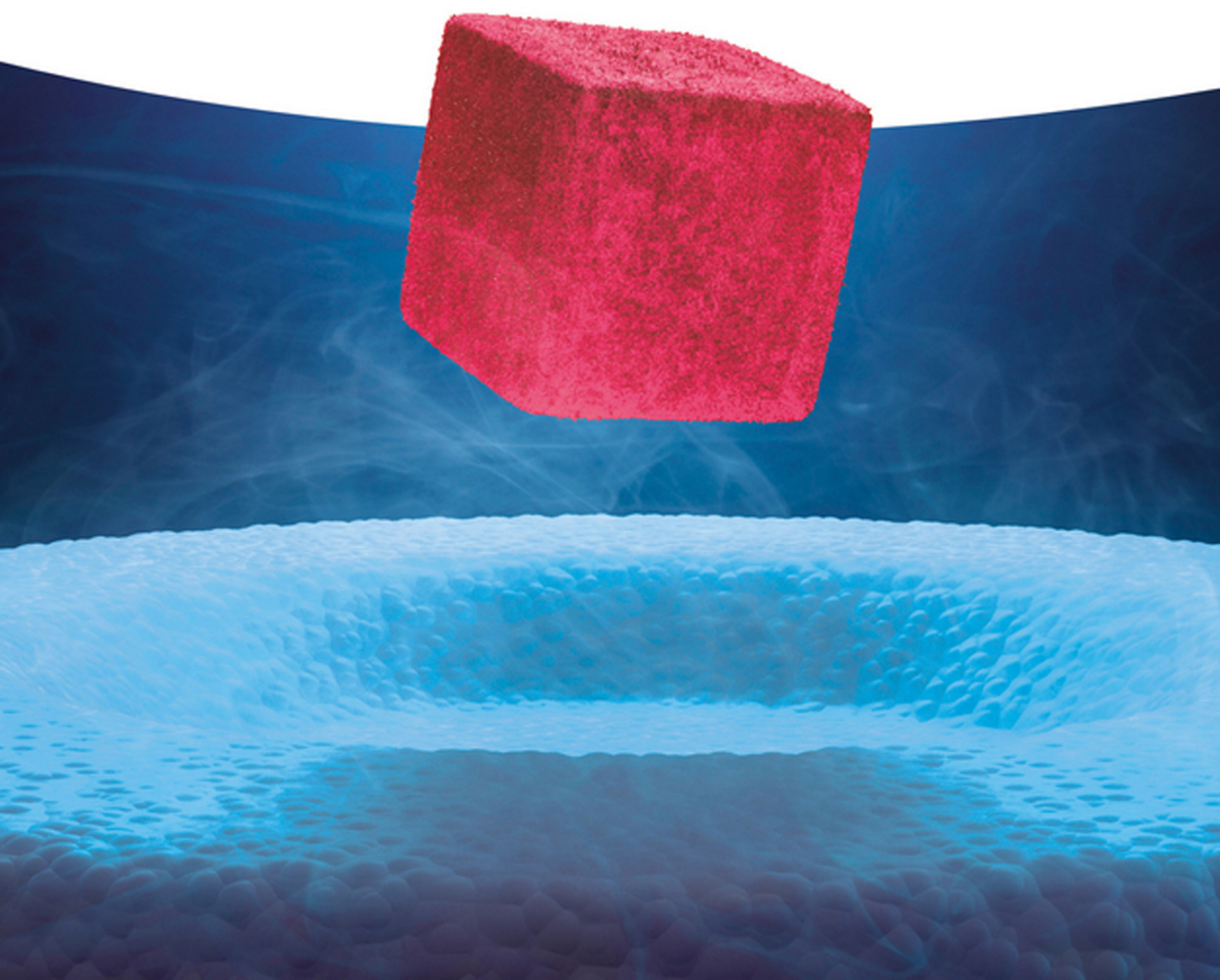


Reinhold Kleiner and Werner Buckel

Superconductivity

An Introduction

Third Edition



Reinhold Kleiner
Werner Buckel

Superconductivity

Related Titles

Bhattacharya, R., Paranthaman, M. (eds.)

High Temperature Superconductors

2010

Print ISBN: 978-3-527-40827-6, also available
in electronic formats

Buzdin, A.I., Ryazanov, V.V.

Superconductor-Ferromagnet Hybrid Structures

2015

Print ISBN: 978-3-527-41033-0, also available
in electronic formats

Bezryadin, A.

Superconductivity in Nanowires

Fabrication and Quantum Transport

2012

Print ISBN: 978-3-527-40832-0, also available
in electronic formats

Hofmann, P.

Solid State Physics

An Introduction, 2nd Edition

2015

Print ISBN: 978-3-527-41282-2, also available
in electronic formats

Altomare, F., Chang, A.M.

