ARCHIVES OF ACOUSTICS
16, 3–4 387–412 (1991)

TECHNOLOGY AND ACOUSTICAL PROPERTIES OF THE CERAMIC HIGH-TEMPERATURE SUPERCONDUCTORS

M. ALEKSIEJUK, J. RAABE*, J. RANACHOWSKI

Institute of Fundamental Technological Research Polish Academy of Sciences
(00-049 Warszawa, Świętokrzyska 21)

Technical University of Warsaw, Department of Chemistry
(00-604 Warszawa, Noakowskiego 3)

1. Introduction

The aim of the paper is to present the acoustic methods of investigating the phenomena taking place in the range of the conductor-superconductor transition in the selected ceramic superconducting materials.

The superconducting materials, used up till recently, which were limited mainly to metals, had the transition temperature of about several Kelvin. During seventy years, beginning from the first studies on superconductivity, the attempts to find materials with higher transition temperature failed, and it was only in 1973 that the Nb_3Ge alloy with the transition temperature of 23 K was discovered. This discovery caused a significant increase of interest in intermetallic alloys of the type Nb_3Ge or V_3X, where X is the metal from the intermediate group. These compounds have had the transition temperature between ten and twenty Kelvin. This allowed to utilize technically the superconductivity phenomenon in generating stable magnetic field. The next important step in this direction was the discovery of superconductivity in lithium titanate $LiTi_2O_4$ which is a typical oxide material. This discovery caused that into the investigation of superconductivity also the oxide materials have been included. The investigations resulted in the discovery, made by BEDNORZ and MULLER [1, 2], the Nobel prize winners, of the superconductivity phenomenon in the perovskites of the $La_{2-x}A_xCuO_y$ system (where A = Ca, Sr or Ba). The superconductivity in this perovskite ceramic has been later confirmed by CHU et al. [3]. That was the reason for directing the interests of theoretical physicists and technologists around the world towards the high-temperature superconductivity (HTS). The main interest of the superconductivity technology consists in the design of magnets generating strong magnetic fields in large volumes.

In all the superconducting devices the current density of about $I \geqslant 5 \cdot 10^4$ Acm^{-2} is demanded. As such values are already comparable with the values obtained for the

Y—Ba—Cu—O superconductors, the real possibility of practical application of HTS exists. The decisive factor for the victory of new materials will be economy, as it occures that the high-temperature superconductor can be competitive, with the respect of prize, with classical superconductors, in low as well as in high temperature. (Fig. 1).

The high-temperature superconductors can cause revolution in the superconductors technology. Their common use is widely planned in the new generation computers based on the switching elements using the Josephson phenomenon. It is possible that in the rearest future the HTS will replace the classical superconductors in the large scale plants.

The significant technological problem is to obtain the possibly dense and fine grained superconducting materials with reproducible microstructural parameters. The high apparent density is one of the basic conditions in this respect. The material should be free from large inter-grain as well as intra-grain pores. The distinct problem is to obtain the ceramic material with small grains, not larger than 10 μm. The exemplary microstructures are shown in Fig. 2.

At present it is generally agreed that the basis of superconductivity in ceramics is their crystallic structure. For the La—Cu—O and as well as for the Y—Ba—Cu—O materials the superconducting phase is orthorhombic in structure. The recent investigations of the La—Ba—Cu—O system demonstrate that two superconducting phases appear in it [5]. Those two phases are: the $La_3Ba_3Cu_6O_{14+x}$ phase and the well known composition "1,2,3", which, from a series of continuous solid solutions. The first ceramic superconductors had mainly the perovskite structure, that was common with such materials as $BaPb_{1-x}Bi_xO_3$ which is a regular perovskite. For the La—Cu—O materials the structure has been described as an intermediate one between a perovskite and NaCl [6], where layers of copper oxide sheets are the only bonding regions for the of Cu and O ions. (Fig. 3).

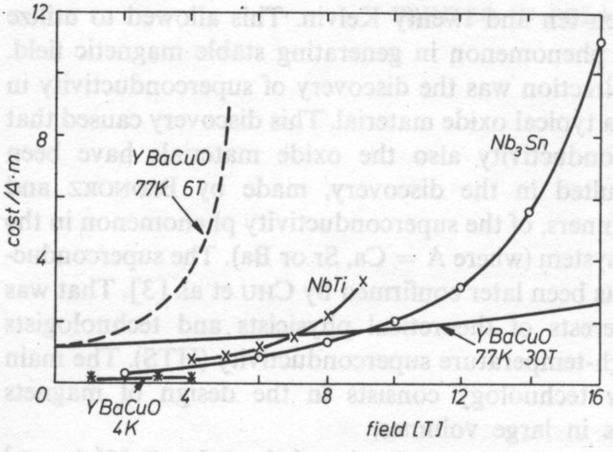

FIG. 1. Worth whileness coefficient of Y—Ba—Cu—O and conventional superconductors.

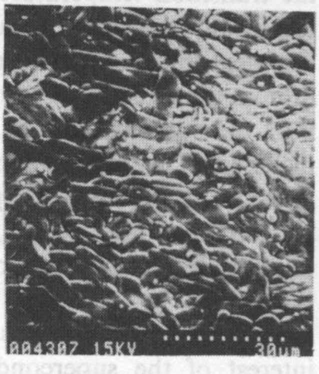

FIG. 2. Example of microstructure of Y—Ba—Cu—O superconductor. Electron scaning microscope. Opton.

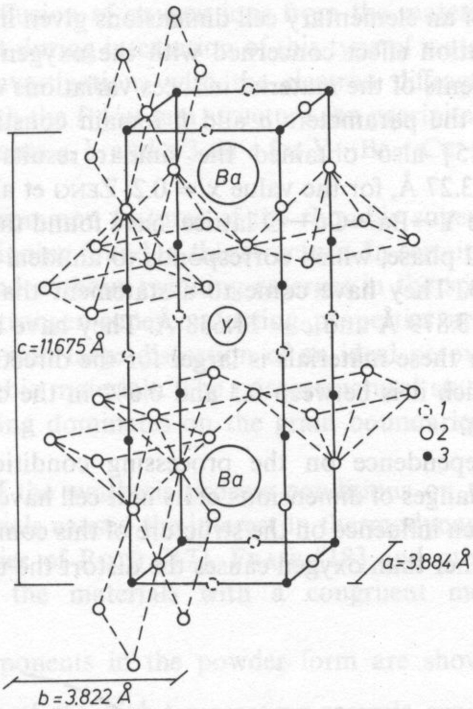

FIG. 3. The orthorhombic perovskite structure Y—Ba—Cu—O 1-vacancy, 2-oxygen, 3-copper.

The superconducting phase in the Y—Ba—Cu—O system deviates even more from the ideal perovskite structure. The oxygen consists in $YBa_2Cu_3O_x$ which could be ideal in respect of superconductivity was found to be $x = 6.95$–6.98 [7]. However the basic cation coordination in the structure corresponds to the structure of K_2NiF_4, structure despite the less than ideal oxygen content for the perovskite structure. In this case the rare earths ions exhibit the 8–fold coordination more frequently than the 12–fold one, barium ions have the 10–fold coordination instead of the 12–fold one, Cu^{2+} ions have the 5–fold coordination instead of the 6–fold one and Cu^{3+} ions have the 4–fold coordination instead of the 6–fold one. Description of the structure of these materials together with their superconducting properties indicates that in their structure the Cu_2O sheets are formed and numerous Cu—O—Cu—O chains are placed along the elementary cell axis [6]. Evidence of the laminar structure of the superconducting phase has been demonstrated by J. MELMED [8] by field image microscopy.

Structural analysis of the superconducting phase in the Y – Ba – Cu – O system ($YBa_2Cu_3O_{7-x}$) demonstrated that it can be classified as belonging to the Pmmm space spatial group with $a = 3.8185$, $b = 3.8856$ and $c = 11.6804$. It has been shown that the variations of the lattice constants are: $a = 3.8185 - 3.839$, $b = 3.883 - 3.908$ and $c = 11.64 - 11.753$ Å [9, 10, 11, 12, 13, 14].

The fluctuations of an elementary cell dimensions given in the literature are due mainly to the deformation effect concerned with the oxygen contents, Linang has stated that heat treatments of the material induces variations of all three dimensions of an unit cell, and if the parameters a and b remain constant, then the value of c increases. Khan [15] also obtained the similar results $Sr_xLa_{2-x}CuO_y$ with $a = 3.775$ Å and $c = 13.27$ Å, for the value $x = 0.2$. Zeng et al. [16], in their studies on the distortion of the Y—Ba—Cu—O lattice, have found the critical phase, which corresponds the critical phase, which corresponds to an ideal orthorhombic layered perovskite $a = b = c/3$. They have come to a statement that the unit cell for the critical phase was $a = 3.879$ Å and $c = 11.638$ Å. They have also observed that the degree of distortion for these materials is larger for the direction $a(-1.3\%)$ than in the direction b, for which it is between 0.3 and 0.6% in the case of the least stable one-component system.

