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SUPERCONDUCTIVITY IN RUSSIA: UPDATE AND PROSPECTS

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Introduction. The researches in high temperature superconductivity in the FSU had been organized and financed since 1988 through **a special State Program**, the scheme being retained for Russia after the regretable decomposition of SU. The scientific supervision is being carried out by the Scientific Council under the chairmanship of Academician Yu. Osipyan. The Council consists of four sections conditionally named "Physics", "Chemistry", "Weak Currents" and "High Currents" and headed by I. Shchegolev (Inst. of Solid State Phys., Chernogolovka), Yu. Tret'yakov (Moscow State Univ.), V.Lemanov (Phys.-Tech. Inst., St.-Petersburg), and N. Chernoplekov (RRC "Kurchatov Inst."), respectively. **I am deeply grateful to each of them for highly valuable discussions of corresponding chapters of this review**.

During the 2 years that passed between the 3d and the 4th World Congresses on Superconductivity, the tendency survived towards curtailing the number of research groups working in the field of high temperature superconductivity and, accordingly, towards cutting back the number of publications on the subject. This process is due basically to the fact that this problem is given up by random people deprived of sufficient financial support and is kept up by high-grade professionals. Therewith the quality of publications raises and their subject matter becomes more and more purposeful. The situation in Russia is developing in the same direction, if only a little bit slower, partly because of less rigid approach to the financing problem. Thus, **in 1993 the HTSC State Program coordinated the activities within 275 projects**, while in 1992 there were 340 of them and 402 in 1991.

Major Research Guidelines. The investigation of high-Tc superconductors is hindered, first of all, by **their equilibrium crystal structures being seemingly always intrinsically deficient**. Some of lattice sites in these structures remain unoccupied which inevitably makes the lattice partially disordered. That is why more and more attention has been paid of late to a possibly thorough analysis of the real structure of the compounds under investigation, their phase composition, etc.

Next, the properties of high-Tc superconductors are in many senses **unusual even in the normal state**. It has been found that anomalies originate because of a strong interaction between electrons in Cu-O planes. However there is still no definite answer to the basic question of whether this electron-electron interaction contributes to the onset of the superconducting state and if so, in what way. To clarify this vague question the mechanism of current carrier formation in Cu-O planes is being studied theoretically and experimentally. A feasibility of realizing nontrivial scenarios of superconductivity is examined, different methods are used for gaining the information on the quantity and symmetry of the superconducting order parameter, etc.

Another stream of works on HTSC worthy of mentioning involves a study into their mixed state predicted by A. Abrikosov as early as in 1957. A giant single-axis anisotropy of electron properties of high-Tc superconductors results in **nearly laminated structure of Abrikosov vortices** which changes essentially their dynamics and the process of their interaction with different defects and dopants. The analysis of these problems creates the basis for a search for possible ways of raising the critical current of high-Tc superconductors, improvement of noise parameters of HTSC-based devices, etc.

1992-93 Developments of Primary Importance.

Ph.1. The precision x-ray structure analysis of $YBa_2Cu_3O_x$ single crystals with various oxygen content held at the Institute of Crystallography of the Russian Academy of Sciences (RAS), Moscow, (head: V.Simonov) has revealed that **there are only three thermodynamically equilibrium phases of this compound**, namely, a dielectric tetragonal phase of the $\mathbf{YBa_2Cu_3O_6}$ composition with T_c = 0K, an orthorhombic phase II of the $YBa_2CuO_{6.5}$ composition with T_c = 60K and an orthorhombic phase I of the $YBa_2Cu_3O_7$ composition with T_c = 92K. Single crystal with $6<x<6.5$ is not, strictly speaking, single crystal but is built of blocks of the tetragonal phase and the orthorhombic phase II, while single crystal with $6.5<x<7$ is built of blocks of orthorhombic phases I and II. On variation of the oxygen index the relation between the volumes of the blocks varies.

Ph.2. Several research teams gained important results concerning the properties and **the role of the electron-electron interaction in HTSC**.

