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### Possible High $T_c$ Superconductivity in the Ba–La–Cu–O System

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Metallc, oxygen-deficient compounds in the Ba–La–Cu–O system, with the composition  $\text{Ba}_x\text{La}_{1-x}\text{Cu}_2\text{O}_{3.0-y}$  have been prepared in polycrystalline form. Samples with  $x=1$  and  $0.75$ ,  $y>0$ , annealed below  $900^\circ\text{C}$  under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally an abrupt decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 30 K range. It is markedly reduced by high current densities. Thus, it results partially from the percolative nature, but possibly also from 2D superconducting fluctuations of double perovskite layers of one of the phases present.

#### 1. Introduction

“At the extreme forefront of research in superconductivity is the empirical search for new materials” [1]. Transition-metal alloy compounds of  $A15$  (Nb<sub>3</sub>Sn) and  $B1$  (NbN) structure have so far shown the highest superconducting transition temperatures. Among many  $A15$  compounds, careful optimization of Nb–Ge thin films near the stoichiometric composition of Nb<sub>3</sub>Ge by Gavalev et al. and Testardi et al. a decade ago allowed them to reach the highest  $T_c = 23.3$  K reported until now [2, 3]. The heavy Fermion systems with low Fermi energy, newly discovered, are not expected to reach very high  $T_c$ 's [4].

Only a small number of oxides is known to exhibit superconductivity. High-temperature superconductivity in the Li–Ti–O system with onsets as high as 13.7 K was reported by Johnston et al. [5]. Their x-ray analysis revealed the presence of three different crystallographic phases, one of them, with a spinel structure, showing the high  $T_c$  [5]. Other oxides like perovskites exhibit superconductivity despite their small carrier concentrations,  $n$ . In Nb-doped  $\text{SrTiO}_3$ , with  $n = 2 \times 10^{19} \text{ cm}^{-3}$ , the plasma edge is below the highest optical phonon, which is therefore unshielded

[6]. This large electron-phonon coupling allows a  $T_c$  of 0.7 K [7] with Cooper pairing. The occurrence of high electron-phonon coupling in another metallic oxide, also a perovskite, became evident with the discovery of superconductivity in the mixed-valent compound  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  by Sleight et al., also a decade ago [8]. The highest  $T_c$  in homogeneous oxygen-deficient mixed crystals is 13 K with a comparatively low concentration of carries  $n = 2.4 \times 10^{21} \text{ cm}^{-3}$  [9]. Flat electronic bands and a strong breathing mode with a phonon feature near  $100 \text{ cm}^{-1}$ , whose intensity is proportional to  $T_c$ , exist [10]. This last example indicates that within the BCS mechanism, one may find still higher  $T_c$ 's in perovskite-type or related metallic oxides, if the electron-phonon interactions and the carrier densities at the Fermi level can be enhanced further.

Strong electron-phonon interactions in oxides can occur owing to polaron formation as well as in mixed-valent systems. A superconductivity (metallic) to bipolaronic (insulator) transition phase diagram was proposed theoretically by Chakraverty [11]. A mechanism for polaron formation is the Jahn-Teller effect, as studied by Hšek et al. [12]. Isolated  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  in octahedral oxygen environment

## Preface

The scientific event that impressed and excited the whole world, without exaggeration, took place precisely 20 years ago, in April 1986. It was when the journal «Zeitschrift für Physik B: Condensed Matter» received the five-page article by the Swiss researchers Georg Bednorz and Alex Müller from the IBM research laboratory in Zürich, that went under a very cautious title (as repeatedly noted), namely «**Possible High- $T_c$  Superconductivity in Ba–La–Cu–O System**», and was published in the September issue [1]. The article reported results of the observation of a rather broad superconducting transition occurring in the ceramic compound  $\text{La}_2\text{CuO}_4$  doped for becoming metallic with alkali-earth metals Ba, Sr or Ca. The critical temperature  $T_c \approx 30\text{--}35$  K of the transition was almost one and a half as high as the previous record of  $T_c \leq 24$  K achieved with great effort in 1973. This publication, as short as it was, launched a new boom of investigations of such an outstanding phenomenon as superconductivity, which, by the way, «marked» its 75th anniversary in the same year 1986. Thus, it can be said with good reason and full certainty that high-temperature (or high- $T_c$ ) superconductivity as a phenomenon of nature, to which this special issue of Low Temperature Physics is dedicated, will be twenty years old this April. It should be noted that the question of the «age» of high- $T_c$  superconductivity of copper or «Zürich oxides», as they are sometimes called, is not just a matter of an idle curiosity since «high-temperature superconductivity» in its true sense, i.e., with  $T_c > 77$  K, was discovered almost a year later [2].

These results gave an onset to an unprecedented world-wide boom, whereby a physical phenomenon attracted tremendous attention, not only of physicists and specialists involved in related areas, but also of the general public\*. Indeed, the article by Bednorz and Müller was a real breakthrough, pioneering a fundamentally new area of scientific exploration, which made the many years old dream of high values of  $T_c$  come true. In fact, all subsequent high- $T_c$  compounds, i.e., the 90-degree yttrium, 110-degree bismuth, 125-degree thallium and, finally, today's record-breaking 164-degree (under pressure) mercury compounds are just the results of explorations by physicists and chemists working in materials science — an unknown area for the majority of experimenters and theoreticians,

which was quite unexpectedly discovered by the Swiss physicists. Whatever the detailed properties of a material exhibiting the high- $T_c$  superconductivity are and whatever type of conductivity or structure it has, all of the compounds known so far feature one common element, i.e., planes of  $\text{CuO}_2$ , where the main action of the play called «high- $T_c$  superconductivity» originates and takes place. That is why only G. Bednorz and A. Müller can be considered to be the authors, and that is why the priority, justifiably confirmed by the Nobel Prize, belongs to them.