The structures dependence on the processing conditions used to produce $YBa_2Cu_3O_\delta$ and the changes of dimensions of its unit cell have been observed during the studies on the oxygen influence on the structure of this compound. Heating in the air or in atmosphere other than oxygen causes the distort the unit cell, what gives an

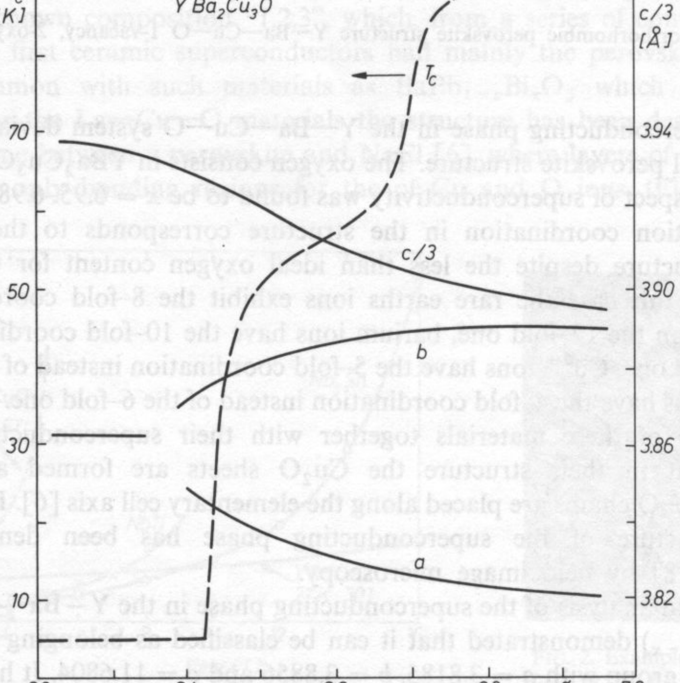

FIG. 4. The dependence T_c and lattice constants a, b and c/3 on δ for Y—Ba—Cu—O.

indication the rapid diffusion of oxygen ions from the material takes place. It has been also observed that during interaction of this type of material with an intensive electron flux, in the investigations with the electron diffraction method, a pseudo-tetragonal phase with the $P4/m$ mm structure can precipitate. The dependence of T_c and the lattice constants a, b, and $c/3$ on σ for Y—Ba—Cu—O has been shown in Fig. 4.

One of the basic common features of the rhombic superconducting phases of this system is heavy twinning found in this structure. In certain conditions, when the rhombic phase with and without twinning emerges in the specimen, in the greatly twinned regions the stronger superconducting properties are usually found. The twinning is concerned with large distortion of an ideal perovskite structure and is common in orthorhombic materials. The microstructural studies of these materials demonstrate that twining dominates on the grain boundaries during the sintering process.

Large influence of the synthesis process conditions on the final properties of superconducting materials caused the interest in thermodynamics of phase systems. According to the studies of ROTH [17], FRASE [18] and others, the $YBa_2Cu_3O_\delta$ "1,2,3" materials are the materials with a congruent melting point (melting temperature).

The starting components in the powder form are shown in Table 1.

2. Technology of the high-temperature ceramic superconductors

2.1. The solid phase reaction method

The investigations, carried out in the last years, on a new class of ceramic materials in the system: yttrium, barium and copper oxides, with the high transition temperature, demonstrated that this temperature depends on the relation $Cu^{3+}:Cu^{2+}$. This relation is strongly conditioned by the technological procedure used in producing this type of ceramic. In general, the ceramic superconductors can be manufactured in two ways: by the reaction in the solid phase or by the co-precipitation method. A typical technological procedure in the case of generation of the $YBa_2Cu_3O_{7-x}$ compound includes a number of following stages. The molar proportions of the yttrium oxide, Y_2O_3, barium carbonate $BaCO_3$ and cuprous oxide CuO are weighed and then mixed intensively in the ball or vibrating mill. The mixture of powders is then pilled with a small pressure about 100 bars and burned in the temperature 950°C for several hours in the atmosphere with higher oxygen content. The obtained sintered material is once again pulverized, pressed and burned. The optimal conditions are obtained for burning in 950°C for 24 hours in the oxygene flux. Also cooling the specimen after burning is an important factor. Slow cooling of the stove e.g. 1.5°C/min and keeping in the temperature of 650°C is applied. The influence of the subsequent stages of the synthesis of ceramic superconducting materials on their properties can be displayed in form of a diagram. (Fig. 5) Below, a detailed description of the method of obtaining $YBa_2Cu_3O_\sigma$ with the solid phase reactions method will be given [20].

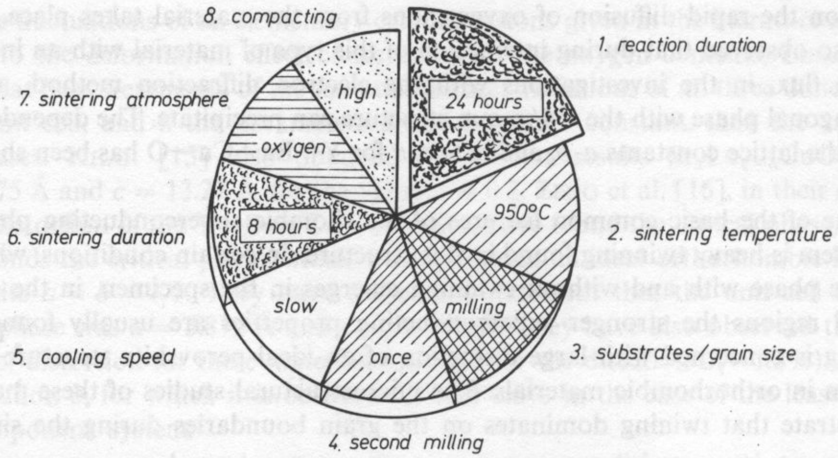

FIG 5. The influence subsequent stages of the synthesis of ceramic superconducting materials on their properties

To make a 30 g specimen of $Y_1Ba_2Cu_3O_\sigma$ the following substrates have been used:

$$Y_2O_3 - 6.11\ \text{g}; \quad BaCO_3 - 27.37\ \text{g}; \quad CuO - 12.92\ \text{g}.$$

The mixture of this quantity of substrates generatees to obtain as a final product the oxide mixture with the stechiometric relation 1–2–3. Attention must be paid to that the substrate should be weighed free from humidity.

Table 1

powder substrates		
material	molecular weight	producer
Y_2O_3	225.8	Aldrich Chemie Co.
BaCO	197.4	Aldrich Chemie Co.
CuO	79.5	Chem. Inc.

The basic technological operation is keeping the specimens in oxygen. The specimens are seasoned in oxygen in the temperature 500°C for 12 hours. The oxygen rotameter should indicate the flow 0.2 m^3/h. For the $Y_1Ba_2Cu_3O_{7-x}$ compound with the stechiometry "1–2–3" the maximum oxygen absorption occurs at about 500°C. This temperature for $Y_1Ba_2Cu_3O_{7-x}$ is below the temperature of transition of the tetragonal structure to the rhombic one, which equals 750°C. The high-temperature superconducting phase is, in principle, conform with the rhombic phase.

After having reasoned the specimens in 500° C for 12 h we switch off the stove and leave the specimens inside, while leaving the oxygen flux on until the temperature decreases down to the ambient temperature. The oxygen flux intensity should remain the same as during seasoning, i.e. 0.2 m^3/h.

After taking the specimens out from the store they should be kept in an oxygen exsiccator in the room temperature. Water causes decay and damage of the specimens.

Among the numerous factors which determine the specimen quality, attention should be paid to the five most important ones. These five quality factors are:

– stoichiometry
– mixture homogeneity
– sintering temperature
– oxygen contents and ordering
– cooling intensity

2.2. *The method of co-precipitation*

In the co-precipitation method the starting point are the substrates in the form of the solution of nitrates from which the mixture of appropriate carbonates is precipitated. The carbonate suspension is then filtered off and heated to remove water. The further procedure is the same as the one applied in the method with the solid phase reaction.

The advantage of the co-precipitation method over the solid phase reaction method is that if an additional, chemical stage of synthesis is included then the stoichiometry of the planned solid phase is known, because the components are mixed in the molecular scale in this case. In respect of this mixing homogeneity it is more probable that only the synthesized solid monophase will emerge and no other "contaminating" phases will be formed. The quick preparation method by the solid phase reaction gives the measurable composition inhomogeneity, despite the mixing and milling stages. This inhomogeneity can favour the forming of additional, contaminating phases.

The two other kinds of co-precipitation methods have also been worked out: the citrate and the oxalate methods. In each of these methods the process starts from the substrates in the form of nitrate powders solved in water. Then, in the citrate method, in primary co-precipitation the citrate acid and the ethylene glycol is applied in place of Na_2CO_3 used in the carbonate method. In the oxalate method as the precipitating agent the calium oxalate is used. In the application of both co-precipitation methods close attention should be paid to the process control, especially in the oxalate method in which the pH must be precisely regulated and it must be seen to that the double salt should not be formed.