One of the manifestations of this interaction is the existence of large strongly correlated fluctuations of electron spins whose existence is reliably established in various experiments. Superconducting pairing owing to spin fluctuations is one of few real alternatives to the conventional electron-phonon mechanism of superconductivity. Most of the theories analyzing the pairing via spin fluctuations predict the origination of so-called d-wave Cooper pairs with a weaker space symmetry rather than s-wave pairs inherent in conventional superconductors. In this connection the clarification of the type of the superconducting pairing not so long ago seemed almost decisive for answering the question of the mechanism of HTSC. In fact, the alternative s- or d-wave pairing ceases to look so meaningful now when there is a very important work made at the Kurchatov Institute (head: Yu. Kagan) late in 1992 which theoretically proves electron spin fluctuations being capable of leading under certain conditions to the formation of s-wave type Cooper pairs.*)

The absence of noticeable anisotropy of a superconducting gap in single crystals of different HTSC systems **directly indicative of the s-wave pairing** was revealed in direct tunnel measurements held in the Moscow State University (head: Ya. Ponomarev) and the Physical Institute, RAS, Moscow (head: S.Vedeneev).

A new approach to this field of problems is offered in the work fulfilled at the Institute of Solid-State Physics, RAS, Chernogolovka (head: V.Timofeev) which searched into reflections of the IR-radiation from the La_2CuO_{4+x} crystals in the insulating phase **under optical pumping of nonequilibrium current carriers**. It has been found that the **carriers** being formed **are strongly bounded due to their spins entering into strong interactions with the spins of copper electrons** (all the phenomena occur in Cu-O planes).

Ph.3. In the work performed at the Kurchatov Institute, Moscow (head: A.Taldenkov) a change in the thermal resistance of a superconductor on switching of the magnetic field has been attributed to phonon scattering by Abrikosov vortices. By means of measuring the effect magnitude the authors show that **Cooper pairs** in crystals of systems Tl-Ba-Cu-O and Bi-Sr-Ca-Cu-O **are always formed by the electrons of one**

*) The same (!) result was obtained independently and a little bit later by J. Appel and A.W.Overhouser.

and the same plane, while in the Y-Ba-Cu-O system the situation varies depending on the oxygen content. In the $YBa_2Cu_3O_7$ phase, for example, superconducting pairs may consist of electrons belonging to adjacent planes. This conclusion is in agreement with other numerous factors known in this respect.

In a sense the same effect of phonon interaction with Abrikosov vortices has been registered in quite a different way in the work of the Institute of Physical Problems RAS, Moscow (head: N.Zavaritskii). Here the appearance of **electric voltage under a sound wave action** was detected in a HTSC sample when in the mixed state. The effect results from phonons dragging the vortices.

Section 2: CHEMISTRY

Within the framework of the Project headed by B.Popovkin (Moscow State University) E.Antipov and S.Putilin synthesized, resting on an original method of the crystal-chemical approach to the HTSC phase structure, **a new family of superconductors** based on complex copper and mercury oxides: $HgBa_2CuO_{4+\delta}$ (T_c = 94 K) and $HgBa_2CaCu_2O_{6+\delta}$ (T_c = 127 K). The latter has a parabolic T_c dependence on the copper oxidation degree. It is the first compound with T_c above 100 K which possesses superconducting properties under deficient and excessive number of holes.

Of late the same researches independently and simultaneously with Swiss scientists have synthesized one more compound of this family, namely **$HgBa_2Ca_2Cu_3O_{8+\delta}$ with the record-high critical temperature of 134 K** increasing up to 158 K at 150-200 kbar, which inspires a hope for synthesizing this phase under the normal pressures by means of selecting proper dopants. The latter member synthesized of the new family, $HgBa_2Ca_3Cu_4O_{10+\delta}$, has a lower T_c value of 133 K - a tendency similar the last members of the bismuth and thallium families. Within the scope of the same Project a new compound, $Eu_{1.6}Sr_{1.8}Ce_{0.6}Cu_3O_{8+\delta}$ (and its samarium analog), have been also synthesized with T_c = 36 K.

On the basis of the **$Sr_2CuO_2CO_3$ phase, earlier found** by E.Antipov's group, a number of laboratories in different countries have produced at present a lot of **oxicarbonate HTSC** akin to oxide HTSC phases. Among other results of a search for new HTSC phases let me point out synthesis of an ordered polytype of Bi-2212 and Bi-2201 phases, namely, $Bi_4Sr_4CaCu_3O_{14+\delta}$ with T_c = 85 K (Project headed by N.Evtikhiev and A.Bush, Moscow Institute of Radio Electronics and Automation). Let me stress out here that the information of **these two results first were published in the "Superconductivity: Physics, Chemistry, Technology" journal** and then they were "rediscovered" by Western investigators. It's a very serious hint for me as an Editor-in Chief!

