PREPARATION, STRUCTURE AND SUPERCONDUCTIVITY
OF HIGH-\(T_c\) COMPOUNDS

(Research of high temperature superconductors in Hungary)

I. Kirschner

Department for Low Temperature Physics, Eötvös University, Budapest, Hungary

Abstract

In this paper the main directions, methods and results of the investigation of high-\(T_c\) superconductors in Hungary are briefly summarized. The fundamental idea of this research is to study the effect of starting conditions on the microstructure of samples and the influence of the latter one on their superconducting parameters. The investigation concerning technical development is also mentioned.

Introduction

At the beginning of this century the fundamental gravitation experiments of Loránd Eötvös and his collaborators made the Hungarian physics to be well-known. Numerous famous results are connected to his name, namely the Eötvös-pendulum (which has an importance in the research of raw materials too), Eötvös-effect and Eötvös-law, etc.

Before the 2nd World War the physical investigation was concentrated in the universities and some big companies, dealing mainly with the applied research referring to the actual needs of the industry. In this way important results have been achieved in the field of research of metals (in particular of wolfram), noble alloys, and physical basis of the production of incandescent lamps and high-power electrical equipments.

Many Hungarian originated physicists and chemists left their native country and worked in the forefront of scientific research in different places of the world. Among them Jenő Wigner (nuclear physics), Ede Teller (nuclear physics), Miklós Kürti (low temperature physics), János Kemény (discovery of basic language of computers), László Tisza
(thermodynamics), Zoltán Bay (radar technology), Frigyes Bárány (vestibular system), Tódor Kármán (mechanics, who was the founder of Jet Propulsion Laboratory), Dénes Gábor (holography), Leó Szilárd (nuclear physics), György Békésy (research of hearing), János Neumann (mathematics), János Polányi (dynamics of chemical process), Kornél Lánczos (mathematical physics), György Hevesy (nuclear chemistry, isotope-traces), Albert Szent-Györgyi (biochemistry) and Bálint Telegdi (nuclear physics) are the most known. The excellent scientific results of Wigner, Gábor, Szent-Györgyi, Hevesy, Békésy, Bárány and Polányi were acknowledged by Nobel-prize.

During the years of fifties a new research and development system was established, having four sections, namely university departments, institutes of the academy of sciences, industrial research institutes and local research and development centers of different companies.

The physical research broadened significantly and the directions covered almost all of the main fields of physics, e.g. quantum-mechanics, solid state physics, thermodynamics, nuclear physics, optics, astrophysics, elementary particles, statistical physics, laser physics, relativity theory, etc.

Some groups were successful in different areas of physical research, namely in the investigation of cosmic rays, molecular spectroscopy, crystal growth, elementary particles, low energy nuclear physics, evolution of the world, magnetism, neutron physics, quantum chemistry, etc. having internationally respected results.

**Activity and co-operation in high-T\(_c\) superconductivity**

The solid state physics and materials science have a rather old tradition in Hungary, and numerous Hungarian research institutions (universities, academic institutes and industrial research centers) act in different fields of condensed matter physics. During this research, remarkable results obtained concerning metals, alloys, semiconductors, surfaces and technical application of the results of the fundamental study. This activity provided the basis of the research of low temperature phenomena, first of all superconductivity.

The main themes of our superconductivity research were the investigation of the magnetic properties of conventional superconductors, namely In-Bi, In-Tl, In-Pb, Sn-Bi, and Sn-Sb alloys, the study of compounds and alloys having an importance from the point of view of application, building magnets and small-scale cable sections, the investigation of the
pinning properties and the use of the irreversible thermodynamics to describe the features of superconductors.

In the last years, after the discovery of the high-temperature superconductivity, we turned mostly to the investigation of the phenomena of these new superconducting compounds.

The investigation of the high-temperature superconductivity was started in Hungary in January 1987, based on our former experiences obtained in the course of the research of the conventional superconductors, which began in 1963.

1. In a small country, like Hungary, the co-operation plays a very important role in the research work, so we have organized a very wide cooperation inside and outside Hungary concerning this field of science. This contains the following institutions:

1. Eight laboratories of the Eötvös University, Budapest, (Department for Low Temperature Physics, Department of Atomic Physics, Department for General Chemistry, Department for Mineralogy, Laboratory for Nuclear Chemistry, Department for Petrology and Geochemistry, Laboratory for Surface Physics and Department for Analytical Chemistry),
2. Central Research Institute of Silicate Industry,
3. Five laboratories of the Budapest Technical University (Physical Institute, Reactor, Department of Electrical Machines, Institute of Mechanical Technology and Department of Electronics Technology),
4. Central Research Institute for Chemistry,
5. University of Debrecen (Institute for Experimental Physics),
6. Institute for Research of Metals,
7. Central Research Institute for Physics,
8. Research Institute of Electrical Industry,
9. EPOS-PVI Electrical Inc.,
10. University of Veszprém (Department of Silicate Chemistry),
11. Research Institute of Technical Physics,
12. National Bureau of Standards,
13. Nuclear Research Institute of the Hungarian Academy of Sciences,
15. Committee of Technical Development.
16. Finland: Wihuri Physical Laboratory (University of Turku), Microelectronics Laboratory (University of Oulu),
17. Great Britain: Center for HTSC (Imperial College of Science and Technology, London), Department of Physics (Glasgow University),
18. Germany: Institut für Festkörperforschung (KFA, Jülich), Lehrstuhl für Tieftemperaturphysik (Humboldt University, Berlin), Forschungszentrum (Geesthacht), Hammelwerke Sensor GmbH (Scheweningen), Physikalisches Institut (University Erlangen-Nürnberg, Erlangen),
19. The Netherlands: Physics Department, (University of Amsterdam), Physical Institute (University of Nijmegen),
20. Russia: Institute for Physical Problems (Moscow), Institute of High Temperature Research (Moscow),
21. Austria: Physikalisches Institut (University of Vienna),
22. Egypt: Department for Physics (Ain Shams University, Cairo),
23. USA: Institute of Chemistry, Drexel University, Philadelphia, etc.

(2). We have developed a complex basis for preparation of samples, which included university laboratories, academic institutes, industrial research centers and local industrial research-development sections. The preparation work covers different profiles, containing different methods form the solid state reaction, through explosion procedure or screen printing, until laser ablation.

(3). In the frame of the above mentioned co-operation we have sent superconducting samples to Italy, Germany, England, The Netherlands, Russia, Austria for investigation and provided more, than 100 Hungarian schools with them giving the possibility for the demonstration of the impressive HTSC effects.

(4). A specific governmental financial support helped us to increase the level of investigation and made possible to carry out some experiments of that kind, which could not be done earlier due to the lack of certain up-to-date experimental equipments.

Research and results in the field of HTSC

The research performed in Hungary in this field is basically experimental, it has, however, some theoretical and application aspects, as well.
The investigation can be treated as a complex one, because it concerns all of the main directions in question, namely the sample preparation, physical properties and possible technical applications.

This study covers all of the known families of HTSC compounds. The properties of La-Ba-Cu-O, Y-Ba-Cu-O, Bi(Pb)-Sr-Ca-Cu-O, Tl-Ca-Ba-Cu-O and in the latest time Hg-Ba-Ca-Cu-O superconductors have been investigated. Different substitutions of ions and doping processes were also performed, which is demonstrated as follows: Sr → Ba, Eu or other RE → Y, Fe or Sn → Cu, F → O₂ and addition of Ag or LiF, in order to change the physical or mechanical parameters of the basic superconducting compounds.

The bulk samples, thick films and thin layers are equally in our interest from the point of view of investigations.

High-Tₐ superconductors, suitable to different specific purposes, (e.g. magnetic screening) were elaborated, as elastic foils, rods and filaments, using organic and inorganic filling materials.

Certain improvements of the experimental technique were also performed concerning the measurement of thermoelectromotive force, critical currents, a.c. resistivity and susceptibility.

During the different directions of investigation we used a rather wide spectrum of the research methods, namely:

The applied methods provide scientific information on the physical properties of the samples, namely:
1. character of the superconducting transition (metallic, semiconducting, percolative), 2. sharpness of it, 3. effect of preparation (starting materials, their mixture, heat treatment), 4. temporal stability or instability (possible change in structural, electrical and magnetic properties), 5. effect of external circumstances, 6. quantity of superconducting material in specimens, 7. number, quality and share-rate of s.c. phases, 8. place and change of ions, 9. type of charge carriers, 10. degree of oxidation, 11. chemical co-ordination, 12. properties of surfaces and grains, 13. critical parameters (Tₒ, Tₐ, Tₜ, Hₕ, Jₑ, ξ, λ, κ), 14. phonon-
electron coupling, 15. gap, 16. conclusion on the fundamental superconducting mechanisms, 17. data for unit cells and their deformation, 18. anisotropy, 19. mechanical properties, dilatation, elasticity, 20. influence of thermal cycling, 21. corrosion, degradation, etc.

(8). Due to the limited length of this paper only a few concrete results of the Hungarian HTS-research can be enumerated to demonstrate the scope of it:

1. Just from the beginning we made the electrical and magnetic measurements together to obtain a good chance to evaluate the Meissner’s state volume of samples.