A large problem, which appears in sintering the materials with smaller contents of rare soils [4], is the formation of a liquid phase in the temperature 950°C. It is known that despite the improvements of sintering conditions, the liquid phase worsens the properties of superconducting materials. HUANG et al. [4] stated that the liquid phase that covers the grains of the superconducting phase can really lower the superconducting properties. Similarly, Guba established recently that prolonging the sintering in 950°C results in forming an eutectic liquid phase which tends not only to noisten the grains of the sintered ceramic, but also the crucible walls [19]. Huang observed also that the liquid phase caused the grain growth in these materials. In connection with the problems concerned with the liquid phase formation in 950°C and with poor sintering characteristics of there materials, i.e. the attained relative densities about 70–80% for pressure-free sintered compacts, their structural and chemical properties can not be considered separately. Indeed, the results of the applied sintering method as well as the gas atmosphere interaction strongly influence the superconducting properties. However, it should be underlined that the formation of the second phase is influenced by both thermal conditions and chemical constitution of the substrates.

In obtaining materials exhibiting the beginning of rapid resistance change by 53% in the temperature 260 K and the end about 240 K (Fig. 6). NARYEN et al. [21] identified the presence of a second phase in which $c = 13.55$ Å and which locates itself mainly the grain boundaries in the sinter. Conditions of synthesis of these materials include sintering in 960°C in oxygen for 12 hours what should gave the formation of an eutectic liquid phase in the regions where, in spite of mixing and calcination in 900°C, the material is poor in Y and Ba. As the phase which emerges at the grain boundaries, which is responsible for the dramatic resistance decrease, was instable when subjected to heat cicles or to nucleation and transformed into a superconductor with $T_c = 90$ K, then also the influence of soaking in oxygen and cooling speed should be studied. The material which exhibited thee largest resistance decrease – by 50%, also shown the superconducting properties concerned with the phase at grain boundaries, with the volume contents of this phase equal to 0.3% [21].

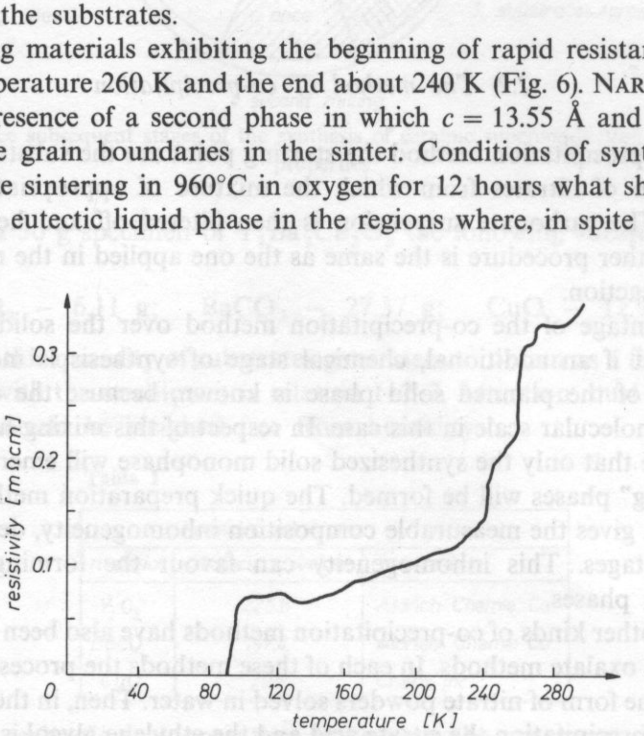

FIG. 6. Resistivity as a function of temperature for a material which exhibited unreproucable anomaly of resistivity at 260 K before reverting to the superconducting phase material

The relation between superconductivity and oxygen contents and ordering in the considered materials was one of the earliest observations since their structure has been discovered. It has been found that the ordering of occupied positions in the plane Cu – O is strictly connected with the high-temperature superconductivity. Even if these positions are occupied only in one fourth, the $YBa_2Cu_3O_{7-x}$. ($x = 0.4$), can be a superconductor in 55 K as long as the occupied positions are ordered. In the opposite case, the material is tetragonal and is a superconductor. If the considered are occupied in half and ordered than the critical superconductivity temperature increases to 90 K [23], the rhombic structure is deformed and twinning takes place. Superconductivity in the materials La—Sr—Cu—O has been demonstrated by TARASCON [24] and its nature is very close to that of the Y—Ba—Cu—O materials. The loss of oxygen from the Cu—O planes destroys superconductivity in these materials. Discurring oxygen restoration in this plane, Tarascon describes oxygen reintercalation. The concept which assumes that the material is intercalated with O_2 is widely accepted because it explains the violent O_2 movement in the material and its influence on the physical phenomena. The proofs for the influence of the slow cooling on the oxygen contents and superconductivity have been presented by GOPALAKRISHNAN et al. [12]. If the sintered ceramics is slowly cooled with 0.1 K/min down to 850°C and 24 K/min down to 400°C then the transition temperature equal to 106 K is obtained. This temperature has been observed for a material which in normal process conditions has the transition temperature 95 K. Another her experiment with slow cooling, 1 K/min, has been carried out by NARAYAN et al. [21], but his specimens were probably overheated while sintering. The abnormalities observed in his material in the temperature 240–260 K were not due to the slow cooling of the specimens. Finally, oxygen in excees $\delta = 7$ influences the saturation of the CuO_2 plane, causes the electrostatic load breakdown through an expanded elementary cell and changes the Ba, Cu and Y coordination. The net effect is the transition into an isulator as it has been previously described.

In the first reports on the discovery of 90 K superconductors formed from the rare earths oxides, it has been said that these materials could be synthesized from ions of the majority of rare earths, irrespective of their magnetic moments. This seems to be in contradiction with the generally accepted theory of superconductivity. It has been established that three rare earths ions adversely affect the superconducting properties of these materials: Ce, Pr and Tb. The first two were not able to form a superconducting compound in the experiments carried out by MCKINNON et al. [25] and the compound containing Tb in place of Y can not exist. Replacing Y by other rare earths had the influence not only the crystallographic structure of the material, but also on its critical temperature. The relation of resistance to temperature for this group of compounds has been shown in Fig. 7 [41, 42]. McKinnon has demonstrated that the addition of rare earths to $La_{16}Sr_{02}CuO_{4-x}$ not larger than 0.2% at did not destroy superconductivity, in spite of the existence of magnetic moment. However, the synthesis temperature changed: it was the lower the larger was the lower the larger was the atomic number of the rare earth element.

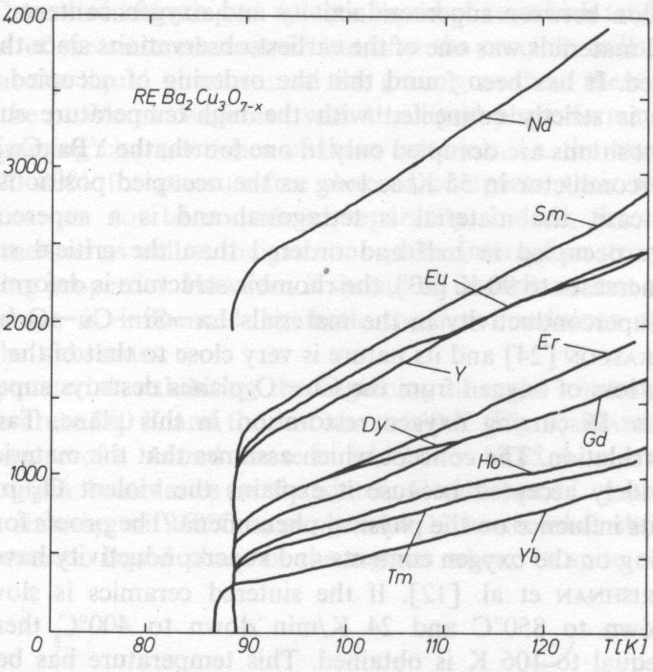

FIG. 7. Resistivity as a function of temperature for the $YBa_2Cu_3O_{7-x}$ perovskite, in which yttrium has been replaced by rare earths cations [42]

Another change which takes place as a result of replacement of the rare earths elements to the considered structures is the influence of the magnetic field on superconductivity. NEUMEIER et al. [26] have demonstrated that by replacing Y with Tm in the “1,2,3” compounds one obtains the materials which are less sensitive to external field.

Replacing copper by bivalent as well as trivalent cathions gains large interest. The primary aim of such investigations was better understanding of the role of Cu—O chains in the links of Cu—O planes, and estimation of the range inside which the dimension and elastic properties of the Ba atom have any influence on the semiconductor transition and the critical current in the new superconducting compounds. The studies carried out by TARASCON et al. [27] demonstrate that in $La_{2-x}SrCuO_4$ the replacement of 0.025 at % Cu by Ni results in the transition temperature decrease from 40 to 22 K. Further increase of Ni concentration leads to lower transition temperatures. The cause of these effects in the disorder introduced to the structure due to the changes of ion magnitude, changes of the oxidation degree of copper and even the possibility of destroying the magnetic couples by a magnetic Ni ion. The substitution by cobalt also reduces superconductivity. The replacement carried out by TARASCON et al. in the $YBa_2Cu_3O_\delta$ materials was limited to Ni. In this case the main difference was the substitution $x = 0.25$ and $x = 0.50$ for

$YBa_{3-x}Ni_xO_\sigma$. It gave the similar results, i.e. lowering the transition temperatures.