One-Dimensional Superconductivity in Nanowires

2013

Print ISBN: 978-3-527-40995-2, also available
in electronic formats

Reinhold Kleiner and Werner Buckel

Superconductivity

An Introduction

Third, Updated Edition

WILEY-VCH
Verlag GmbH & Co. KGaA

The Authors

Professor Dr. Werner Buckel deceased
Technische Universität Karlsruhe
Kösliner Str. 87
76139 Karlsruhe
Germany

Professor Dr. Reinhold Kleiner
Physikalisches Institut
Auf der Morgenstelle 14
72076 Tübingen
Germany

Translator

Professor Dr. Rudolf Hübener
Physikalisches Institut
Auf der Morgenstelle 14
72076 Tübingen
Germany

Translation of the 7th German edition

Cover

Photo courtesy: © Kiyoshi Takahase
Segundo/Stockami

All books published by **Wiley-VCH** are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at
<<http://dnb.d-nb.de>>.

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Print ISBN: 978-3-527-41162-7
ePDF ISBN: 978-3-527-68652-0
ePub ISBN: 978-3-527-68654-4
Mobi ISBN: 978-3-527-68653-7
oBook ISBN: 978-3-527-68651-3

Cover Design Schulz Grafik-Design,
Fußgönheim, Germany
Typesetting SPi Global, Chennai, India
Printing and Binding Markono Print
Media Pte Ltd., Singapore

Printed on acid-free paper

Contents

Preface to the Third Edition *IX*

Introduction *1*

References *9*

1	Fundamental Properties of Superconductors	<i>11</i>
1.1	The Vanishing of the Electrical Resistance	<i>11</i>
1.2	Ideal Diamagnetism, Flux Lines, and Flux Quantization	<i>21</i>
1.3	Flux Quantization in a Superconducting Ring	<i>30</i>
1.4	Superconductivity: A Macroscopic Quantum Phenomenon	<i>33</i>
1.5	Quantum Interference	<i>45</i>
1.5.1	Josephson Currents	<i>47</i>
1.5.2	Quantum Interference in a Magnetic Field	<i>59</i>
	References	<i>71</i>
2	Superconducting Elements, Alloys, and Compounds	<i>75</i>
2.1	Introductory Remarks	<i>75</i>
2.1.1	Discovery, Preparation, and Characterization of New Superconductors	<i>75</i>
2.1.2	Conventional and Unconventional Superconductors	<i>76</i>
2.2	Superconducting Elements	<i>78</i>
2.3	Superconducting Alloys and Metallic Compounds	<i>83</i>
2.3.1	The β -Tungsten Structure	<i>84</i>
2.3.2	Magnesium Diboride	<i>86</i>
2.3.3	Metal–Hydrogen Systems	<i>87</i>
2.4	Fullerides	<i>88</i>
2.5	Chevrel Phases and Boron Carbides	<i>89</i>
2.6	Heavy-Fermion Superconductors	<i>92</i>
2.7	Natural and Artificial Layered Superconductors	<i>94</i>
2.8	The Superconducting Oxides	<i>96</i>
2.8.1	Cuprates	<i>96</i>
2.8.2	Bismuthates, Ruthenates, and Other Oxide Superconductors	<i>103</i>
2.9	Iron Pnictides and Related Compounds	<i>104</i>

2.10	Organic Superconductors	107
2.11	Superconductivity at Interfaces	110
	References	111
3	Cooper Pairing	117
3.1	Conventional Superconductivity	117
3.1.1	Cooper Pairing by Means of Electron–Phonon Interaction	117
3.1.2	The Superconducting State, Quasiparticles, and BCS Theory	124
3.1.3	Experimental Confirmation of Fundamental Concepts about the Superconducting State	129
3.1.3.1	The Isotope Effect	130
3.1.3.2	The Energy Gap	133
3.1.4	Special Properties of Conventional Superconductors	150
3.1.4.1	Influence of Lattice Defects on Conventional Cooper Pairing	150
3.1.4.2	Influence of Paramagnetic Ions on Conventional Cooper Pairing	157
3.2	Unconventional Superconductivity	163
3.2.1	General Aspects	163
3.2.2	Cuprate Superconductors	170
3.2.3	Heavy Fermions, Ruthenates, and Other Unconventional Superconductors	186
3.2.4	FFLO-State and Multiband Superconductivity	193
	References	196
4	Thermodynamics and Thermal Properties of the Superconducting State	201
4.1	General Aspects of Thermodynamics	201
4.2	Specific Heat	205
4.3	Thermal Conductivity	209
4.4	Ginzburg–Landau Theory	212
4.5	Characteristic Lengths of the Ginzburg–Landau Theory	216
4.6	Type-I Superconductors in a Magnetic Field	221
4.6.1	Critical Field and Magnetization of Rod-Shaped Samples	221
4.6.2	Thermodynamics of the Meissner State	226
4.6.3	Critical Magnetic Field of Thin Films in a Field Parallel to the Surface	230
4.6.4	The Intermediate State	231
4.6.5	The Wall Energy	235
4.6.6	Influence of Pressure on the Superconducting State	239
4.7	Type-II Superconductors in a Magnetic Field	244
4.7.1	Magnetization Curve and Critical Fields	246
4.7.2	The Shubnikov Phase	256
4.8	Fluctuations above the Transition Temperature	268
4.9	States Outside Thermodynamic Equilibrium	272
	References	277

