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韩汝珊 主编

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# "中外物理学精品书系"
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# 序　言

物理学是研究物质、能量以及它们之间相互作用的科学。她不仅是化学、生命、材料、信息、能源和环境等相关学科的基础，同时还是许多新兴学科和交叉学科的前沿。在科技发展日新月异和国际竞争日趋激烈的今天，物理学不仅囿于基础科学和技术应用研究的范畴，而且在社会发展与人类进步的历史进程中发挥着越来越关键的作用。

我们欣喜地看到，改革开放三十多年来，随着中国政治、经济、教育、文化等领域各项事业的持续稳定发展，我国物理学取得了跨越式的进步，做出了很多为世界瞩目的研究成果。今日的中国物理正在经历一个历史上少有的黄金时代。

在我国物理学科快速发展的背景下，近年来物理学相关书籍也呈现百花齐放的良好态势，在知识传承、学术交流、人才培养等方面发挥着无可替代的作用。从另一方面看，尽管国内各出版社相继推出了一些质量很高的物理教材和图书，但系统总结物理学各门类知识和发展，深入浅出地介绍其与现代科学技术之间的渊源，并针对不同层次的读者提供有价值的教材和研究参考，仍是我国科学传播与出版界面临的一个极富挑战性的课题。

为有力推动我国物理学研究、加快相关学科的建设与发展，特别是展现近年来中国物理学者的研究水平和成果，北京大学出版社在国家出版基金的支持下推出了"中外物理学精品书系"，试图对以上难题进行大胆的尝试和探索。该书系编委会集结了数十位来自内地和香港顶尖高校及科研院所的知名专家学者。他们都是目前该领域十分活跃的专家，确保了整套丛书的权威性和前瞻性。

这套书系内容丰富，涵盖面广，可读性强，其中既有对我国传统物理学发展的梳理和总结，也有对正在蓬勃发展的物理学前沿的全面展示；既引进和介绍了世界物理学研究的发展动态，也面向国际主流领域传播中国物理的优秀专著。可以说，"中外物理学精品书系"力图完整呈现近现代世界和中国物理

科学发展的全貌，是一部目前国内为数不多的兼具学术价值和阅读乐趣的经典物理丛书。

“中外物理学精品书系”另一个突出特点是，在把西方物理的精华要义“请进来”的同时，也将我国近现代物理的优秀成果“送出去”。物理学科在世界范围内的重要性不言而喻，引进和翻译世界物理的经典著作和前沿动态，可以满足当前国内物理教学和科研工作的迫切需求。另一方面，改革开放几十年来，我国的物理学研究取得了长足发展，一大批具有较高学术价值的著作相继问世。这套丛书首次将一些中国物理学者的优秀论著以英文版的形式直接推向国际相关研究的主流领域，使世界对中国物理学的过去和现状有更多的深入了解，不仅充分展示出中国物理学研究和积累的“硬实力”，也向世界主动传播我国科技文化领域不断创新的“软实力”，对全面提升中国科学、教育和文化领域的国际形象起到重要的促进作用。

值得一提的是，“中外物理学精品书系”还对中国近现代物理学科的经典著作进行了全面收录。20 世纪以来，中国物理界诞生了很多经典作品，但当时大都分散出版，如今很多代表性的作品已经淹没在浩瀚的图书海洋中，读者们对这些论著也都是“只闻其声，未见其真”。该书系的编者们在这方面下了很大工夫，对中国物理学科不同时期、不同分支的经典著作进行了系统的整理和收录。这项工作具有非常重要的学术意义和社会价值，不仅可以很好地保护和传承我国物理学的经典文献，充分发挥其应有的传世育人的作用，更能使广大物理学人和青年学子切身体会我国物理学研究的发展脉络和优良传统，真正领悟到老一辈科学家严谨求实、追求卓越、博大精深的治学之美。

温家宝总理在 2006 年中国科学技术大会上指出，“加强基础研究是提升国家创新能力、积累智力资本的重要途径，是我国跻身世界科技强国的必要条件”。中国的发展在于创新，而基础研究正是一切创新的根本和源泉。我相信，这套“中外物理学精品书系”的出版，不仅可以使所有热爱和研究物理学的人们从中获取思维的启迪、智力的挑战和阅读的乐趣，也将进一步推动其他相关基础科学更好更快地发展，为我国今后的科技创新和社会进步做出应有的贡献。

“中外物理学精品书系”编委会 主任
中国科学院院士，北京大学教授
**王恩哥**
2010 年 5 月于燕园

# Preface

It has been one hundred years since the discovery of superconductivity.