Other studies [28] in which Cu was substituted with Co and Fe in $YBa_2Cu_3O_\delta$ led to semiconducting materials. When Co was substituted, what led to Cu_3—Cu_2Co, the oxygen contents in this material correspond to $\delta = 7.25$. If Fe was substituted, what led to Cu_3—$Cu_{2.5}Fe_{0.5}$ oxygen contents in the obtained material corresponded to $\delta = 7.15$. Oxygen concentrations lower than $O_{6.7}$ for Co and $O_{6.4}$ for Fe gave disintegration of the respective materials. In the discussed works only the set containing $Cu_{2.963}O_{0.037}$ had the rhombic structure. The tests of single crystals of the "1,2,3" materials carried out by Collin et al. (not published) demonstrated the presence of rhombic highly twinned crystals with vacances in Cu positions. According to calculations, the Cu defficiency reached 8%, what has been confirmed by other authors. The reason of this deficiency in these single crystals could be the heating over 940–950°C, which is the temperature range corresponding to the thermal stability threshold of the "1,2,3" phase. Collin reports this as a reason why the green tetragonal phase is usually bound with a powder from which single crystals issue (Fig. 8). The Meissner magnetic effect for materials substituted with Ag indicates that the 0.7% admixing leads to reducing the superconducting part in these materials [29]. Lack of influence on the transition temperature has been ascribed to nonhomogeneity of the materials, so that the superconductivity in mass was not changed even though some regions of a specimen were superconducting. Trials were also made to substitute Ba in the YBa_2CuO materials. In particular, the substitution of Ba with Sr in $YBa_{2-x}Sr_xCu_3O_4$, for $x = 0.2$; 0.5; 0.75; 1.0; 1.25; 1.5 and 2.0 has been studied. The effect has the continuous decrease of transition temperature in this material, together with the increase of Sr contents. Also the resistance over the critical temprature increased continuously. Veal et al. [30] stated also that the lattice parameters *b* and *c* decreased together with the increase of Sr concentration.

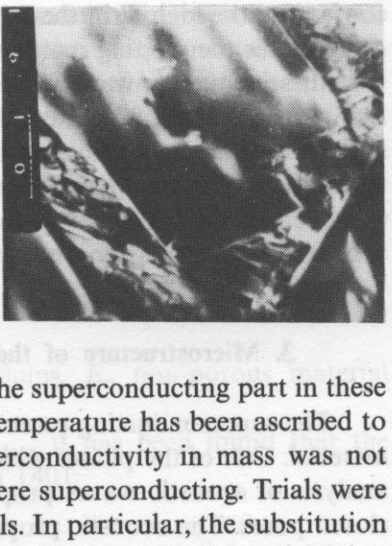

FIG. 8. $YBa_2Cu_3O_6$ crystals which emerged during cooling the alloy, usually crystalizing together with the so called "green" phase "211"

M. F. Yan et al. [31] also worked upon the materials with variable Ba and Y contents. He concentrated mainly upon the materials with Ba as well as Y excess, or with only Ba excess. Because the applied substrates gave multiphase specimens after sintering, it has been stated that it was difficult to correlate the high transition temperatures with the material phases. The possibility of having superconducting properties has been ascribed to the phase which emerged at the grain boundaries of four different phases in the specimens with the $Y_{4.1}Ba_{2.51}Cu_1O$ composition. The reason why it has been assumed that the phase at grain boundaries is probably a superconductor results from the measurement of diamagnetism which indicate that for 0.3% of the specimen the starting point of transition is in 550 K and that for long sintering time (113 h) in 950°C the "1, 2, 3" phase could pass to solution and precipitate at the grain boundaries of other phases formed during the cooling process. The superconducting phase at the grain boundary, observed also in other investigations, can give satisfactory explanation of the large resistance drop with the temperature decrease in such materials which should be classified as insulators.

The papers where the studies on introducing the F and Cl anions are described report that in partial substitution high T_c temperatures are obtained (more than 200 K). Investigations carried out in Energy Conversion Devices have indicated that the implementation of F to the material generates the oriented crystal growth, as it has been reported by Ovshinsky and Young. They have obtained the start of T_c in 265 K and zero resistance in 148 K for YBa_2Cu_3O treated with the ions of F with the parameters 180 keV and 1×10^{15} ions/cm^2 [4]. At the same time the attempts of confirming the high T_c in these materials reported by YAN [31] with the use of BaF_2 or $BaCl_2$ as the starting materials gave 91 K as a result. It has been also found out that these materials were multi-phase and contained the grains of CuO, $BaCl_2$ or BaF_2. In the "1, 2, 3" material Evibil studied also the use of BaF_2 as one of the substrate powders. In one, nonreproducible specimen he found a certain proof of transition to the superconducting state in the temperature 260 K. This transition remained in the specimen of the approximate contents $YBa_2Cu_3O_5F_2$ even after a couple of months of the specimen's life.

3. Microstructure of the high-temperature superconducting ceramic

The superconducting ceramic made from diverse compounds is the multi-phase material. One of the phases which should always be taken into consideration in the analysis of acoustic waves propagation is the gas phase contained in the open or closed pores. The acoustic properties of superconducting ceramic we influenced not only by the more value of porosity but also by its statistical parameters, such as pore diameters distribution, pores geometry, i.e. shape and mutual displacement, as well as volume shaves of different phases. The same remarks, although to smaller extents refer to the crystallic phases. In Fig. 9 the shapes of the pores in ceramic materials have been shematically shown.

The process of sintering and recrystallization leads to the decrease of porosity of the whole bath. In general, the increase of sintering temperature leads to deterioration of small pores with irregular shapes and to formation of spherical pores, mainly as a result of the tendency to minimize the free surface of the system. The histogram of pore dimension have the Poisson distribution. However, it should be taken into

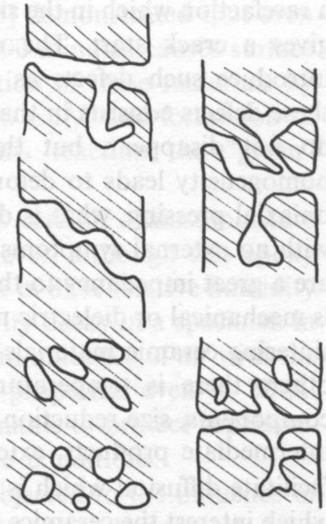

FIG. 9. Shape of pores found in ceramic materials

account that because of the complexity of pore shapes the microscopic studies not always give completely reliable results. In the microscopic measurement of absolute porosity the surface distribution of pore diameter does not correspond to the volume distribution, which is significant in calculation of mechanic stress fields, electric fields and acoustic wave propagation parameters. These problems have been solved in a number of papers and experimentally verified in a variety of ceramic materials and sintered metallic powders.

In general, the relation of elasticity modulus to absolute porosity is [40]:

$$E = E_0 e^{-kp}$$

where: E — porous materials elasticity modulus, E_0 non-porous material elasticity modulus, p — porosity, k — constant.

For the superconducting ceramic $YBa_2Cu_3O_{7-x}$ it has been found that the relation of the modulus to porosity has the form [40]:

$$E = E_0(1-p)^3$$

An equally important parameter for the acoustic properties of a specimen are the microstructural parameters of the solid phase, which include: dimension and shape of grains, type and shaves of different crystallic phases and glass, and the material texture. These parameters are dependent on all the technological operations. In the process of preparing powders an important operation is milling, which should lead to destroying the agglomerates of substrate materials and to precise mixing of the whole bath. If the process of preparation leaves the non-disintegrated grain agglomerates, the rigid configuration of these forms can be left uncharged in the process of pressing the powders. The non-disintegrated aglomerate can be a rarefaction which in the sintering process, develops into a pore or a lamination that gives a crack start. The next technological operation, i.e. powder pressing can introduce such defects as density inhomogeneity or laminations. Noxiousness of these defects consists in that in the sintering process it is not only that those defects do not disappear, but they rather grow bigger. For example the density inhomogeneity leads to deformation of the specimen or to wide cracks especially in uniaxial pressing, what is due to different contractions in sintering. Invisible cracks with no external symptoms of deformation are much more dangerous. These cracks are a great impedancy to the specimens, for which the basic exploitational condition is mechanical or dielectric resistance. A number of factors influence the corectness of sintering ceramic materials and the concerned mass transport mechanisms. Among others there is temperature and time of sintering, crystal lattice defects in the components, size reduction and initial grain system geometry, formation of reactive intermediate products, external pressure and sintering atmosphere. Lattice defects facilitate diffusion which is the main mass transport mechanism. In the oxide links, which interest the ceramics researchers, a typical lattice disordering is an easy formed solid solution. Also the presence of a liquid phase interact with the sintering process. Depending on the amount of the liquid phase and its ability to moisten the grains one obtains different sinter structures. With a large volume shave of the liquid phase, which ensures filling the inter-grain spaces, there exists a possibility of completely eliminating porosity. Finally, the output sinter structure is formed by recrystallization. This process is concerned with the movement of grain boundaries which leads to minimization of the free surfaces of the system and is related to eliminating small grains in favour of the large ones. The basic technological problem at this stage of the process is not to allow the pores to detach from the grain boundaries and to remain behind the moving recrystallization front. This would lead to the intra-grain porosity, which is practically unremovable.