5	Critical Currents in Type-I and Type-II Superconductors	283
5.1	Limit of the Supercurrent Due to Pair Breaking	283
5.2	Type-I Superconductors	285
5.3	Type-II Superconductors	291
5.3.1	Ideal Type-II Superconductor	291
5.3.2	Hard Superconductors	296
5.3.2.1	Pinning of Flux Lines	296
5.3.2.2	Magnetization Curve of Hard Superconductors	301
5.3.2.3	Critical Currents and Current–Voltage Characteristics	310
	References	318
6	Josephson Junctions and Their Properties	321
6.1	Current Transport across Interfaces in a Superconductor	321
6.1.1	Superconductor–Insulator Interface	321
6.1.2	Superconductor–Normal Conductor Interfaces	328
6.1.3	Superconductor–Ferromagnet Interfaces	335
6.2	The RCSJ Model	337
6.3	Josephson Junctions under Microwave Irradiation	342
6.4	Vortices in Long Josephson Junctions	346
6.5	Quantum Properties of Superconducting Tunnel Junctions	357
6.5.1	Coulomb Blockade and Single-Electron Tunneling	358
6.5.2	Flux Quanta and Macroscopic Quantum Coherence	363
	References	368
7	Applications of Superconductivity	373
7.1	Superconducting Magnetic Coils	374
7.1.1	General Aspects	374
7.1.2	Superconducting Cables and Tapes	375
7.1.3	Coil Protection	386
7.2	Superconducting Permanent Magnets	388
7.3	Applications of Superconducting Magnets	390
7.3.1	Nuclear Magnetic Resonance	390
7.3.2	Magnetic Resonance Imaging	394
7.3.3	Particle Accelerators	395
7.3.4	Nuclear Fusion	397
7.3.5	Energy Storage Devices	398
7.3.6	Motors and Generators	401
7.3.7	Magnetic Separation and Induction Heaters	404
7.3.8	Levitated Trains	405
7.4	Superconductors for Power Transmission: Cables, Transformers, and Current Fault Limiters	406
7.4.1	Superconducting Cables	407
7.4.2	Transformers	409
7.4.3	Current Fault Limiters	411
7.5	Superconducting Resonators and Filters	412

7.5.1	High-Frequency Behavior of Superconductors	413
7.5.2	Resonators for Particle Accelerators	417
7.5.3	Resonators and Filters for Communications Technology	420
7.6	Superconducting Detectors	425
7.6.1	Sensitivity, Thermal Noise, and Environmental Noise	426
7.6.2	Incoherent Radiation and Particle Detection: Bolometers and Calorimeters	427
7.6.3	Coherent Detection and Generation of Radiation: Mixers, Local Oscillators, and Integrated Receivers	431
7.6.4	Quantum Interferometers as Magnetic Field Sensors	440
7.6.4.1	SQUID Magnetometer: Basic Concepts	440
7.6.4.2	Environmental Noise, Gradiometers, and Shielding	450
7.6.4.3	Applications of SQUIDS	454
7.7	Superconductors in Microelectronics	459
7.7.1	Voltage Standards	460
7.7.2	Digital Electronics Based on Josephson Junctions	463
	References	468
	Monographs and Article Collections	477
	History of Superconductivity	477
	General Books	477
	Special Materials	477
	Tunnel Junctions, Josephson Junctions, and Vortices	477
	Nonequilibrium Superconductivity	478
	Applications of Superconductivity	478
	General Overview	478
	Magnets, Cables, Power Applications	478
	Microwaves, Magnetic Field Sensors, Electronics	478
	Low Temperature Physics and Technology	478
	Index	479

Preface to the Third Edition

Because 8 years have passed since the last edition of this book, it was time to revise the text and to cover new developments. With the iron-pnictides a new class of superconductors has been found. Among the physicists, this discovery generated almost the same excitement as the discovery of the cuprate superconductors in the 1980s. Furthermore, there were many interesting applications, say, in the area of superconducting cables or magnets, or with the qubits in the area of microelectronics. In order to keep the size of this book within reasonable limits, by far not all results could be included. For this I apologize.

As in the previous editions, the guiding principle, followed by Werner Buckel, remained to explain superconductivity as simple as possible. Also the nonexperts should be able to gain insight into this exciting field at its age of 100 years by now.