Procedures have been developed for separation of individual fullerens of C_{60} and C_{70} on modified sorbents (silica gel, modified with diphenylsilile groups, or graphite) which accelerate noticeably the separation process (Project headed by M.Vol'pin, Institute of Element-Organic Compounds, and Project headed by A.Dityatiev, Science and Research Center of Chemical Technologies). **Methods of extraction of higher (up to C_{200}) fullerens and metalfullerenides have been devised**. In order to raise T_c a search for new endohedral metalfulleren complexes and methods of their testing is being performed.

Along with physical methods of HTSC film deposition the State Program supports the development of **chemical methods of films manufacturing**, such as aerosol pyrolysis, a sol-gel technique. Special attention has been paid to the fundamentals of the chemical vapor deposition (CVD) method, most suitable for epitaxial HTSC film production, and its MetalOrganic modification (MOCVD).

The results of the researches performed under Projects headed by A.Kaul', Moscow State University, and Project headed by F.Kuznetsov, Institute of Inorganic Chemistry, the Siberian Branch of RAS, indicate at **indubitable perspective technological character of the MOCVD method**. Superconducting properties of films are by no means worse than of those produced by physical methods, that is, films have been produced with the MOCVD method had the critical temperature $T_c > 90$ K, critical current density j_c (77 K) > 10^6 A/cm^2 and surface resistance R_s (77 K, 10 GHz) < 500 μOhm). This method has made it possible to achieve deposition rate of 30 μm/h while retaining high critical parameters of HTSC films and produce high-quality films on substrates of 100 cm^2 in area.

The major promising directions of developing this methods in the nearest years to come seem to be the following:

a) a search for **new metalorganic precursors**; clarification of chemical transformations of precursors in the vapor phase;

b) development of single-source systems of precursor evaporation as the most straightforward method to achieve **high reproducibility of the deposition process**; development of the *in situ* methods of the deposition process control;

c) mathematical **modeling of the deposition** process;

d) **investigation into the pinning mechanism** in MOCVD films, directed synthesis of films with preset distribution and prevailing type of pinning centers;

e) production of **heterostructures** containing HTSC layers.

Researchers of the Institute of General and Inorganic Chemistry RAS (Project headed by V. Nefedov) analyzed changes occurring in HTSC ceramics and thin films after a long-term (10 days) exposure to the electrical current action and found that **passing the current is accompanied with redistribution of the content of active oxygen** (enrichment near the positive electrode) and impurities; the concentration of the HTSC phase increases in the middle of the sample and the critical current drops. It has also been found that the epitaxial films degrade much slower than nonepitaxial ones do.

Section 3: WEAK CURRENTS

The works carried out by this Section in last two years covered the following problems:

1. **Substrate** manufacturing for HTSC film deposition, a search for new crystalline materials to be used as substrates and perfecting the quality of existing materials;

2. **Control and optimization** of the methods of high-quality HTSC film production, including those on large-diameter substrates;

3. Elaboration of a reproducible production **process for Josephson junctions, development of SQUIDs**;

4. Development of **bolometers** of high sensitivity;

5. Application of HTSC materials in **microwave devices**;

6. Manufacturing of multilayer structures of the "metal-insulator-superconductor" type and analysis of the **electric field** (or polarization) **effect** on electrical properties of a superconductor;

7. Working out a production process for micron-scale superconducting structures on the basis of **high-Q tunnel transitions** Nb-AlO_x-Nb (low temperature superconductivity).

The following results may be regarded as the most significant for each of these problems (**at the end of each paragraph a name for proper references is offered**):

1) Buffer layers made of cerium oxides (CeO_2, a=5.411Å (100) and a=3.826Å (110); Ce_2O_3, a=3.891Å; $CeAlO_3$, a=3.767Å) well chemically and chrystallographically compatible with YBCO films (a=3.824Å) have been found to be particularly promising. It opens up perspectives of producing microwave and other devices on **large area HTSC material** (integrated variant). Eu.Gol'man, St.-Petersburg Electro-Tech. Inst.

2) HTSC film were produced by molecular-beam epitaxy on substrates of up to 76 mm in diameter. Smooth-surface films of 10 cm in diameter were laser deposited on Al_2O_3 substrates without a sublayer. **The critical current densities in the films run up**

to 10^7 A/cm^2 at 77 K. An average surface resistance value in the films is 0.5 mOhm (77 K, 10 GHz). Double-coat films were produced on Al_2O_3 substrates. On Si substrates with a sublayer films with T_c = $3.5x10^6$ A/cm^2 (at 77K) are produced. M.Predtechenskii, Inst. of Thermal Physics, Novosibirsk.