Superconductivity was discovered in 1911 by Kamerlingh Onnes when he was measuring the resistance of Hg at the temperature of 4 K. Below this transition temperature, the metal Hg has no resistivity, and it is called zero-resistivity effect. After years of research, in 1933, people realized another basic property of superconductors, the perfect diamagnetism, which is also called Meissner effect. Based on that, BCS theory was established in the 1950s, more than 40 years after the discovery of superconductivity, which shows the abstruseness of this theory and the difficulty of the work. There have been four Nobel Prizes given to 6 scientists because of their contributions to the superconductivity research. And the concept of pairing condensation has been expanded to 13 orders of magnitude in temperature, from $^3$He ($T_c \sim 10^{-3}$ K) to the nucleus ($T_c \sim 10^{10}$ K), without considering the quark condensate. BCS theory has affected the condensed matter physics and even the whole physics world over half a century. But the unusual features of the superconducting state and normal state of high $T_c$ superconductors challenge the authority of conventional BCS theory and even the Landau-Fermi liquid (FL) theory. In the last century, especially in the latter half, FL theory and BCS theory made important contributions to a deeper understanding of physics based on lots of experiments. In addition, the study of high $T_c$ superconductivity broke through the framework of FL theory and BCS theory on the shoulder of this "giant" again, and developed the condensed matter physics. At the same time of looking for materials with higher $T_c$s, the study of the mechanism of high $T_c$ superconductors attracts the attention of nearly the whole physics community. Although people have not reached a consensus until now, as a leading subject, the scope of the research field involved and the depth of the problems discussed in it are both rare in recent decades. It challenges the conventional condensed matter physics completely and promotes research greatly. It can be imagined and expected that the work in future will be difficult, and we will go on making efforts to explore. "Looking upon this unfinished scientific Tower of Babel" (P. W. Anderson).

In the dialogue between P. W. Anderson and R. Schrieffer in 1991 about the theory of cuprates (Physics Today, June 1991, P55), how to write the second volume of *solid state physics* was mentioned. They said like this: "Bednorz and Müller's 1986 discovery did mark the beginning of a remarkable period of development in condensed matter physics. Before that time, strongly correlated fermion systems were an interesting byway of the field, but most serious many-body theorists believed Fermi-liquid theory could cover the most interesting materials. We are now rewriting the condensed matter textbooks of the future by adding volume II, in which interactions must be included in zero order, on an equal footing with one-body kinetic effects ... but rather how to develop concepts and methods to handle such systems in general ... Just as BCS was the dawning of a new type of physics now extending over 13 orders of magnitude in temperature, so we are perhaps witnessing the beginning of a major advance in our understanding of systems most of which are yet to be discovered." The two physics masters pointed out that high-temperature superconductivity physics would play an extremely important role in the development of physics.

A paper about Hg system high-temperature superconductor [Nature **363**, 56 (1993)] was selected as one of the most important ten articles in the twentieth century by Nature magazine, and included in Physics Century Anthology, which shows the full affirmation to the importance of superconductivity research and its important role in physics in the last century. The $T_c = 133$ K (it can reach 160 K under high pressure) of $HgBa_2Cu_3O_{8+x}$ reported in this article still keeps the highest record in the family of cuprates. There are Chinese scientists among its authors.

This book attempts to collect the important contributions in superconductivity research made by Chinese scientists, and combine them into a book as centennial of superconductivity. Because Chinese scientists participate in many important stages and problems, I collect these twenty papers in an appreciated and respectful mood, most of which have been published and others are articles engaged by special arrangement. This book is the companion book of another two books: *Advances in Theoretical and Experimental Re-*

*search of High-Temperature Cuprate Superconductivity*, and *High-Temperature Superconducting Physics*, the Second Edition. (Peking University Press, forthcoming in 2012.) *Superconductivity Centennial* is from the perspective of looking back at the history over twenty years, and *Advances in Theoretical and Experimental Research of High-Temperature Cuprate Superconductivity* is from the perspective of more comprehensive physical properties, while *High-Temperature Superconducting Physics* focuses on the special properties of copper oxides high-temperature superconductors. These three books complement one another. Of course they are more complement to the *Superconductivity Century Anthology* pressed internationally, among which some of the articles have been accepted, but we focus more on the contributions of Chinese authors in *Superconductivity Centennial.*

