute of Solid State Physics 1972-2002*, ed. A. G. Petrov, Sofia, (2002) p. 125.
2. N. **Tonchev**, K. **Kalaydjiev**, M. **Bushev**, C. **Popov**, N. **Todorov**, M. **Kirov**, M. **Baychev**, Department: Low Temperature and Magnetic Phenomena, *Jubilee Collection 30-th Anniversary of the Institute of Solid State Physics 1972 – 2002*, ed. A. G. Petrov, Sofia, (2002) p. 151.
3. Е. **Леяровски**, М. **Захариева**, *Известия на Физическия институт с АНЕБ*, **19,** с. 73 (1969).
4. L. **Leyarovska**, E. **Leyarovski**, *A* search for superconductivity below 1^{O}K in transition metal borides, *Journal of the Less Common Metals*, **67**(1) 249-255 (1979).
5. E. **Leyarovski**, L. **Leyarovska**, E. **Krasnopyorov**, L. **Kokot**, R. **Horin**, T. **Midlarz**, Superconductivity and Magnetic Properties of Nb-Al Phases: Nb_2Al and $NbAl_3$, *Zeitschrift für Physik B*, **27**, 57-60 (1977).
6. N. **Alekseevskii**, E. **Leyarovski**, L. **Leyarovska,** V. **Tsebro**, Magnetic phase transition in $Mo_5SnGa_{0.5}S_6$, *Journal of Physics C*, **8**, L585 (1975).
7. V. **Kovachev**, K. **Nenkov**, Power Losses of Nb_3Ge-clad Tapes in Superposed AC and DC Magnetic Fields, *Materials Letters*, **2**(2) p. 111 (1983).
8. V. **Kovachev**, D. **Dew-Hughes**, AC Losses of V_2Hf, *Proceed. ICEC 10*, July 31 – August 3 1984, Helsinki, Butterworths, Surrey, 708 (1984).
9. V. **Kovachev**, V. **Lovchinov**, K. **Nenkov**, E. **Nazarova**, M. **Bichkova**, A. **Korjov**, AC Losses of NbN, *Physica Status Solidi A*, **91**, K151 (1985).
10. J. **Bussiere,** V. **Kovachev**, AC losses of bronze processed $(Nb_{1-x}Zr_x)_3Sn$ between 5 and 16^{O}K, *Journal of Applied Physics*, **50,** 3510-3513 (1979)**.**
11. V. **Kovachev**, E. **Nazarova**, Minimum in AC Losses of Low Bulk Pinning Nb_3Sn, *Physica Status Solidi A*, **71**, 357 (1982).
12. V. **Kovachev**, E. **Nazarova**, Minimal of Power Losses of Nb_3Sn in superposed AC and DC Magnetic Fields, *Proceed. ICMC 9*, Kobe, Japan, 1982, Butterworths, Surrey, 162 (1982).
13. V. **Kovachev**, *Energy dissipation in superconducting materials*, Oxford Science Publication, Clarendon Press, Oxford (1991).
14. V. **Kovachev**, E. **Vlakhov**, K. **Nenkov**, V**. Lovchinov**, M. **Gospodinov**, A. **Stojanova**, D. **Dimitrov**, T. **Mydlarz**, Antiferromagnetic Ordering in Y-Ba-Cu-Pt-O, *International Journal of Modern Physics B,* **1**(2) p. 479 (1987).
15. V. **Kovachev**, E. **Vlakhov**, K. **Nenkov**, V. **Lovchinov**, M. **Gospodinov**, A. **Stojanova**, D. **Dimitrov**, M. **Czyczek**, T. **Mydlarz**, Superconducting Properties of Y-Ba-Cu-Pt-O, *International Journal of Modern Physics B*, **1**(2) p. 223 (1987).
16. P. **Peshev**, G. **Gyurov**, I. **Khristova**, K. **Petrov**, D. **Kovacheva**, Ya. **Dimitriev**, N. **Nencheva**, E. **Vlakhov**, Comparative study of some methods of synthesis of the high-T_c superconductor $YBa_2Cu_3O_{7-x}$, *Materials Research Buletin*, **23,** p. 1765 (1988).
17. D. **Kovacheva**, K. **Petrov**, V. **Lovchinov**, E. **Nazarova**, P. **Dochev**, G. **Melnikliev**, V. **Kovachev**, *Phase* formation and superconductivity in Bi-Pb-Sr-Ca-Cu-O, *Physica C*, 162-164, p. 1227 (1989).