3) A reproducible production process for Josephson junctions on bicrystalline substrates has been worked out. The voltage-current characteristics have marked Shapiro steps up to the 4-th order. The VvsI characteristics obtained register the highest for the moment characteristic voltage $V_c = j_c R_N$ = 1 mV. **For the first time** the existence of Josephson junctions of the "HTSC - semiconductor - HTSC" type was experimentally corroborated.

Realized are **DC SQUIDs** with the flux sensitivity (1.2 - 1.5)x10^{-5} Φ_0/Hz$^{1/2}$ in the incoming signal band of 30-10,000 Hz and the slew rate up to 10^4 Φ_0/sec. On using an external magnetic flux concentrator the field sensitivity makes 6.6x10^{-13} T/Hz$^{1/2}$. Two dimensional magnetic flux scanners based on LTSC and HTSC d.c. squids have been worked out. M.Kupriyanov, Moscow State Univ.

RF SQUIDs have been made with a 100x100 μm quantization loop and a magnetic flux concentrator of 3 mm in diameter. The measurements revealed that the spectral noise density diminishes rapidly with the frequency increase and for frequencies above 3 Hz attains the fixed level of 6.5x10^{-5} Φ_0/Hz$^{1/2}$. The power sensitivity was 5.6x10^{-29} J/Hz and the field sensitivity made 2.3x10^{-13} T/Hz$^{1/2}$ (at 3 Hz). S.Gaponov, Inst. Appl. Phys., Nizhnii Novgorod.

4) A layout is calculated and a production process is elaborated of **antenna microbolometers** on $NdGaO_3$ substrates with a threshold sensitivity of 1.6x10^{-11} W/Hz$^{1/2}$ and time constant 30x10^{-7} sec.

The following receiving devices have been worked out and manufactured: **a double-channel receiving device** based on HTSC bolometers for scientific researches in the IR and submillimeter ranges and a four-channel receiving device based on antenna microbolometers for investigations in thermonuclear plasma in the submillimeter range.

A bolometer of a new type has been suggested with the operation principle based on the temperature dependence of the kinetic inductance for a strip resonator.

Further investigations envisage a study of **ultrafast electron processes** in thin HTSC films and an elaboration of receiving and commutating devices with extremely high speed of response (involving a mechanism of electron heating in the resistive state). Eu.Gershenzon, Moscow Pedagogical Institute.

5) Film resonators are already available with the Q-factor (at 10 GHz) **three times better than that for copper** devices.

Suggested and investigated is an electrically small antenna for the frequency range of about 2 GHz. The antenna has a radiator sized 0.07 of the wavelength and a compact matching system (resonator) sized 20x13x2 mm^3. The calculated efficiency has turned out to be **75% for HTSC materials and 14% for copper (at 77 K)**. O.Vendick, St.-Petersburg Electro-Tech. Institute.

6) **The electric field effect in multilayer "superconductor-insulator-metal"** (SIM) structures open up new prospects of investigating into physical properties of HTSC materials and provide the grounds for posing the question of HTSC field-effect transistor development. A production process has been worked out for multilayer structures where $SrTiO_3$, $PbTiO_3$ - $PbZrO_3$ and $SrTiO_3$- $BaTiO_3$ films are used as insulators (ferroelectrics). With ferroelectric 0.5 mm films of $PbZr_{0.75}Ti_{0.25}O_3$ solid solutions the dielectric constant (at 1 kHz) was found to be ~600, the loss tangent 0.02 and the remanent polarization was 24 $\mu C/cm^2$ at the cohercivity field of 80 kV/cm^2. V.Lemanov, St.-Petersburg Phys. Tech. Institute.

7) The manufacturing practice for **high-quality submicron Nb - AlO_x - Nb transitions** has been optimized. A production process of multilayer superconducting structures on the basis of such transitions has been developed which ensured the manufacturing of microcircuits with the spread in parameters below 7% for transitions sized 3x3 μm^2 and the level of integration 10^3 per chip.

Threshold parameters of one-quantum digital elements were experimentally analyzed. The number of "error-free switchings" was more than 10^{15} for the buffer cascade and not less than 10^{14} for the NOT element. V.Kosheletz, Inst. of Radio Electronics, Moscow.