As to the memories of the first, remarkable and romantic, period of investigations into high- $T_c$  superconductivity that rapidly involved almost all centers of physical, chemical and applied research at universities, institutes, companies and enterprises, it is worthwhile to note numerous newspaper or TV reports of increasingly high  $T_c$ 's, as well as positive forecasts and strong, although exaggerated, hopes for prompt and universal world-wide energy well-being.

Alas, this has not happened as yet!

There are many reasons for this, but the main one probably consists in the fact that the new materials turned out to be dramatically different from conventional superconductors, and they posed problems which nobody could foresee or anticipate. And although, as expressed by V.L. Ginzburg [3], copper oxides «should not be separated by a Chinese wall from other superconducting materials», they constitute a special and, despite an incredible number of publications (already about 100,000), yet not totally understood class of conductors. In particular, the fact that the conductivity of cuprates is formed by starting from insulating antiferromagnetic systems (which is due to strong on-site electron-electron correlations) is an issue that is hard to understand and, moreover, hard to describe.

Nevertheless, during the twenty years of superintensive investigations, high- $T_c$  superconductivity changed into an independent and vast area of research, where much has already been done, but still more has to be done in the future. In particular, missing is a solution of the question about the crucial interaction underlying pairing, which, in turn, is anisotropic. Also unsolved are many seemingly particular issues, which, at the same time, are very important for further development of physics of superconductivity and its appli-

\* It is interesting to note that in 1987 President Ronald Reagan made a speech at the Plenary Meeting of the American Physical Society, and at that same time the National Program «High-Temperature Superconductivity» headed by Prime Minister N.I. Ryzhkov was launched in the USSR with generous funding. Similar measures for the investigation of new materials and for a hopefully rapid and free application of the results were taken in all industrialized countries.

cation. This fact can be explained (but not justified): as it turned out soon, the discovery and subsequent experimental investigation of specially synthesized and increasingly more perfect high- $T_c$  compounds demonstrated an insufficient development of important aspects of condensed matter theory, which proved to be «unfit» for an adequate description of properties of strongly correlated doped metals. Moreover, if we add to it that the latter exhibit, simultaneously, the features of magnetic, disordered and low-dimensional systems, which before the discovery of high- $T_c$  superconductivity were usually studied separately, then the problems accompanying investigations of these fascinating materials should be clear even to nonspecialists.

Being guest editors, we wished the special issue of Low Temperature Physics dedicated to the jubilee of high- $T_c$  superconductivity to contain experimental and theoretical articles summarizing results in this area of research, or in related ones. This was indeed the case for a number of articles, and the reader will really have the opportunity to get acquainted with history and state-of-the-art in a number of issues. On the other hand, many authors understood the task in a wider sense and decided to report on the latest results relating not only to copper oxides, but also to other systems, the investigation of which was caused by and derived from the high- $T_c$  superconductivity. Equally favorable treatment was also given to such articles, following the rule that «everything not prohibited should be allowed».

The spectrum of the covered problems is quite large: various experimental techniques used to study the electronic states and the response to electromagnetic fields are presented. Special and unexpected properties, such as the electronic pseudogap in the normal state, the «stripe phase» and the competition of superconductivity with orbital current structures are discussed and «justified» by model calculations. The question whether «good old» electron-phonon interaction, possibly combined with the effect of Coulomb repulsion and acting through a nonadiabatic mechanism, or other collective modes like spin fluctuations are responsible for the electronic pairing is analyzed in detail. Theoreticians develop quite heavy machinery, such as Gutzwiller projection for the ground state or the dynamic mean-field approach for the Hubbard model, in order to get hold of the secrets of strongly correlated electrons. Applying these ideas to superconductivity in organic compounds and in systems of ultra-cold atoms brings the reader back to interesting domains of low-temperature superconductivity.

We thought that joining under the same cover articles on superconductivity of such different orientation would not merely be a «tribute to fashion or eclecticism», but a direct reflection of the present-day rea-

lity, where specialists of different scientific orientation could find nontrivial relationships between branches of a wide area of knowledge, which the physics of superconductivity became after the discovery of Bednorz and Müller. The time of groundless advertisement promises, such as forthcoming levitated trains, very fast and cheap computer techniques, resistless energy and current transportation in wires over long distances, large-scale applications for powerful magnets, motors, generators — and many others — has gone long ago. But there comes the time of serious, in-depth research in one of the major, promising and actively developing exciting areas of solid state physics.

On the other hand, specialists, as well as anybody interested in the latest achievements and topical (by no means all) problems of physics of superconductivity, can see how long the way is that high- $T_c$  superconductivity has gone through and how great the progress is in this area. Finally, and one should not wonder about that, many challenges have not yet been overcome, despite much success. Probably the ways for solving some of them can be found to some extent in the articles immediately following our introductory words.

Twenty years have passed by very quickly, and now we are entering the next, third decade. The order of the day is to achieve maximum  $T_c$  under conditions which are not too different from the normal ones. Of course, room temperature under ambient pressure would be an ideal variant in terms of possible applications. The answers to this, as well as to many other important questions, including practical ones, will hopefully be given in the foreseeable future.

In the conclusion, in the name of the Editorial Board of Low Temperature Physics and on our personal behalf, we are expressing our sincere gratitude to all our colleagues for their kind consideration in preparing their contribution to this jubilee issue. Also, we are sincerely asking for the understanding of those authors whose articles for technical reasons or because of late submission could not be included in the present issue of the journal, although it is of a double volume. They will be published in the next issue.

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