As it has been mentioned above, pores change the acoustical properties of the tested material. An equally unprofitable phenomenon engendered by recrystallization is a discontinuous grain growth. As its consequence in the microstructure the large grains emerge, the dimensions of which are larger than those of an average grain by one or to orders of magnitude. Grain boundaries of such large grains also cause the changes in velocity and damping of ultrasound waves, with respect to a medium without such boundaries.

4. Degradation of properties in ambient conditions

The greatest threat in application of the $YBa_2Cu_3O_\delta$ superconductors is their sensibility to moisture. This problem is particularly vital in all those measurements where it is necessary to cover the superconducting specimens with metallic films. The introductory studies on this problem pursued by Yan [32] demonstrated that even air with 85% rh at 85°C interacting with a specimen for 90 minutes causes surface amorphization of the Y—Ba—Cu—O ceramic. Degradation of these materials by H_2O is caused by reduction of a trivalent cation Cu^{3+} to Cu^{2+} and formation of $Ba(OH)_2$ with the evolution of O_2. Further, after this reaction the "green" polycrystalline ceramic phase and CuO formed.

Barns and Landise tried to protect the Y—Ba—Cu—O ceramic against moisture influence by applying 0.5 mm thick epoxy coating. However, although this epoxy coating should protect against moisture, the influence of air of 85% relative humidity in the temperature 85°C for 70 min causes superconductivity decay in a specimen in 77 K, while a specimen not protected by a coating under an influence of air with the same parameters for 50 min looses its superconducting properties even in 22 K. Barns and Landise anticipated that their method would enable to protect superconductivity for 1000 h in room humidity and temperature conditions.

There were also tests in which the materials were subjected to the influence of air with relative humidity 100% and temperature 23°C. These tests demonstrated the formation of $Cu(OH)_2$ and $BaCO_3$, (probably as a result of noncomplete removal of CO in sintering) even after exposure for 3 h. The main effect of such interaction of air saturated with vapour was the formation of an amorphous layer. In this case the time of saturation was 120 h. The amorphic layer formed during this time inhibited further decay reaction in the material.

Karios and Vance [4] found out that in the temperature 21°C the sulphuvic acid of pH = 1.2 completely dissolves the superconducting ceramic in 2–4 minutes.

Trolier et al. [33] studied the influence of various solvents on the Y—Ba—Cu—O ceramic surface. They found that for short exposure times at 25°C in the solvents Cu can be found. Aromatic solvent have the tendency to form surfaces richer in Y while alcohols created Y–deficient surfaces in relation to Cu concentration. Isoamyl alcohol caused the complete decomposition of the superconductor, with CuO, $BaCO_3$ and a phase containing yttrium as products. Similarity, the decomposition of superconducting ceramic was caused by the acetic and formic acids. In the Fig. 10 the diffractograms of layers formed at the surface of $YBa_2Cu_3O_{7-x}$ ceramic under the influence of various solvents.

An alternative technology of protecting the superconducting materials has been described by Mankiewicz et al. [34]. He has stated that the layers of Y, Ca and BaF_2 formed with the vapour deposition technique before the oxidating heating are resistant to water. This suggests the possibility of manufacturing and storing the layers vapour deposited with fluoride and then doing the oxidating heating, i.e. before hermetization in the appropriate glass, metal or organic containers used in many practical applications.

The superconducting materials are also sensitive to electron or neutron bombardement. Clark et al. [35] demonstrated that the inpingement with the by O ions doses of 1.1×10^{14} ions/cm^2 completely destroys superconductivity in these

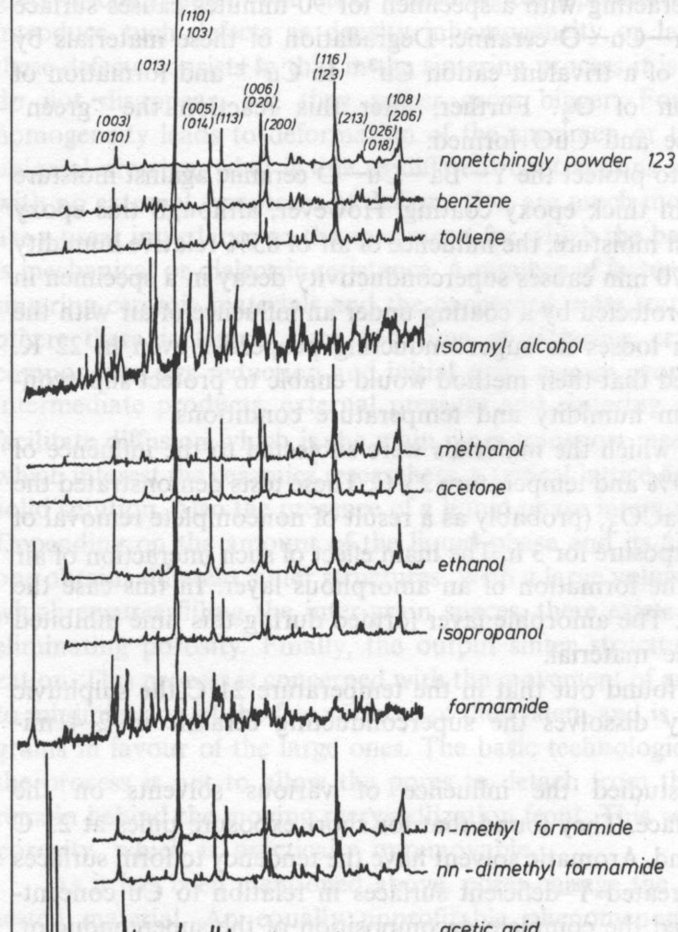

FIG. 10. Difractogrames of layers creating on surface $YBa_2Cu_3O_7$ as result interactions different solvents

materials. Also the ion flux with the intensity of 10^{13} ions/cm² initiates the loss of superconductivity.

The mechanism of superconductivity destruction resulting form the emergence of oxygen ions in the lattice consists in the reduction of vacancy ordering degree and in the transition from twinned orthorhombic structure to an amorphous material, after surpassing the threshold density of point defects [35, 36].

Irradiating the superconducting ceramic with a neutron beam has a relatively less destructive influence on the properties of these materials. Interaction of a neutron beam of the intensity 1.3×10^{18} n/cm² with a $La_{1.85}Sr_{0.15}CuO_y$ causes only the reduction of the critical temperature to 27 K [37].

KUPFER et al. [38] after having investigated the $YBa_2Cu_3O_7$ ceramic irradiation with neutrons found out that the radiation intensity for these materials shouldn't exceed 5×10^{17} n/cm^2. A neutron flux with intensity equal to 6×10^{18} n/cm^2 lowers the critical temperature by a half. The results of studies of the influence of irradiation, which demonstrate loss of superconductivity of a superconducting ceramic, indicate that the perspectives of application of these materials in applications producing a high neutron flux as e.g. Tokamak, or with high-energy particles, as e.g. in the super-collider superconducting accelerators, can be problematic.

However the effective application of superconducting materials in the heavy particles environment can be improved by screening. In electronic applications the γ and X radiation can be more dangerous. BOHANDY et al. [39] found out, that the γ and X radiation, within the limits of experiment errors, does not interfere with the superconducting properties of the material for the intensities up to 1.3 Mrad. They have also found out that this radiation results in electron excitation and not the excitation of ion structure, so that the electrons return to the initial superconductivity state after the radiation emission stop.

From the above carried out review of problems concerned with manufacturing the ceramic oxide superconductors the sources of difficulties with the appropriate choice of the methods of measuring their properties clearly arise. These are connected with large sensitivity of the oxide superconductors to influences of typical organic investions and oxide solutions. The use of these reagents (in rinsing or submerging of metal coatings) can result in dissolving the measured layers. For these reasons, the acoustic methods, in particular those which do not necessitate for coating the durable contacts, can find wide application, especially in testing new superconducting materials of unknown properties.

5. Thin-layer superconductors technology

Most of the structural defects in ceramic superconductors of larger thicknesses, which have been described above, can be avoided by using thin HTS layers in acoustic measurements. There are several methods of coating: chemical, laser, and the most frequently used method of magneton spatering [43, 44]. The magneton spatering with the constant current method is done in the room temperature. As a target an element made at pressed superconductor powder is used; as a base the strontium titanate $SrTiO_3$ zirconium oxide ZrO_2, magnesium oxide MgO, galium lantanate $LaGaO_3$, aluminium lantanate $LaAlO_3$, and lithium niobate $NbLiO_3$ are applied. Coating is carried out at the pressure 0.01 Tr and with the coating speed 45 A/s. The layers can have high resistivity and then should be subjected to a heat treatment. They undergo quick heating up to 925°C in 5 minute time, in a helium atmosphere. Then, they are slowly cooled for 2–3 hours in the oxygen flow. The specimens obtained in this way are tested for surface homogeneity in a scanning microscope. The obtained 1, 2, 3 – compound microstructures in form of a thin layer coated on a ZrO_2 substrate are shown in Fig. 11.

The resistivity of the layers as a function of temperature has been measured. The current characteristic vs. temperature for a 1, 2, 3 layer coated on a base is displayed in Fig. 12. A sharp resistivity drop in 91 K, with the transition width below 3 K (10–90%) is observed.