2. We have investigated in detail some important questions of high-T\textsubscript{c} compounds, namely the preparative chemistry consequences on Y-Ba-Cu-O superconductors, the possible role of percolation effects in establishment of superconductivity, characteristic parameters of Tl-Ca-Ba-Cu-O compounds based on a very wide spectrum of preparation methods, surface structure of different samples by STM method, effect of thermo-mechanical and water corrosion, proximity effect, complex study of Bi-based samples, effect of neutron irradiation, diamagnetism above T\textsubscript{c}, effect of particle size on the mechanism of the development of HTSC, improvement of the plastic properties of samples, etc.

3. Similarly to other laboratories, we also observed superconductivity at higher, than usual T\textsubscript{c} in an Y-based, temporally unstable specimen in April, 1987, but in contrast with other results, the value of its T\textsubscript{c} was only 105 K.

4. The elaboration of superconducting ceramic magnets with a new energy feeding, small-scale electrical rotating machines, cryogenic liquid level sensors, magnetic field detectors and magnetically screening elastic foils, rods and thin filaments can be mentioned among our works for the purpose of technical development.

5. Some Hungarian researchers were dealing with the study and application of Josephson’s tunnelling and with the high-T\textsubscript{c} SQuID experiment having some new and valuable information on these questions and on their application in measuring technique.

6. The employment of the Mössbauer-spectroscopy to find out the details of structure and some fine effects represents an important contribution to the HTSC-research in Hungary. It was very wide, and based on replacing sites by \textsuperscript{151}Eu, \textsuperscript{119}Sn, \textsuperscript{57}Fe and \textsuperscript{57}Co nuclides in order to get information about site preference, structural changes, temporal instability and change of the phonon properties.

7. Hungarian researchers have attained remarkable results in the investigation of fullerenes, certain part of those can be superconducting. If the chains of C60 molecules contain some alkaline metals (e.g. K, or Rb), they can develop in the form of filaments and produce
electrically conducting polymer-crystals, which show a metallic behaviour. This research is also accomplished in an international (American and Swiss) co-operation. The structure of fullerenes of different kinds of conductivity are under investigation in Hungary, using unlike methods, e.g. ESR-, IR-, and Mössbauer-spectroscopy. These investigations include alkaline fullerenes, fullerene polymers and ligandum-containing fullerenes as well.

8. Optically induced changes of the magnetic properties, created by laser beam in La-Ba-Cu-O superconductors have been observed. According to our investigation, the light-induced change of the magnetic moment strongly depends on the temperature at low temperatures. The results obtained in the magnetic field of 1-26 Oe suggest, that the observed effects have contributions from the weakening Josephson’s junctions under illumination and from the additional part of the optically induced flux creep, which depends on the applied magnetic field.

9. In order to examine the fine details of superconducting-normal or normal-superconducting transition, a new, so-called thermometric mapping method was elaborated. By the essence of this method, the samples are submitted to a large and variable temperature gradient, which broadens significantly the transition to reveal its gradual nature. This procedure is in a strong contrast with the conventional electrical and magnetic measuring practice of superconductivity, where a homogeneous temperature distribution is used generally to avoid the uncertainty of results. The method is sensitive enough to detect not only the fine structure of the transition, or to select the unlike properties of different specimens, but to trace the change of the features of a given sample too.

(9). Comparing to the international research of HTSCs, we investigated firstly some important questions of this field, which were as follows:

1. building high-$T_c$ superconducting ceramic magnets, 2. synthesis and application of a new precursor $\text{Ba}_2\text{Cu}_3\text{O}_5$, 3. investigation of the corrosion effects, 4. elaboration of the thermometric mapping method, 5. Mössbauer-study of Tl-based superconductors, 6. cryogenic liquid level sensor based on TEMF, 7. a new method for preparing Y-based superconductors, 8. observation of the fine structure of S-N or N-S transition, and 9. elaboration of a microwave magnetic field detector. At the same time Hungarians were among the first groups to measure TEMF, to develop ceramic HTSCs workable by machine-tool, to elaborate elastic foils, rods and filaments and to build small electrical rotating HTSC machines.
Publications

In the course of investigation of high-\(T_c\) superconductors we have reached internationally respected results, published over 150 scientific papers, elaborated some patents and introduced the fundamental phenomena of high-temperature superconductivity into the education of universities and secondary schools. Among them, we have the exact number of the publications of one of the Hungarian high-\(T_c\) laboratories. This is the Department for Low Temperature Physics, Eötvös University, which published 75 scientific papers, 3 patents and 15 studies and dissertations on the methods, results and applications between 1987 and 1993.

Conclusions

On the basis of the facts analyzed in this paper, certain conclusions can be drawn, as follows:

1. A small country can also be effective in the field of a given branch of scientific research, if the aim is chosen right, the powers are concentrated rationally and the co-operations are organized operatively [1].

2. Hungarian scientists attained significant results in different areas of high-\(T_c\) superconductivity and contributed successfully to the world-wide research, because they utilized effectually the internal and the possibilities of international co-operations [2].

References