I am thanking all colleagues who have contributed to the new edition by means of ideas and suggestions, in particular Vera Palmer, Ulrike Werner, as well as Harald Reiss, Paul Seidel, and Peter Kes. Particularly I want to thank Rudolf Huebener for his excellent translation of the 7th German edition. I thank Klaus Schlenga, Bruker EST, for helping with the text of Section 7.3.1. For allowing to reproduce unpublished figures I thank Mrs. van Bühl, Nexans, Cheri Hart, AMSC, as well as Joachim Albrecht, Hochschule Aalen, Alexander Henning, Bruker ASC, Tom H. Johansen, Superconductivity Laboratory of Oslo University, Hans Henning Klauss, TU Dresden, Hubertus Lütken, Paul Scherrer Institut, S. Mahieu, IRAM, Xiaofeng Qian, MIT, Daniel Schmickler, Zenergy GmbH, and Convertteam UK Ltd, Wolfgang Schmidt, Siemens AG, Michael Strasik, Boeing, and CERN.

Tübingen
July 2015

Reinhold Kleiner

Introduction

In physics, many phenomena result from the activity of specific mutual interactions. An important example is the relation between the uncorrelated thermal motion of the atomic building blocks of matter and the ordering forces between these building blocks. With increasing temperature, the thermal motional energy eventually becomes sufficiently large compared to some relevant ordering interaction energy that the ordered state of matter, established at low temperatures, breaks down. All phase transitions, say, from the liquid to the gaseous state, as well as the construction of the atoms themselves from the elementary constituents of matter, follow this rule. Therefore, it is not surprising that often unexpected new properties of matter, which subsequently also may become important for technology, are discovered in experiments performed under extreme conditions. Superconductivity is an example of such a discovery.

In the year 1908, Kamerlingh-Onnes [1],¹⁾ Director of the Low-Temperature Laboratory at the University of Leiden, finally achieved the liquefaction of helium as the last of the noble gases. He had founded this laboratory, which became world-famous under his leadership. At atmospheric pressure the boiling point of helium is 4.2 K. It can be reduced further by pumping. The liquefaction of helium extended the available temperature range near to the absolute zero point. The first successful experiment still needed the total combined manpower of the Institute. However, earlier Kamerlingh-Onnes was able to perform extended experiments at these low temperatures. At first, he started an investigation of the electrical resistance of metals.

At that time, ideas about the mechanism of electrical conduction were only poorly developed. It was known that it must be electrons affecting the charge transport. Also the temperature dependence of the electrical resistance of many metals had been measured, and it had been found that near room temperature the resistance decreases linearly with decreasing temperature. However, at low temperatures, this decrease was found to become weaker and weaker. In principle, there were three possibilities to be discussed:

1) A biography can be found in *Spektrum der Wissenschaft*, May 1997, pp. 84–89 (German edition of *Scientific American*).

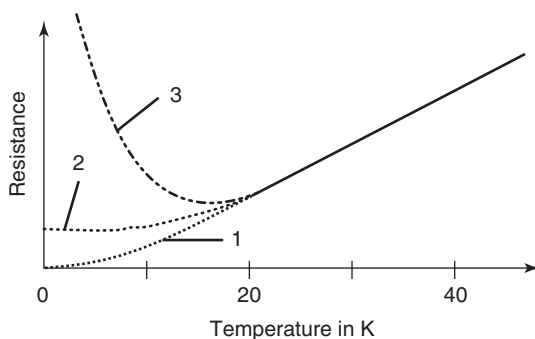


Figure 1 Schematics of the temperature dependence of electrical resistance at low temperatures. See text for details of curves.

- 1) The resistance could approach zero value with decreasing temperature (James Dewar, 1904; Figure 1, curve 1).
- 2) It could approach a finite limiting value (Heinrich Friedrich Ludwig Matthiessen, 1864; Figure 1, curve 2).
- 3) It could pass through a minimum and approach infinity at very low temperatures (William Thomson = Lord Kelvin, 1902; Figure 1, curve 3).

In particular, the third possibility was favored by the idea that at sufficiently low temperatures, the electrons are likely to be bound to their respective atoms. Hence, their free mobility was expected to vanish. The first possibility, according to which the resistance would approach zero at very low temperatures, was suggested by the strong decrease with decreasing temperature.

Initially, Kamerlingh-Onnes studied platinum and gold samples, since at that time he could obtain these metals with high purity. He found that during the approach to zero temperature, the electrical resistance of his samples reached a finite limiting value, the so-called residual resistance, a behavior corresponding to the second possibility discussed earlier. The value of this residual resistance depended on the purity of the samples. The purer the samples, the smaller was the residual resistance. After these results, Kamerlingh-Onnes expected that in the temperature range of liquid helium ideally pure platinum or gold should have a vanishingly small resistance. In a lecture at the Third International Congress of Refrigeration in Chicago in 1913, he reported on these experiments and arguments. There he said [2]: “Allowing a correction for the additive resistance I came to the conclusion that probably the resistance of absolutely pure platinum would have vanished at the boiling point of helium.” These ideas were supported further by the quantum physics rapidly developing at that time. Albert Einstein had proposed a model of crystals, according to which the vibrational energy of the crystal atoms should decrease exponentially at very low temperatures. Since the resistance of highly pure samples, according to the view of Kamerlingh-Onnes (which turned out to be perfectly correct, as we know today), is only due to this motion of the atoms, his hypothesis mentioned above appeared obvious.