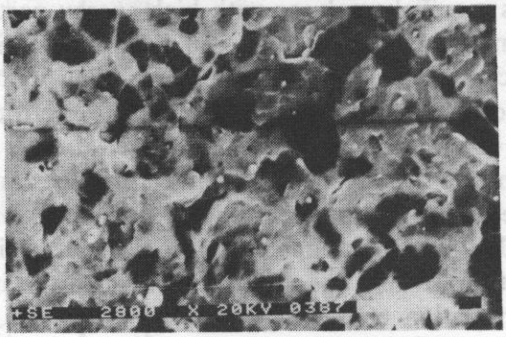

FIG. 11. Image of the 1, 2, 3 compound thin layer spreaded on the zirconium oxide

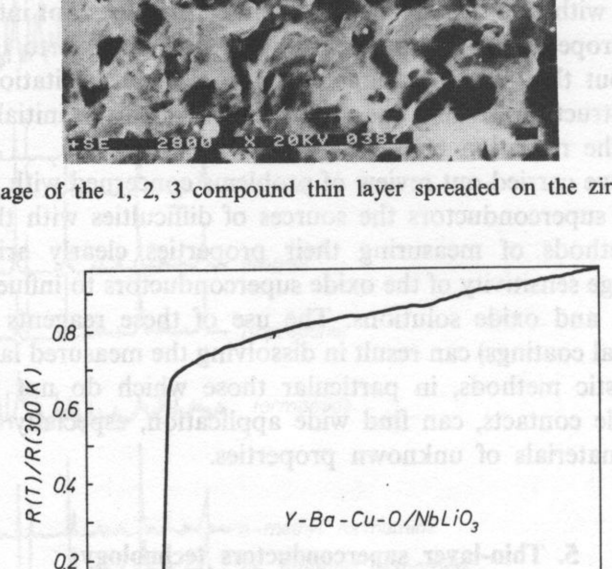

FIG. 12. Resistivity-temperature characteristic of the 1, 2, 3 – type compound spreaded on the $NbLiO_3$ substrate

6. Acoustic properties of superconductors

The measurements of macroscopic acoustic wave propagation parameters in conventional superconductors have played a significant role in confirming the BCS theory [45, 46]. The BCS theory satisfactorily explains the temperature relations of damping acoustic ways in superconductors. According to this theory in a superconductor for $T = 0$ two mechanisms of damping acoustic waves are possible: quasi-

-particles excitation or dispersion on them [45]. Excitation of quasi-particles can take place only with high frequencies, i.e. with $\hbar\omega > 2\Delta$, where $\hbar$ – Planck constant, ω – acoustic wave frequency, 2Δ – superconductor energetic gap width.

The fonon absorbtion probability in the superconducting state is expressed with the following realation [48]:

$$W_s = 2\int_{\Delta}^{\infty}\left(1-\frac{\Delta^2}{E_k E_{k'}}\right)\{f(E_k)[1-f(E_{k'})][1-f(E_k)\}\, N_s(E_k)\, dE$$

where: $f(E)$ – Fermi function, E_k, $E_{k'}$ – energy of the initial and final state of transition, $f(E_k)$, $f(E_{k'})$ – Fermi functions, N_s – density of states in a superconductor.

In the case of small frequencies of an acoustic wave ($\hbar\omega \ll 2\Delta$) we obtain

$$W_s = 2\int_{\Delta}^{\infty} N_N^2\{f(E_k)-f(E_k+\hbar\omega)\}\, dE = -2N_N^2\frac{df}{dE}\hbar\omega N_N^2 f(\Delta).$$

An analogous relation for absorbtion probability can be obtained for a metal in normal state:

$$W_N = 2\int_{0}^{x} N_N^2\{f(E_k)-f(E_k+\hbar\omega)\}\, dE = 2\hbar\omega N_N^2 f(0) = \hbar\omega N_N^2.$$

By comparing the two expressions we obtain:

$$\frac{W_s}{W_n} = \frac{\alpha_s}{\alpha_N} = 2f(\Delta)$$

where α_s – acoustic waves damping coefficient in superconducting state, α_N – acoustic waves damping coefficient above the critical temperature.

In the Fig. 13 an experimental relation $\frac{\alpha_s}{\alpha_N}$ for a lead crystal obtained for frequency 10 MHz has been shown.

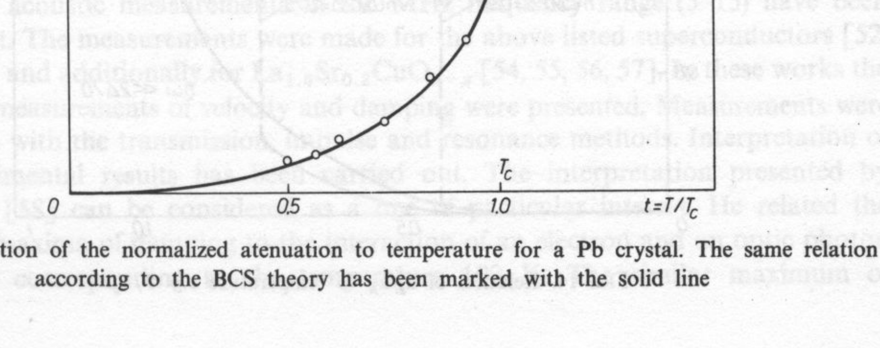

FIG. 13. Relation of the normalized atenuation to temperature for a Pb crystal. The same relation according to the BCS theory has been marked with the solid line

In the case of large frequencies $\hbar\omega > 2\Delta$ where the phenomenon of forming quasi-particles in the Cooper pairs fragmentation [18] the damping ratio is expressed with the following relation:

$$\frac{\alpha_s}{\alpha_n} = \frac{1}{\hbar\omega} \int_{-\infty}^{\infty} \left(1 - \frac{\Delta^2}{E_k E_{k'}}\right) [f(E_k) - f(E_{k'})]\, q_s(E_k)\, q_s(E_k)\, dE$$

where $q_s(E_k)$ – relative density of states $\dfrac{N_s}{N_N}$ equal to

$$q_s(E_k) = \begin{cases} 0 & \text{for } E_k \leqslant \Delta \\ \dfrac{|E_k|}{(E_k^2 - \Delta^2)^{1/2}} & \text{for } E_k > \Delta \end{cases} .$$

The integral in the above relation can be rewritten in the following form:

$$\frac{\alpha_s}{\alpha_n} = \frac{2}{\omega} \int_{\Delta}^{\infty} [f(E) - f(E + \hbar\omega)] \frac{[E(E + \hbar\omega) - \Delta^2]\, dE}{(E^2 - \Delta^2)\,[(E + \hbar\omega)^2 - \Delta^2]} - \frac{1}{\hbar\omega} \cdot \int_{s - \hbar\omega}^{s} (1 - 2f(E + \hbar\omega))$$

where the first component has been analyzed above, and the second component corresponds to formation of quasi-particles pairs and can not be calculated analytically. Numerical calculations give the results shown in Figs. 14 and 15. It can be seen on the graphs in Fig. 14 that when $\hbar\omega$ becomes larger than 2Δ by an arbitrarily small value there is a jump of damping value to a different curve.

In Fig. 15 the relation of α_s/α_N and for given values of T has been shown. For $\hbar\omega$ larger than 2Δ we obtain also the jump of damping. The above theoretical results have been confirmed in the analysis of working conditions of the supercon-

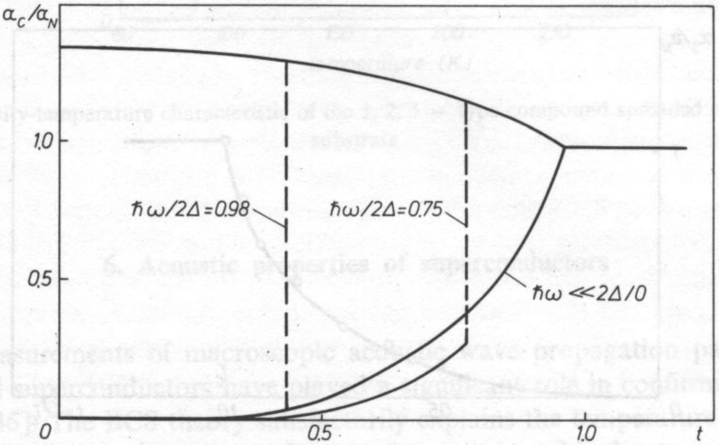

FIG. 14. Relation of α_s/α_N to temperature $t = T/T_c$

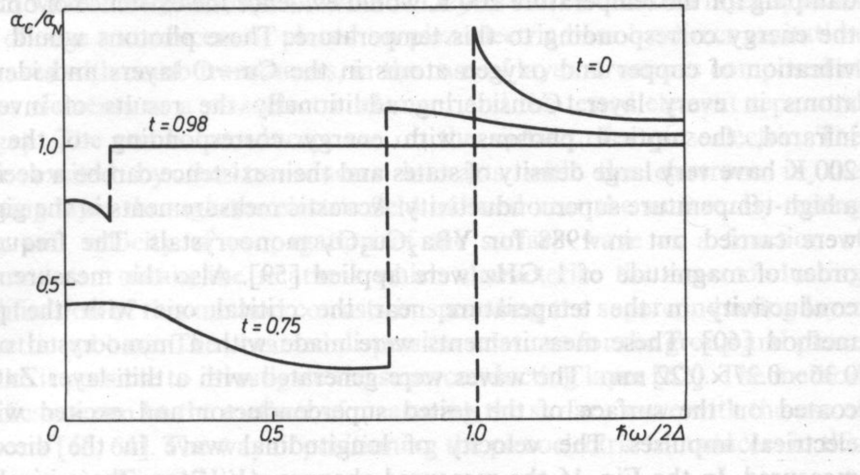

FIG. 15. Relation of α_s/α_N to $\hbar\omega/2\Delta$

ducting tunnel junctions applied as generators and detectors of hypersound tunnel vibrations [47].