The works involved in the collected twenty articles are all on important problems of high-temperature superconductivity and are attached great importance by our peers. For examples, the paper about Y system high-temperature superconductors with $T_c$ = 90 K by Wu Maokun and Zhu Jingwu's research group was the earliest report in the world of material with $T_c$ over liquid nitrogen temperature, the paper of Zhao Zhongxian and Chen Liquan's group reported this nearly at the same time; the research about Hg superconductivity in which Guo Jiandong participated still keeps the world record of superconducting transition temperature. The book also includes pairing symmetry research by Cui Zhangqi's group, NMR research by Zheng Guoqing's group, research of *d*-wave symmetry spectra by Ding Hong's group, measurement of the superconducting gap by Dai Pengcheng's group, the article about microscopic electrical heterogeneity by Pan Shuheng's group, the earliest research of ARPES by Shen Zhixun's group, the research of "Kinks" by Zhou Xingjiang's group. This book collects the important articles about iron-based superconductors too, such as the article by Chen Xianhui's group, the article which gives the highest superconducting transition temperature of iron-based superconductors by Zhao Zhongxian's group, the article about Zn doping in iron-based superconductors by Xu Zhuan's group, and the article about the spectra by Wang Nanlin's group. In order to fully introduce the physical properties of the condensed matter, this book collects the research about thermodynamic properties by Wen Haihu's group, the research about low temperature heat transport by Sun Xuefeng's group, and the research about Raman spectra by Zhang Qingming's group. In addition, there are three important theoretical papers separately given by Ding Qinsheng's group, Su Gang and Guo Wei. Ding Qinsheng's group made the computing research to the magnetism and superconductivity of 122 iron-based materials. Su Gang discussed the off-diagonal long-range order in condensed quantum phase and reviewed the superconductivity, superfluids and Bose-Einstein Condensation, especially the discussion on super states. After pointing out the magnetic origin of the superfluid, Guo Wei suggested that the fluctuations in spin of O caused by hole doping in $CuO_2$ plane could lead to a resonating-valence-bond (RVB) state with quantum number $S = 1$, $S_z = 0$ and cause the magnetic ordering via the local exchange interaction which is called Kramers super-exchange. And the complete phase diagram was given from ferromagnetic insulator to superconductor.

In the 21st century, there is still a lot of work to be done about the mechanism of high-temperature superconductivity, especially the research of spin pairing mechanism. The key experiments like the isotope effect in conventional superconductors are needed. I think that we should search them from the special properties of high-temperature superconductors. Therefore I collect the special and maybe the universal properties in this system and compile them into a book, supply it to the readers for analysis and consideration, and I hope it could push the further research forward. I also wish the readers to give criticisms, modifications and supplements for this book.

*Han Rushan*
Peking University
July 2012

# Contents

# 1

# Superconductivity at 93 K in a New Mixed-Phase Y-Ba-Cu-O Compound System at Ambient Pressure*

M. K. Wu[1], J. R. Ashburn[1], C. J. Torng[1], P. H. Hor[2], R. L. Meng[2], L. Gao[2], Z. J. Huang[2], Y. Q. Wang[2] and C. W. Chu[2,3]

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A stable and reproducible superconductivity transition between 80 and 93 K has been unambiguously observed both resistively and magnetically in a new Y-Ba-Cu-O compound system at ambient pressure. An estimated upper critical field $H_{c2}(0)$ between 80 and 180 T was obtained.

The search for high-temperature superconductivity and novel superconducting mechanisms is one of the most challenging tasks of condensed-matter physicists and material scientists. To obtain a superconducting state reaching beyond the technological and psychological temperature barrier of 77 K, the liquid-nitrogen boiling point, will be one of the greatest triumphs of scientific endeavor of this kind. According to our stud studies [1], we would like to point out the possible attainment of a superconducting state with an onset temperature higher than 100 K, at ambient pressure, in compound systems generically represented by $(L_{1-x}M_x)_a A_b D_y$. In this letter, detailed results are presented on a specific new chemical compound system with $L$ = Y, $M$ = Ba, $A$ = Cu, $D$ = O, $x$ = 0.4, $a$ = 2, $b$ = 1, and $y \leqslant 4$ with a stable superconducting transition between 80 and 93 K. For the first time, a "zero-resistance" state ($\rho < 3 \times 10^{-8}$ $\Omega$-cm, an upper limit only determined by the sensitivity of the apparatus) is achieved and maintained at ambient pressure in a simple liquid-nitrogen Dewar.