In order to test these ideas, Kamerlingh-Onnes decided to study mercury, the only metal at the time that he hoped could be extremely well purified by means of multiple distillation. He estimated that at the boiling point of helium he could barely just detect the resistance of mercury with his equipment, and that at still lower temperatures it should rapidly approach a zero value.

The initial experiments carried out by Kamerlingh-Onnes, together with his coworkers Gerrit Flim, Gilles Holst, and Gerrit Dorsman, appeared to confirm these concepts. At temperatures below 4.2 K the resistance of mercury, indeed, became immeasurably small. In his lecture of 1913, Kamerlingh-Onnes summarized this phase of his experiments and ideas as follows: “With this beautiful prospect before me there was no more question of reckoning with difficulties. They were overcome and the result of the experiment was as convincing as could be.”

However, during his further experiments using improved apparatus, he soon recognized that the observed effect could not be identical to the expected decrease in resistance. The resistance change took place within a temperature interval of only a few hundredths of a degree and, hence, it resembled more of a resistance jump than a continuous decrease.

Figure 2 shows the curve published by Kamerlingh-Onnes [3]. As he himself commented [2]: “At this point (slightly below 4.2 K) within some hundredths of a degree came a sudden fall not foreseen by the vibrator theory of resistance, bringing the resistance at once to less than a millionth of its original value at the melting

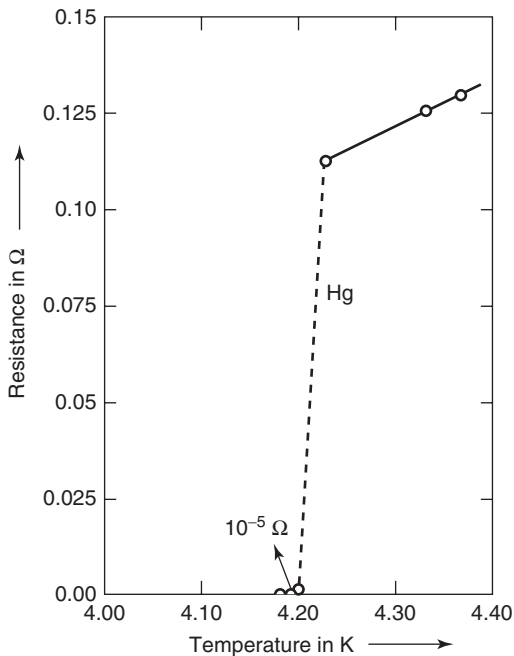


Figure 2 The superconductivity of mercury. (After Ref. [3].)

point. ... Mercury had passed into a new state, which on account of its extraordinary electrical properties may be called the superconductive state.”

In this way, also the name for this new phenomenon had been found. The discovery came unexpectedly during experiments that were meant to test some well-founded ideas. Soon it became clear that the purity of the samples was unimportant for the vanishing of the resistance. The carefully performed experiment had uncovered a new state of matter.

Today we know that superconductivity represents a widespread phenomenon. In the Periodic Table of the elements, superconductivity occurs in many metals. Here, at atmospheric pressure, niobium is the element with the highest transition temperature of about 9 K. Thousands of superconducting compounds have been found, and this development is by no means closed.

The scientific importance of the discovery of superconductivity can be seen from the fact that in 1913 Kamerlingh-Onnes was awarded the Nobel Prize in physics. At that time, hardly anybody could have foreseen the richness in fundamental questions and interesting concepts resulting from this observation, and it took nearly half a century until superconductivity was understood at least in principle.²⁾

The vanishing of the electrical resistance below a “critical temperature” or “transition temperature” T_c is not the only unusual property of superconductors. An externally applied magnetic field can be expelled from the interior of superconductors except for a thin outer layer (“ideal diamagnetism” or “Meissner–Ochsenfeld effect”), or superconductors can concentrate the magnetic field in the form of “flux tubes.” Here, the magnetic flux is quantized³⁾ in units of the “magnetic flux quantum,” $\Phi_0 = 2.07 \times 10^{-15}$ Wb. The ideal diamagnetism of superconductors was discovered by Walther Meissner and Robert Ochsenfeld in 1933. It was a big surprise, since based on the induction law one would only have expected that an ideal conductor conserves its interior magnetic field and does not expel it.

The breakthrough in the theoretical understanding of superconductivity was achieved in 1957 by the theory of John Bardeen, Leon Neil Cooper, and John Robert Schrieffer (“BCS theory”) [4]. In 1972, they were awarded the Nobel Prize in physics for their theory. They recognized that at the transition to the superconducting state the electrons condense pairwise into a new state, in which they form a coherent matter wave with a well-defined phase, following the rules of quantum mechanics. Here the interaction of the electrons is mediated by the “phonons,” the quantized vibrations of the crystal lattice.

2) For a summary of the history of superconductivity, we refer to monograph [M1].