Application of the hitherto discussed formulae to the description of damping acoustic waves in high-temperature superconductors is not justified, as up till now the coherent theory of high-temperature superconductivity is missing. Despite that, the experimental acoustic methods are already widely used. The reduction of damping with the decrease of temperature in the superconducting state is one of the more important proofs for that in normal metals large damping of acoustic waves is concerned with the existence of free electrons.

First acoustic measurements of superconductors were made with the frequencies of several kHz. The measurements were carried out with the resonance method for plates and disks [49, 50, 51]. With this method the resonance frequency and the internal friction coefficient were measured in the $YBa_2Cu_3O_{7-x}$ and $EuBa_2Cu_3O_{7-x}$ superconductors. Also the Young modulus was estimated with the resonance method. Relations have been found between the observed temperature peaks of the internal friction coefficient and the structural transitions concerned with the transition to the state of superconductivity and movements of oxygen vacancies. Then, the acoustic measurements in the MHz frequency range (5–15) have been carried out. The measurements were made for the above listed superconductors [52, 53, 54, 55] and additionally for $La_{1.8}Sr_{0.2}CuO_{4-x}$ [54, 55, 56, 57]. In these works the results of measurements of velocity and damping were presented. Measurements were performed with the transmission, impulse and resonance methods. Interpretation of the experimental results has been carried out. The interpretation presented by Y. HORIE [58] can be considered as a one of particular interest. He related the observed maxima of damping to the interaction of an electron and an optic photon of energy corresponding to the temperature 100 K. The similar maximum of damping for the temperature 200 K would evidence the existence of optic photons of the energy corresponding to this temperature. These photons would be related to vibration of copper and oxygen atoms in the Cu—O layers and identical La—O atoms in every layer. Considering additionally the results of investigations in infrared, the optical photons with energy corresponding to the temperature 200 K have very large density of states and their existence can be a decisive factor of a high-temperature superconductivity. Acoustic measurements in the gigahertz range were carried out in 1988 for $YBa_2Cu_3O_7$ monocrystals. The frequencies of the order of magnitude of 1 GHz were applied [59]. Also the measurements of heat conductivity in the temperature near the critical one with the photothermal method [60]. These measurements were made with a monocrystal of dimensions $0.36 \times 0.27 \times 0.22$ mm. The waves were generated with a thin-layer ZnO transducer coated on the surface of the tested superconductor and excited with 10–20 ns electrical impulses. The velocity of longitudinal wave in the direction C was measured. In the Fig. 16 the measured changes $\Delta V/V$ near the critical temperature

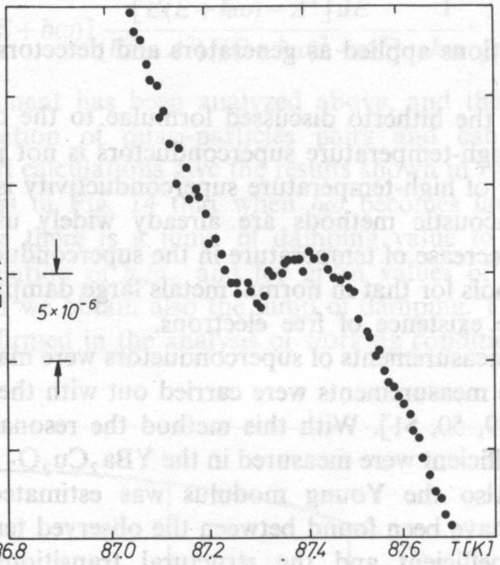

FIG. 16. Ultrasound waves travel velocity changes near the critical temperature for a 1, 2, 3-type superconductor 59

have been presented. In the work concerning the heat conductivity the conductivity increase in the temperature near to the critical temperature has been stated. The analysis made in this work relates these changes with the disturbancies of the copper atom position in the Cu—O layers [61].

It seems that more explicit measurement results can be obtained with thin superconducting layers dielectrically spreaded on the substrate. These measurements are carried out with surface acoustic waves. Such layers can be tested in layer systems with the use of edge transducers or placed on piezoelectric base by direct excitation of acoustic waves with comb transducers, in the case of layer structures composed of two continous elements or a piezoelectric element and the tested element separated by a small gap. The comb transducers are on the surface of a piezoelectric. The surface wave excited by the transducers interacts with the electrons in the superconducting layer through the electric field induced near the surface. By testing the damping and velocity of propagation of the surface wave as a function of temperature one can obtain the relations which characterize the superconducting layer. A modification of this method consists in spreading the superconducting layer on a piezoelectric subbase. The obtained dispersion relations for the group and phase velocities make it possible to investigate the superconducting layer [62]. The method of great significance can be the method of measuring the surface wave with the use of edge transducers [63, 64]. The way of positioning the piezoelectric transducers in this method is shown in Fig. 17.

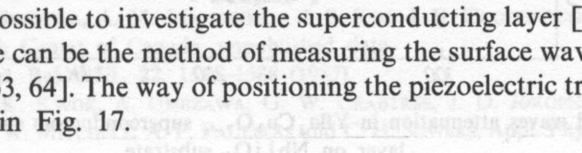

FIG. 17. Setup of transducers for the measurements of the relation between the surface wave amplitude and the distance *h* between a free surface and a transducer: *1* — sender, *2* — receiver, *3* — medium

Piezoelectric tile transducers are easy to manufacture and can be applied in the case of piezoelectric materials as well as the non-piezoelectric ones. The only limitation is frequency; this is concerned with the technological conditions and with the difficulty of manufacturing the adequately narrow and thin transducers (the upper bound is 100 MHz). The substantial novelty of the work is the theoretical analysis of surface waves generation in the case of title transducers, estimation of the optimal wave generation conditions and the original way of finding the coefficient of wave transmission from one surface to another. With this method the layers of the 1, 2, 3 superconductors spreaded on the strontium titanate and lithium niobate have been measured.

The measurements of damping for the above mentioned layer spreaded on the lithium niobate substrate with the use of edge transducers has been shown in Fig. 18. In the critical temperature a considerable increase of damping (by the order of magnitude of 10 dB) has been observed. Below the critical temperature the damping decreases. During passing through the critical point strong deformation of the sequence of acoustic echoes can be seen. This can evidence the increase of local mechanical stresses or the structural changes of the medium. In transition through the critical point the change of the acoustic wave velocity by the order of magnitude of $\Delta V/V = 10^{-3}$ is observed.

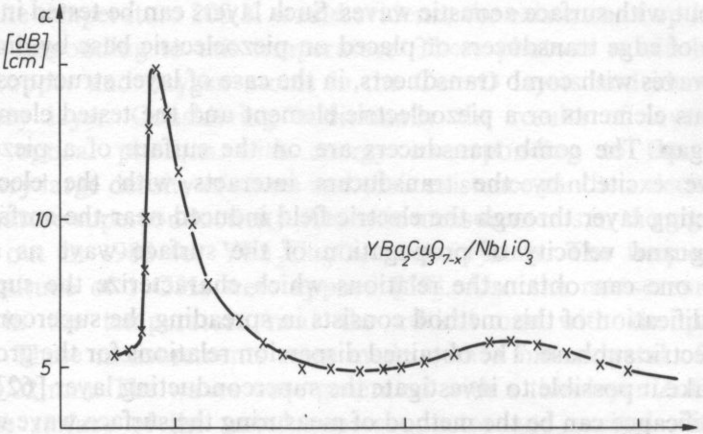

FIG. 18. Ultrasound waves attenuation in $YBa_2Cu_3O_{7-x}$ superconductors spreaded in a form of thin layer on $NbLiO_3$ substrate

References

[1] T. G. BEDNORZ, K. A. MULLER, Z. Phys. B: Condens. Matter. **64**, 189–193 (1986).

[2] G. BEDNORZ, N. TAKASHIGE, K. A. MULLER, Europhys Lett. **3**, 379 (1987).

[3] M. K. WU, J. R. ASHBURN, C. J. TORNG, P. H. HOR, R. L. MENG, L. GAO, Zl. HUANG, Q. WANG, C. W. CHU, Phys. Rev. Lett. **58**, 908 (1987).

[4] G. FISHER, Ceramic Bulletin, **67**, 4, 725–735 (1988).

[5] D. KLIBANOW, K. SUJATA, T. O. MASON, Appl. Phys. Lett., **53**, 125–127 (1988).

[6] A. W. SLEIGHT, 1–12 The Chemistry of High Temperature Superconductors, Ed. D. L. Nelson, M. S. Whittingham and T. F. George, American Chemical Society, Washington, DC 2–12 (1987).