18. D. **Radev**, M. **Marinov**, V. **Tumbalev**, I. **Radev**, L. **Konstantinov**, Mechanically activated self-propagated high-temperature synthesis of nanometer-structured MgB_2, *Physica C*, **418,** p. 53 (2005).
19. *An Overview Dedicated to the 25 Anniversary of the Institute of Electronics*, The Bulgarian Academy of Sciences, Sofia (1988).
20. S. **Tinchev**, L. **Blieck**, V. **Kose**, A consistent model for 1/f noise in thin film devices such a bolometers, Josephson junction and SQUIDs, *Physics Letters*, **94**(8) p. 381 (1983).

21. S. **Tinchev**, Input impedance of the SQUID in high bias frequency regime, *IEEE Trans. MAG-19* (3) p. 594 (1983).
22. Z., **Genchev**, Z. **Ivanov**, B. **Todorov**, Effect of a periodic perturbation on radio frequency model of Josephson junction, *IEEE Trans. Circuits and Systems, CAS-30* (9) p. 633 (1983).
23. I. **Nedkov**, I. **Iliev**, S, **Tinchev**, M. **Taslakov**, V. **Kojucharov**, AC susceptibility of monovalent metal substituted high-Tc suprconducting oxides, *Superconductors Science and Technology* (1) 324-325 (1989).
24. A. **Veneva**, I. **Nedkov**, V. **Lovchinov**, Superconducting properties and microstructure of YBCO HTSC materials with K_2CO_3 addition, *Physica C*, **235-240**, 805-806 (1994).
25. P. **Atanasov**, R. **Tomov**, V. **Serbesov,** Plasma assisted in situ laser deposition of $Y_1Ba_2Cu_3O_{7-x}$ superconducting thin films with laser heating and annealing, *Vacuum*, **45**, p. 1215 (1994).
26. Z. **Ivanov**, T. **Nurgaliev**, T. **Donchev**, A. **Chernakova**, B. **Todorov**, Superconducting Bi-Sr-Ca-Cu-O films prepared by RF magnetron sputtering, *Modern Physics Letters B*, p. 785 (1989).
27. V. **Tsaneva**, T. **Donchev**, R. **Tomov**, D. **Ouzunov**, A. **Veneva**, T. **Nurgaliev**, Plasma optical emission studies of high-T_c superconducting and buffer thin film physical vapour deposition, *Vacuum*, **48**, p. 803 (1997).
28. T. **Nurgaliev**, V. **Tsaneva**, R. **Chakalov**, T. **Donchev**, A. **Spasov**, Contactless characterization of YBCO films on different substrates, *Physica C*, **235-240,** 3215-3216 (1994).
29. S. **Tinchev**, Ion Modified High-Tc Josephson Junctions and SQUIDs, *Superconductivity: Theory, Materials and Applications*, ed. Vladimir Rem Romanovskii, Novapublisher, USA, (2011) 381-404.
30. E. **Vlakhov**, K. **Nenkov**, Y. **Dimitriev**, V. **Kovachev**, Influence of Ag Additions on Superconducting Transition of R $Ba_2\ Cu_3\ O_{7-x}$ (R = Y, Eu) Ceramics in Magnetic Field, *Physica C*, **162-164**(2) p. 975 (1989).
31. E. **Vlakhov**, E. **Gatteff**, Y. **Dimitriev**, A. **Staneva**, Synthesis and superconductivity of $YBa_2Cu_3O_y$ ceramics doped with Sb, Ag and Te, *Journal of Materials Science Letters* (13) p. 1654 (1994).
32. Y. **Dimitriev**, E. **Gatteff**, E. **Kashchieva**, A. **Staneva**, E. **Vlakhov**, High-T_c superconducting glass-ceramics prepared by the melt-quenching methods in the bismuthate system with additives, *Materials Research Bulletin*, **28** p. 1185 (1993).
33. E. **Vlakhov**, K. **Nenkov**, M. **Ciszek**, A. **Zaleski**, Y. **Dimitriev**, Superconducting and magnetic properties of melt-quenched Bi-2223 superconductors doped with Pb and Te, *Physica C*, **225** p. 149 (1994).