In spite of the great efforts of the past 75 years since the discovery of superconductivity, the superconducting transition temperature $T_c$ has remained until 1986 below 23.2 K, the $T_c$ of $Nb_3Ge$ first discovered [2] in 1973. In the face of this gross failure to raise the $T_c$, nonconventional approaches [3] taking advantage of possible strong nonconventional superconducting mechanisms [4] have been proposed and tried. In September 1986, the situation changed drastically when Bednorz and Müller [5] reported the possible existence of percolative superconductivity in $(La_{1-x}Ba_x)Cu_{3-\delta}$ with $x$ = 0.2 and 0.15 in the 30-K range. Subsequent magnetic studies [6–8] confirmed that high-temperature superconductivity indeed exists in this system. Takagi *et al.* further attributed the observed superconductivity in the La-Ba-Cu-O system to the $K_2NiF_4$ phase [9]. By the replacement of Ba with Sr [8,10,11], it is found that the La-Sr-Cu-O system of the $K_2NiF_4$ structure, in general, exhibits a higher $T_c$ and a sharper transition. A transition width [10] of 2 K and an onset [11] $T_c$ of 48.6 K were obtained at ambient pressure.

Pressure [8,12] was found to enhance the $T_c$ of the La-Ba-Cu-O system at a rate of greater than $10^{-3}$ K bar$^{-1}$ and to raise the onset $T_c$ to 57 K, with a "zero-resistance" state [13] reached at 40 K, the highest in any known superconductor until now. Pressure reduces the lattice parameter and enhances the $Cu^{+3}/Cu^{+2}$ ratio in the compounds. This unusually large pressure effect on $T_c$ has led to suggestions [8,12] that the high-temperature superconductivity in the La-Ba-Cu-O and La-Sr-Cu-O systems may be associated with interfacial effects arising from mixed phases; interfaces between the metal and insulator layers, or concentration fluctuations within the $K_2NiF_4$ phase; strong superconducting interactions due to the mixed valence states; or yet an unidentified phase. Furthermore, we found that when the superconducting transition width is reduced by making the compounds closer to the pure $K_2NiF_4$ phase, the onset $T_c$ is also reduced while the main transition near 37 K remains unchanged.

Extremely unstable phases displaying signals indicative of superconductivity in compounds consisting of phases in addition to or other than the $K_2NiF_4$ phase have been observed by us [8,14], up to 148 K, but only in four samples, and in China [15] at 70 K, in one sample. Therefore, we decided to investigate the multiple-phase Y-Ba-Cu-O compounds instead of the pure $K_2NiF_4$ phase, through simultaneous variation of the lattice parameters and mixed valence ratio of Cu ions by chemical means at ambient pressure.

The compounds investigated were prepared with nominal compositions represented by $(Y_{1-x}Ba_x)_2CuO_{4-\delta}$ with $x = 0.4$ through solid-state reaction of appropriate amounts of $Y_2O_3$, $BaCO_3$, and CuO in a fashion similar to that previously described [8]. Bar samples of dimensions $1 \times 0.5 \times 4\ mm^3$ were cut from the sintered cylinders. A four-lead technique was employed for the resistance ($R$) measurements and an ac inductance bridge for the magnetic susceptibility ($\chi$) determinations. The temperature was measured by means of Au+0.07% Fe-Chromel and Chromel-Alumel thermocouples in the absence of a magnetic field, and a carbon-glass thermometer in the presence of a field. The latter was calibrated against the former without a field. Magnetic fields up to 6 T were generated by a superconducting magnet.

The temperature dependence of $R$ determined in a simple liquid-nitrogen Dewar is shown in Fig. 1.1. $R$ initially drops almost linearly with temperature $T$. A deviation of $R$ from this $T$ dependence is evident at 93 K and a sharp drop starts at 92 K. A "zero-$R$" state is achieved at 80 K. The variation of $\chi$

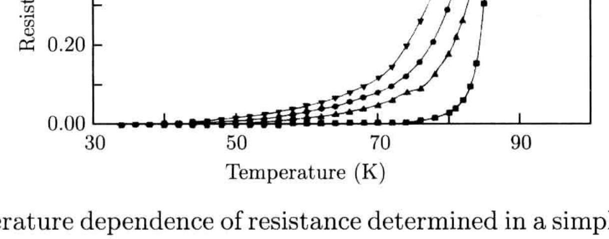


Fig. 1.1 Temperature dependence of resistance determined in a simple liquid-nitrogen Dewar.