[7] P. K. GALLAGHER, Adv. Ceram. Mater., **2** (3B), 632–39 (1987).

[8] A. J. MELMED, R. D. SHULL, C. K. CHIANG, H. A. FOWLER, Science Washington, DC **239**, 176–78 (1988).

[9] M. O. EATOUGH, D. S. GINLEY, B. MOROSIN, and E. L. VENTURINI, Appl. Phys. Lett., **51** (5), 367–8 (1987).

[10] J. K. LIANG, G. C. CHE, W. CHEN, K. Q. LU, Q. S. YANG, G. H. CHEN and Y. M. NI, J. Mater. Sci. Lett., **6**, 1321–22 (1987).

[11] R. S. ROTH, K. L. DAVIS and J. R. DENNIS, Adv. Ceram. Mater., **2** (**38**), 303–12 (1987).

[12] I. K. GOPALAKRISHNAN, J. V. YAKHAMI, M. A. VAIDYA and R. M. IYER, Appl. Phys. Lett., **51**, 17, 1367–69 (1987).

[13] R. BEYERS, G. LIM, E. M. ENGLER and R. J. SAVOY, Appl. Phys. Lett. **50** (26), 1918–20 (1987).

[14] H. HANEDA, M. ISOBE, S. HISHITA, Y. ISHIZAWA and S. SHIRASAKI, Appl. Phys. Lett. **51** (22), 1848–50 (1987).

[15] Y. KHAN, J. Mater. Scie. Lett., **6**, 1221–2 (1987).

[16] X. ZENG, X. JIANG, H. QI, D. PANG, N. ZHU and Z. ZHANG, Appl. Phys. Lett., **51** (9), 692–33 (1987).

[17] R. S. ROTH, K. L. DAVIS and J. R. DENNIS, Adv. Ceram. Mater., **2** (3B), 303–12 (1987).

[18] K. G. FRASE and D. R. CLARKE, Adv. Ceram. Mater., **2** (3B), 295–302 (1987).

[19] *Superconducting ceramics*, British Ceramic Procedings Nr 40. The Institut of Ceramics, Stoke-on-Trent, 1987.

[20] H. Wang et al. Inorg. Chem., **26**, 1474, (1987).

[21] J. Narayan, V. Shukla, S. J. Łukasiewicz, N. Biunno, R. Singh, A. F. Schreiner and S. J. Pennycook, Appl. Phys. Lett. **51** (12), 940–42 (1987).

[22] K. N. Tu, S. I. Park and C. C. Tsuei, Appl. Phys. Lett., **51** (25), 2158–60 (1987).

[23] B. G. Bagley, L. H. Greene, J. M. Tarascon and G. W. Hull, Appl. Phys, Lett., **51** (8), 622–624 (1987).

[24] J. M. Tarascon, L. H. Greene, W. R. McKinnon, Pergamon Journals Ltd., **63** (6), 499–505 (1987).

[25] W. R. McKinnon, J. M. Tarascon, L. H. Greene and G. W. Hull, *Extended abstracts of high temperature superconductors*, Mat. Res. Soc. 1987 Spring Meetinh Edition 185–87 (1987).

[26] J. J. Neumeier, Y. M. Ferreira, R. R. Hake, B. W. Lee, M. B. Maple, M. S. Tokorikachvili, K. N. Yang and H. Zhou, Appl. Phys. Lett. **51** (5), 371–73 (1987).

[27] J. M. Tarascon, L. H. Greene, W. R. McKinnon, G. W. Hull, T. P. Orlando, K. A. Delin, S. Foner and E. J. McNiff Jr., Phys. Rev. B: Condens Matter, **36**, 16 (1987).

[28] Y. K. Tao, J. S. Swinnea, A. M. Manthiram, J. S. Kim, J. B. Goodenough and H. Steiñfink, National Research Center of Canada, unpublished data.

[29] Cahen et al., Mat. Res. Bull., **22**, 1581–1588 (1987).

[30] B. W. Veal, W. K. Kwok, A. Umezawa, G. W. Crabtree, J. D. Jorgenson, J. W. Downey, L. J. Nowicki, A. W. Mitchell, A. P. Paulikas and C. H. Sowers, Appl. Phys. Let., **51** (4), 279–81 (1987).

[31] M. F. Yan, W. W. Rhodes, P. K. Gallagher, An International Symposium Denver, Colorado, October 19, 1987.

[32] M. F. Yan, R. L. Barns, H. M. O'Bryan, Jr., P. K. Gallagher, R. C. Sherwood and S. Jin, Appl. Phys. Lett., **51** (7), 532–34 (1987).

[33] S. E. Trolier et al. Am. Cer. Soc. Bull. **67**, 4, 759–762 (1988).

[34] P. M. Mankewich, J. H. Scolfied, W. J. Skocpol, R. E. Howard, A. H. Dayem, E. Good, Appl. Phys. Let., **51** (21), 1753–55 (1988).

[35] G. J. Clark, A. D. Marwick, R. H. Koch and R. B. Laibowitz, Appl. Phys. Let., **51** (2), 139–41 (1987).

[36] G. J. Clark, F. K. LeGoues, A. D. Marwick and R. D. Laibowitz, R. Koch, Appl. Phys. Let., **51** (18), 1462–64 (1987).

[37] D. K. Christen, J. R. Thompson, S. T. Sekula, L. A. Boatner, B. C. Sales and S. J. Pennycock, Jpn. J. Appl. Phys., **26**, 1057–58 (1987).

[38] H. Kupfer, I. Apfelstedt, W. Schauer, R. Flukiger, R. Meier-Hirmer, W. Wuhl and H. Scheurer, Z. Phys. B: Condens. Matter., **69**, 167–71 (1987).

[39] J. Bohandy, J. Suter, B. F. Kim, K. Moorjani and F. J. Adrian, Appl. Phys. Let. **51** (25), 2161–63 (1987).

[40] J. Ranachowski, F. Rejmund, Z. Librant, *Acoustics in ceramic investigations* (in Polish), 28 IPPT Warsaw 1981.

[41] J. Stankowski, *High-temperature superconductivity* (in Polish), Report for the Session of the General Meeting of PAS, Warsaw, May 1988.

[42] C. V. Chu, K. A. Müller, Zeitschr. f. Phys., B64, 189 (1986).

[43] W. Kula, R. Sobolewski, P. Gierłowski, G. Jung, A. Konopka, J. Konopka, S. Lewandowski, Thin Solid Films, **174**, 249–254 (1989).

[44] G. Jung, A. Dąbkowski, P. Gierłowski, W. Kula, Physica C 158, 419–423 (1989).

[45] J. Bardeen, C. N. Cooper, J. R. Schrieffer, Phys. Rev., **108**, 11, 75 (1957).

[46] G. Rickayzen, *Theory Superconductivity*, New York 1965.

[47] M. Aleksiejuk, M. Dobrzański, W. Larecki, Arch. of Acoustics, 1, 157–172 (1981).

[48] V. M. Bobetic, Phys. Rev. 136A, 1535–1541 (1964).

[49] Wang Yening et al. Int. J. of Modern Phys., B. 1 273–276 (1987).

[50] C. Cannelli, R. Cannelli, F. Cordero, G. A. Costa, M. Ferreti, G. L. Olcese, Phys. Rev. B. **36**, 8907–8910 (1987).

[51] C. Duran, P. Esquinazi, C. Fainstein, M. Nurvi Requiro, Sol. Stet. Comm., **65**, 957 (1988).
[52] D. P. Almond, E. F. Lambson, G. A. Sanders, Wang Hong, J. Phys. F., Met. Phys., 457–460 (1987).
[53] S. Bhattacharya et al., Phys. Rev. Lett., **60**, 1181–83 (1988).
[54] M. Lang et al., Z. Phys. B69, 45–51 (1988).
[55] V. Muller, K. De Groot, Jap. of Appl. Phys., **26**, 2139–2141 (1987).
[56] T. Legreid, K. Fosshim, F. Vassendem, Proc. from HTS., Interloken 1988.
[57] B. Luhti, B. Wolf, T. Kim, W. Grill, Jap. of Appl. Phys., **26**, 26–3, 1127–1130 (1987).
[58] Y. Horie, T. Fukami, S. Masc, Sol. Stet. Comm., **63**, 653–655 (1987).
[59] B. Golding, W. H. Haemmerle, C. F. Schneemeyr, J. V. Waszczuk, Ultrasonic Symposium, 1079–83 (1988).
[60] J. Fanton, G. S. Kino, B. T. Khuri-Jakub, 1988 Ultrasonic Symposium, 1093–96 (1988).
[61] M. Levy, M. F. Xu, Bimal K. Sarma, Z. Zhco, S. Adenwallo, O. Robinson, J. B. Ketterson, 1988 Ultrasonic Symposium, 1097–1103 (1988).
[62] Z. Kubik, A. Opilski, Acta phys. slov., **37**, 359–362 (1987).
[63] W. Pajewski, Arch. Akustyki, **12**, 3, 235–243 (1977).
[64] N. Gyen Viet Kink, W. Pajewski, Arch. Akustyki **14**, 4, 367–376 (1979).
[65] Z. Librant, A. Gładki, L. Hozer, M. Pawłowska, *Report of the Association of Polish Electricians* No. 07/16/89 (unpublished).