3) The magnetic flux Φ through a loop of area F carrying a perpendicular and spatially homogeneous flux density B is given by $\Phi = BF$. In the following, we denote B simply by “magnetic field.” In the general case of an arbitrarily oriented and spatially inhomogeneous magnetic field \mathbf{B} one must integrate over the area of the loop,

$\Phi = \int_F \mathbf{B} d\mathbf{f}$. The unit of magnetic flux is the weber (Wb), and the unit of magnetic field is the tesla (T). Frequently, the unit gauss (G) is used also ($1 \text{ G} = 10^{-4} \text{ T}$). We have $1 \text{ Wb} = 1 \text{ T m}^2$. If a loop is placed at a large distance around the axis of an isolated flux tube, we have $\Phi = \Phi_0$.

The formation of a coherent matter wave, often referred to as a “macroscopic wave function,” represents the key property of the superconducting state. We know similar phenomena from other branches of physics. The laser is based on a coherent wave represented by photons. In the phenomenon of superfluidity below the so-called lambda point, the helium atoms condense into a coherent matter wave [5, 6]. For the isotope ^4He the lambda point is 2.17 K, and for ^3He it is about 3 mK. Under the proper conditions, these superfluids can flow without any friction. Furthermore, recently the condensation of gases of alkali atoms such as rubidium or potassium into a coherent quantum state has also been achieved. This “Bose–Einstein condensation” was predicted by Bose and Einstein in 1925. Only in 1995 could such condensates consisting of a few thousand atoms be prepared by means of special optical and magnetic refrigeration techniques at temperatures below 1 μK [7]. Also the discoveries of the laser, of superfluidity, and of the Bose–Einstein condensation were honored by the awards of Nobel Prizes.⁴⁾

For more than 75 years, superconductivity represented specifically a low-temperature phenomenon. This changed in 1986, when J. G. Bednorz and K. A. Müller discovered superconductors based on copper oxide. For their discovery, the two scientists were awarded the Nobel Prize in physics in 1987 [8]. In the September 1986 issue of the journal *Zeitschrift für Physik B*, Bednorz and Müller published a paper with the cautionary title “Possible high T_c superconductivity in the Ba–La–CuO system” [9]. In this paper the authors reported that this material loses its resistance at about 30 K. Surprisingly, the paper received only little attention. There were doubts that superconductivity was really observed. The samples consisted of mixtures of several phases among which there were also electrically insulating substances. Therefore, they had large values of the specific electrical resistance. It could well be possible that some phase transition within the texture caused the drop in resistance.⁵⁾ Hence, a convincing proof of superconductivity in these samples was still needed.

This proof was achieved by Bednorz, *et al.* [11] by demonstrating the existence of the Meissner–Ochsenfeld effect. Figure 3 shows the key measurement of this paper. Above 40 K both samples displayed the well-known paramagnetism of metals, which is nearly independent of temperature. Around 30 K, that is, in the same temperature range where the drop in resistance appears, during cooling in a magnetic field, an increasing diamagnetism due to the Meissner–Ochsenfeld effect can be seen, and the magnetic susceptibility turns negative.

This result was highly surprising for the scientific community, because already in the mid-1960s Bernd Matthias and his coworkers had started a systematic study of the metallic oxides (see [12]). They searched among the substances based on the

4) To Landau in 1962 (^4He); to Townes, Basov, and Prokhorov in 1964 (laser); to Lee, Osheroff, and Richardson in 1996 (^3He); and to Cornell, Wieman, and Ketterle in 2001 (Bose–Einstein condensation).

5) In the mid-1940s during cooling below about 70 K, sharp drops of the resistance in metallic sodium ammonia solutions were observed, which initially were interpreted in terms of superconductivity. However, in fact, they were due to sodium threads precipitating from the solution [10].

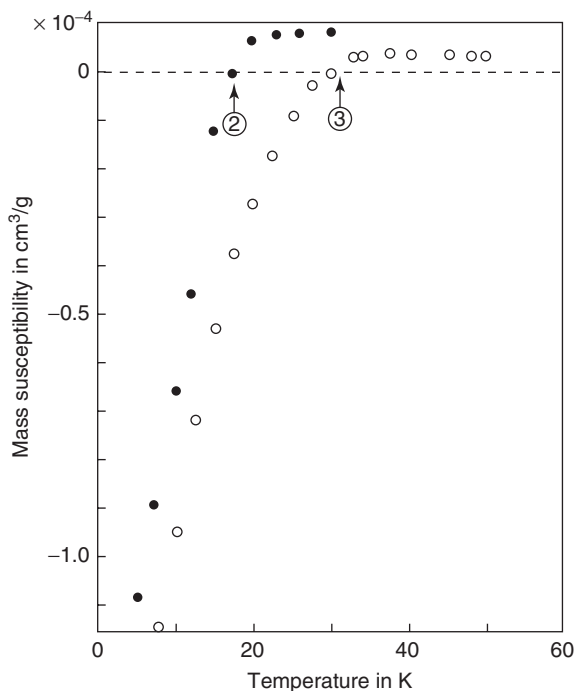


Figure 3 The magnetic susceptibility of two samples of the Ba–La–Cu–O system versus temperature [11].

transition metal oxides, such as W, Ti, Mo, and Bi. They found extremely interesting superconductors, for example, in the Ba–Pb–Bi–O system; however, no particularly high transition temperatures were found.