Section 4: HIGH CURRENTS

Realization of high expectation of the Technical Revolution connected with the HTSC practical application are obviously dragged out by **the absence of large-scale production of long-lengh wires** and current-carrying elements on their basis. The difficulty in working out corresponding technological processes consists in the necessity of meeting (over the whole volume of HTSC wire) the three classical requirements of ensuring high current-carrying ability:

- no weak links between crystallites;
- favorable pinning structure; and
- formation of a crystallographic structure with well-expressed texture along the expected transport current direction.

A success in solving the problem is undoubtedly feasible only on the basis of a sufficiently deep insight into the nature of HTSC materials and its interconnection with the microstructure and phase composition of samples.

Thus, in Project headed by I.Voloshin, Energy Institute, Moscow most promising molten textured HTSC samples with the critical current density of about 10^5 A/cm^2 were analyzed. Magnetic field and temperature dependencies of the critical current density were studied. The investigation was performed with **an original noncontact technique** worked out by the Project participants ensuring the variations of the magnetic domain structure of the indicating film contacting with the sample. A nontrivial result has been obtained, namely, the magnetic flux penetration in well-textured samples occurs through macroscopic strip of the scale of about 1 mm rather than via crystallite boundaries.

As to HTSC wires, the majority of the technology teams in Russia are successfully developing the "powder-in-tube" method which looks most promising for the moment. Current-carrying ability values (0 T, 77 K) at the level of 10^4 A/cm^2 for Bi-2223 based wire are quite common but the transition to greater lengths results in noticeable decreasing of the critical transport current. The most advanced, to my mind, are the works performed at the All-Russia Research Institute of Inorganic Materials, Moscow, head: A. Nikulin. The critical current density of their short-length (5 cm) Bi-2223 wires runs to 3.5×10^4 A/cm^2 in the self field and at 77 K featuring **high reproducibility** and relatively weak decreasing of current-carrying ability on the application of an external magnetic field.

Perspective and, by all means, **pioneer method of long-length high-current HTSC composite wire production** is a technology being jointly developed within the scope of Project headed by V.Kruglov by the researchers from the RRC "Kurchatov Institute", Moscow, and Moscow Institute of Steels and Alloys. The technology is based on the high temperature gas-dynamic extrusion of amorphous or crystallized semiproducts produced by pumping of the melt into silver containers followed by operations of drawing, rolling and thermal treatment, see Fig.

This process ensures a nearly theoretical density of the HTSC core, low contamination of crystallite boundaries, a possibility of introducing structure variations within a broad range and at any stage of the technological process and a multi-axial loading principle with one-shot extrusion deformation degrees up to 98%. In consequence it is possible to produce **long-length (up to 10 m) wire stretches** with a high degree of homogeneity along the whole length (as confirmed by weak smearing of the V vs I characteristics, not exceeding those of commercial niobium-titanium alloys) and with high transport properties yielding the critical current densities for Bi-2212 based compounds (4.2 K) of the order of 10^5 A/cm^2 and 7x10^4 A/cm^2 in the fields of 5 T and 8 T, accordingly.

A research team from the Moscow State Technology University (head: Drs. O.Polushchenko) has produced bulky highly textured rods and plates based on the 1-2-3 compound with the critical current density above 10^4 A/cm^2 at the liquid nitrogen temperature and 1 T magnetic field. It allowed specialists from the Moscow Aviation Institute (head: L.Kovalev) to devise prototypes of a new face-type hysteresis motor (stature diameter: 60 mm; power: >10 W) and a synchronous jet-propulsion stepping motor with an external diameter of 108 mm.

Good progress in the development of a so-called "topological generator" has been made by a group headed by Yu.Baurov from the Central Science and Research Institute of Machine Building, Moscow. They designed a generator on the basis of bulk ceramics as well as films. In the produced prototype generator of this type sized 80 mm in diameter and 100 mm in length the current in the closed circuit was about 10 A at 77 K. The experience acquired in the course of tests allows one to hope that it is possible to design a high current (1,000 A) topological generator using the now available technology for HTSC elements manufacturing.

The Project headed by Eu.Krasnoperov, RRC "Kurchatov Institute", Moscow, envisages working out "hybrid" magnetic systems. Outer sections are superconducting and inner ones are resistive water-cooled. The total stationary field will be 30 T. An outer section is made of niobium-titanium wires and comprises 16 compounded modules. During the tests of a section the field in the center was 4.9 T which is 0.5 T higher than the calculated value. The water-cooled section consists of two "polyhelix"-type optimized windings connected in series. Their production has been launched. The contribution of the superconducting section into the total field will make 9-10 T and that of the water-cooled section will be 20 T.