34. T. **Nedeltcheva**, S. **Georgieva**, L. **Vladimirova**, A. **Stoyanova-Ivanova**, Increasing the sensitivity of the spectrophotometric determination of the oxygen content in YBCO superconducting samples using the I_3 – starch compound, *Talanta*, **77,** p. 1745 (2009).
35. E. **Leyarovski**, L. **Leyarovska**, N. **Leyarovska**, C. **Popov**, M. **Kirov**, Low-field magnetocaloric effects in YBaCuO superconductors, *Physica C*, **153-155**, 1527-1528 (1988).
36. V. **Kovachev**, E. **Vlakhov**, High magnetic field studies of high-temperature superconductors, *Studies of high-temperature superconductors,* ed. A. Narlikar, v. 4, (1990) p. 59.
37. N. **Balchev**, K. **Nenkov**, B. **Kunev**, J. **Pirov**, A. **Souleva**, Synthesis and Phase composition of $FeSr_2YCu_2O_z$, *Journa of Superconductivity: Incorporating Novel Magnetism*, **16**(3) p. 513 (2003).
38. N. **Balchev**, K. **Nenkov**, G. **Mihova**, B. **Kunev**, J. **Pirov**, Superconducting and Magnetic Properties of Sn - Doped Ru-1222, *Physica C*, **467**, 174-178 (2007).
39. N. **Balchev**, K. **Nenkov**, G. **Mihova**, B. **Kunev**, J. **Pirov**, D. **Dimitrov**, Structure, Magnetic and Superconducting Properties of $MoSr_2HoCu_2O_{8-\delta}$, *Journal of Magnetism and Magnetic Materials*, **321**, 388-391 (2009).
40. E. **Nazarova**, K. **Nenkov**, A. **Zaleski**, K. **Buchkov**, A. **Zahariev**, Investigations of the overdoped state in policrystalline$R_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ samples (R=Y, Eu, Gd, Er), *Superconductivity: Theory, Materials and Applications*, ed. Vladimir Rem Romanovskii, Novapublisher, USA (2011) 327-361.
41. V. **Lovchinov**, D. **Dimitrov**, P. **Simeonova**, G. **Kallias**, E. **Moraitakis**, Phase formation and microstructure of silver sheathed B(Pb)SCCO tapes influenced by Te additive, *Journa of Superconductivity: Incorporating Novel Magnetism*, **13** p. 1042 (2000).
42. H. **Ignatov**, E. **Nazarova**, A. **Zahariev**, V. **Lazarova**, J. **Georgiev**, A. **Stoyanova-Ivanova**, S. **Terzieva**, K. **Kliavkov**, V. **Kovachev**, Deformation effects on the structure and properties of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (x=0; 0.3) tapes produced by OPIT method in the Ag tube, *Journal of Superconductivity*, **21**, p. 69 (2008).
43. J. **Bednorz**, K. **Müller**, *Zeitschrift für Physik B*, **64** p. 189 (1986).
44. I. **Kostadinov**, M. **Mateev**, I. V. **Petrov**, P. **Vasilev**, J. **Tihov**, Superconducting glass behavior in high-temperature superconductors, *Physica C*, **153-155,** p. 320 (1988).

45. T. **Mishonov**, J. **Indekeu**, E. **Penev**, The 3d to 4s by 2p highway to superconductivity in cuprates, *International Journal of Modern Physics B* **16,** 4577-4585 (2002).
46. T. **Mishonov**, J. **Indekeu**, E. **Penev**, Superconductivity of overdoped cuprates: The modern face of the ancestral two electron exchange, *Journal of Physics: Condensed Matter*, **15** (2003).
47. M. **Iliev**, V. **Hadjiev**, V. **Ivanov**, Raman spectroscopy of local structure and reordering processes in $YBa_2Cu_3O_{7-\delta}$-type compound, *Journal of Raman Spectroscopy*, **27,** p. 333 (1996).
48. M. **Iliev**, C. **Thomsen**, V. **Hadjiev**, M. **Cardona**, Resonant Raman scattering of oxygen-deficient $YBa_2Cu_3O_{7-\delta}$: Evidence for the coexistence of ortho-I, ortho-II and tetragonal microstructures, *Physical Review B*, **47,** p. 12341 (1993).
49. V. **Hadjiev**, M. **Iliev**, K. **Sasmal**, Y. **Sun**, C. W. **Chu**, Raman spectroscopy of RFeAsO (R=Sm, La), *Physical Review B*, **77,** p. 220505 (R) (2008).