During the turn of 1986/1987 the “gold rush” set in, when it became known that the group of S. Tanaka in Japan could exactly reproduce the results of Bednorz and Müller. Now scientists in countless laboratories all over the world began to study these new oxides. Soon this extraordinary scientific effort yielded successful results. One could show that within the La–Sr–Cu–O system, superconductors with transition temperatures above 40 K could be produced [13]. Only a few weeks later, transition temperatures above 80 K were observed in the Y–Ba–Cu–O system [14, 15]. During this phase, new results were more often reported in press conferences than in scientific journals. The media anxiously followed this development. With superconductivity at temperatures above the boiling point of liquid nitrogen ($T = 77$ K), one could envision many important technical applications of this phenomenon.

Today we are familiar with a large series of “high-temperature superconductors” based on copper oxide. Here the most studied compounds are $\text{YBa}_2\text{Cu}_3\text{O}_7$ (also “YBCO” or “Y123”) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (also “BSCCO” or “Bi2212”), which display maximum transition temperatures around 90 K. Many compounds

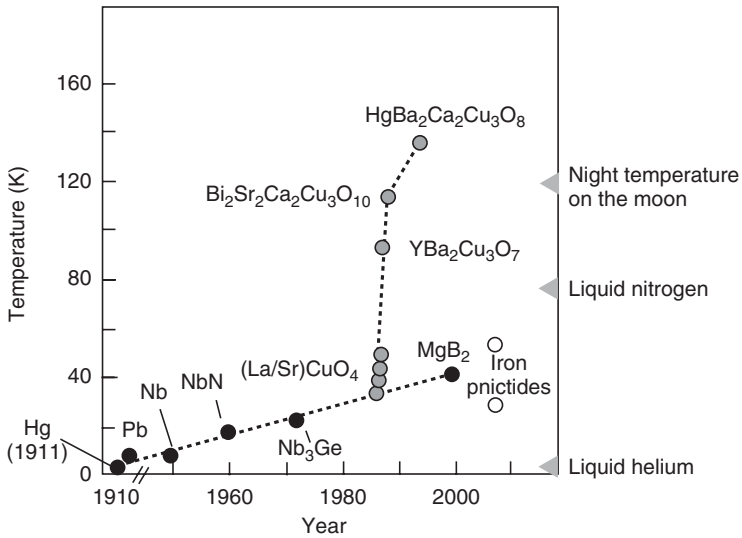


Figure 4 Evolution of the superconducting transition temperature since the discovery of superconductivity. (After Ref. [16].)

have transition temperatures even above 100 K. The record value is claimed by $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$, having a T_c value of 135 K at atmospheric pressure and a value as high as $T_c = 164$ K at a pressure of 30 GPa. Figure 4 shows the evolution of transition temperatures since the discovery by Kamerlingh-Onnes. The jump-like increase due to the discovery of the copper oxides is particularly impressive.

In this figure, we have included the metallic compound MgB_2 , as well as the group of the iron pnictides. It is surprising that in the case of MgB_2 superconductivity with a transition temperature of 39 K was discovered only in the beginning of 2000, although this material has been commercially available for a long time [17]. This discovery also generated much activity in the physics community, and in the two following years important properties of this material were clarified. MgB_2 shows similar behavior as the “classical” metallic superconductors. The excitement at the discovery of the iron pnictides in 2008 was also large [18]. These are compounds in the form $\text{LaFeAsO}_{0.89}\text{F}_{0.11}$ or $\text{Ba}_{0.6}\text{KFe}_2\text{As}_2$, showing transition temperatures up to 55 K. In the case of these materials, layers of iron–arsenic represent the central building block, analogous to the copper-oxide planes in the case of the cuprates.

Many properties of the cuprates, and also of other superconducting compounds, are very unusual, as we will see during the course of this book. More than 25 years after their discovery, it is still unclear how Cooper pairing is accomplished in these materials. However, magnetic interactions are likely to play an important role. Perhaps we can learn more from a comparison with the iron pnictides.

Another important aspect concerns the maximum electric current, the “critical current,” which a superconductor can carry without electrical resistance. We will see that the property “zero resistance” is not always valid. In the case of AC, the resistance remains finite and increases with increasing frequency of the alternating current. However, the critical current is limited also in the case of DC. It depends on the temperature and the magnetic field, and also on the material and the geometry of the conductor. Even today, it is still a special art to develop a conductor that hundreds of amperes can flow without resistance.

Due to the discovery of the high-temperature superconductors, the phenomenon of superconductivity is not restricted anymore to a temperature range far away from that relevant for all organic life. One hopes that one day materials are found showing this phenomenon at room temperature or even above it.