The realization of this project (which is inhibited by serious financial difficulties) will provide a means of carrying out physical investigations in stationary magnetic fields up to 30 T. Evidently, it is of primary necessity for studying the properties of HTSC materials.

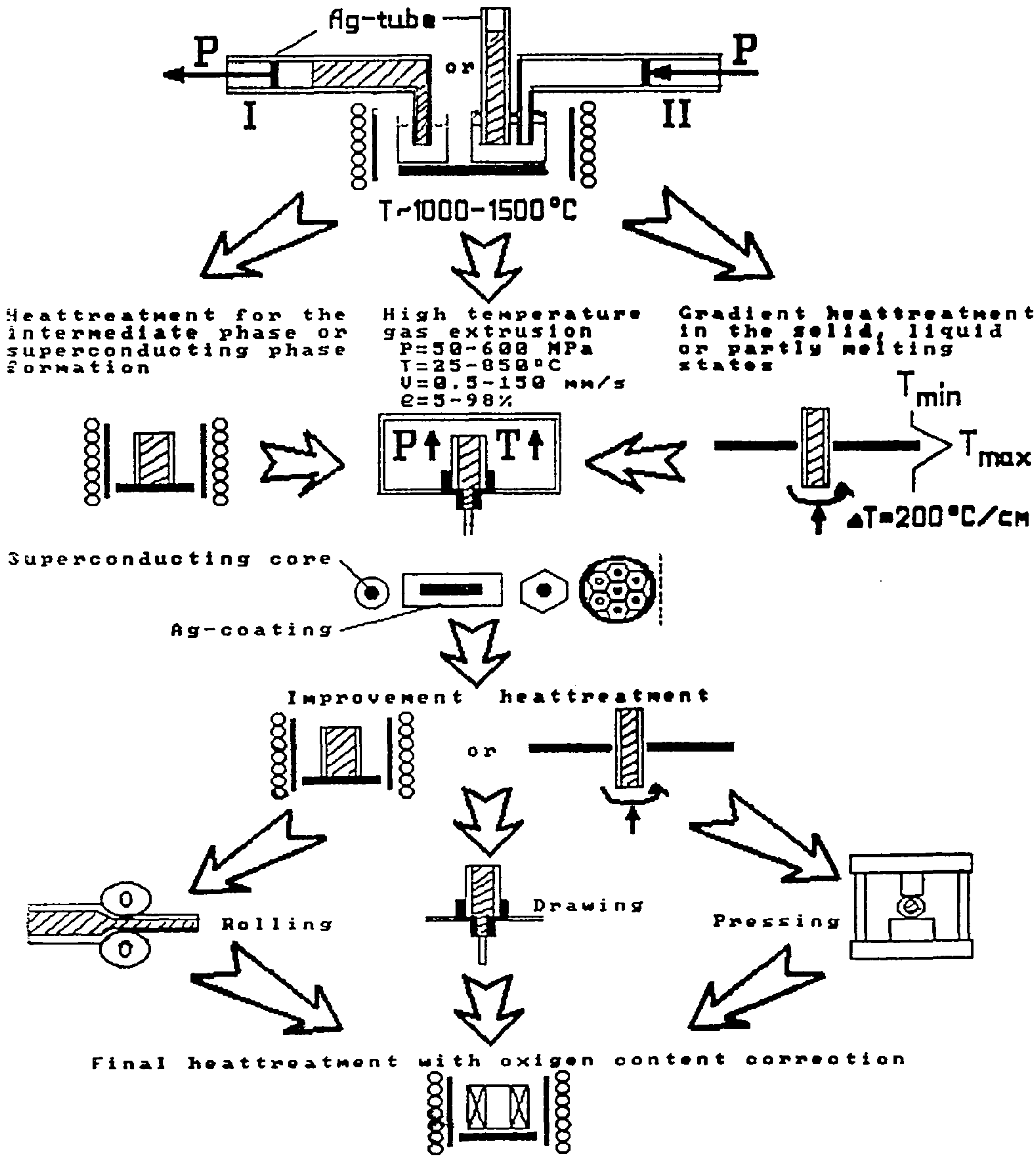

Figure 1.- NoveL method of the LongLength current carrying HTSC structures formation.