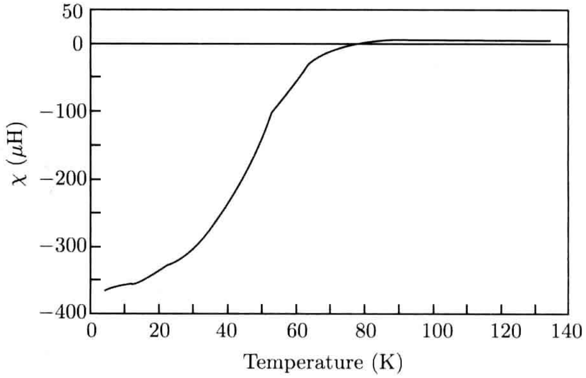


Fig. 1.2 Temperature dependence of magnetic susceptibility.

with $T$ is shown in Fig. 1.2. It is evident that a diamagnetic shift starts at 91 K and the size of the shift increases rapidly with further cooling. At 4.2 K, the diamagnetic signal corresponds to 24% of the superconducting signal of a Pb sample with similar dimensions. In a magnetic field, the $R$ drop is shifted toward lower $T$. At our maximum field of 5.7 T, the "zero-$R$" state remains at a $T$ as high as 40 K. Preliminary X-ray powder diffraction patterns show the existence of multiple phases uncharacteristic of the $K_2NiF_4$ structure in the samples. Detailed analyses and under way.

The above results demonstrate unambiguously that superconductivity occurs in the Y-Ba-Cu-O system with a transition between 80 and 93 K. We have determined the upper critical field $H_{c2}(T)$ resistively. If the positive curvature at very low fields is neglected, one gets a value of $dH_{c2}/dT$ near $T_c$ of 3 T/K or 1.3 T/K, depending on whether $H_{c2}(T_c)$ is taken at the 10% or the 50% drop from the normal-state $R$. In the weak-coupling limit, $H_{c2}(0)$ is thus estimated to be between 80 and 180 T in the Y-Ba-Cu-O system investigated. We believe that the value of $H_{c2}(0)$ can be further enhanced as the material is improved. The paramagnetic limiting field at 0 K for a sample with a $T_c \sim 90$ K is 165 T. Because of the porous and multiphase characteristics of the samples, it is therefore difficult to extract any reliable information about the density of states from the slope of $H_{c2}(T)$ at $T_c$ on the basis of the dirty-limit approximation.

On the basis of the existing data, it appears that the high-temperature superconductivity above 77 K reported here occurs only in compound systems consisting of a phase or phases in addition to or other than the $K_2NiF_4$ phase.

While it is tempting to attribute the superconductivity to possible nonconventional superconducting mechanisms as mentioned earlier, all present suggestions are considered to be tentative at best, especially in the absence of detailed structural information about the phases in the Y-Ba-Cu-O samples. However, we would like to point out here that the lattice parameters, the valence ratio, and the sample treatments all play a crucial role in achieving superconductivity above 77 K. The role of the different phases present in superconductivity is yet to be determined.

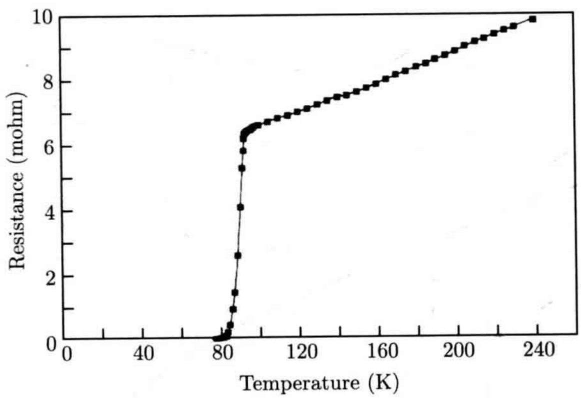


Fig. 1.3 Magnetic field effect on resistance.

The work at the University of Alabama at Huntsville is supported by NASA Grants No. NAG8-032 and No. NAGW-A12, and National Science Foundation Alabama EPSCoR Program Grant No. R11-8610669, and at the University of Houston by National Science Foundation Grant No. DMR 8616537, NASA Grants No. NAGW-977 and No. NAG8-051, and the Energy Laboratory of the University of Houston. Technical assistance from D. Campbell, A. Testa, and J. Bechtold is greatly appreciated.

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[3] See, for example, C. W. Chu and M. K. Wu, in *High Pressure in Science and Technology*, edited by C. Homan, R. K. MacCrone and E. Whalley (North-Holland, New York, 1983), Vol. 1, p. 3; C. W. Chu, T. H. Lin, M. K. Wu,