On the other hand, low temperatures become more and more accessible for day-to-day utilization. Refrigerators and cold boxes are regular household items. Just recently, large advances have been achieved in refrigeration techniques. Modern cryo-coolers today reliably reach temperatures of 30 K, or in some cases even 4.2 K and lower [19].⁶⁾ Also cooling with liquid nitrogen is a standard procedure in many branches of industry. Hence, superconductivity will enter our daily lives more and more in the fields of energy technology or microelectronics, for example.

By using liquid helium as a cooling liquid, for sometime one uses metallic superconductors in medical applications, say, for the generation of high magnetic fields in nuclear-spin tomographs or in magnetic-field sensoric. Also voltage standards are based on superconducting devices. In the case of these applications, the compounds NbTi, Nb₃Sn, and the elementary superconductor Nb are particularly important. Also the high-temperature superconductors are more and more utilized. In the field of energy technology, the first superconducting cables are operating. Superconducting motors, say, for the driving of ships are being fabricated. Superconducting filters made of YBa₂Cu₃O₇ are applied in communication technology. Magnetic-field sensors made of this material are utilized in the field for the detection of minerals or for nondestructive testing of materials. High-temperature superconductors can levitate above magnets or can hang even under the magnets. This provides the possibility of a contact-free and nearly frictionless mounting and motion, which is attractive in the case of many areas of technology.

This book is meant to provide an initial exposure to the phenomenon of superconductivity. Only selected aspects could be dealt with. Some subjects have had to be summarized only briefly in order to keep the size of the book within reasonable limits. However, it is hoped that the book transmits some of the fascination that superconductivity has offered now for nearly a century.

6) In the laboratory, by means of various refrigeration methods, temperatures down to only a few millikelvins can be sustained continuously. Based on nuclear spin demagnetization, final temperatures in the microkelvins range and below are reached. For a summary, see the monographs [M32] and [M33].

References

1. H. Kamerlingh-Onnes: *Proc. Roy. Acad. Amsterdam* **11**, 168 (1908).
2. H. Kamerlingh-Onnes: *Comm. Leiden*, Suppl. No. **34** (1913).
3. H. Kamerlingh-Onnes: *Comm. Leiden* **120b** (1911).
4. J. Bardeen, L. N. Cooper, J. R. Schrieffer: *Phys. Rev.* **108**, 1175 (1957).
5. D. R. Tilley, J. Tilley: "Superfluidity and Superconductivity", Van Nostrand Reinhold Company, New York (1974).
6. D. M. Lee: *Rev. Mod. Phys.* **69**, 645 (1997); D. D. Osheroff, *Rev. Mod. Phys.* **69**, 667 (1997); R. C. Richardson: *Rev. Mod. Phys.* **69**, 683 (1997).
7. E. A. Cornell, C. E. Wieman: *Rev. Mod. Phys.* **74**, 875 (2002); W. Ketterle: *Rev. Mod. Phys.* **74**, 1131 (2002).
8. J. Bednorz, K. A. Müller, *Rev. Mod. Phys.* **60**, 585 (1988).
9. J. G. Bednorz, K. A. Müller: *Z. Phys. B* **64**, 189 (1986).
10. R. A. Ogg Jr., *Phys. Rev.* **69**, 243 and 668 (1946); **70**, 93 (1946).
11. J. G. Bednorz, M. Takashige, K. A. Müller: *Europhys. Lett.* **3**, 379 (1987).
12. Ch. J. Raub: *J. Less-Common Met.* **137**, 287 (1988).
13. R. J. Cava, R. B. van Dover, B. Batlogg, E. A. Rietmann: *Phys. Rev. Lett.* **58**, 408 (1987); C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang: *Phys. Rev. Lett.* **58**, 405 (1987).
14. M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. O. Wang, C. W. Chu: *Phys. Rev. Lett.* **58**, 908 (1987).
15. Z. X. Zhao: *Int. J. Mod. Phys. B* **1**, 179 (1987).
16. Kirtley, J.R. and Tsuei, C.C. (1996) *Spektrum der Wissenschaft*, p. 58 (German edition of Scientific American).
17. J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu: *Nature* **410**, 63 (2001).
18. H. Takahashi, K. Igawa, K. Arii, Y. Kamihara, M. Hirano, H. Hosono: *Nature* **453**, 376 (2008).
19. C. Heiden: In monograph [M26], S. 289; C. Lienert, G. Thummes, C. Heiden: *IEEE Trans. Appl. Supercond.* **11**, 832 (2002).

1

Fundamental Properties of Superconductors

The vanishing of the electrical resistance, the observation of ideal diamagnetism, or the appearance of quantized magnetic flux lines represent characteristic properties of superconductors that we will discuss in detail in this chapter. We will see that all of these properties can be understood, if we associate the superconducting state with a macroscopic coherent matter wave. In this chapter, we will also learn about experiments convincingly demonstrating this wave property. First we turn to the feature providing the name “superconductivity.”

1.1

The Vanishing of the Electrical Resistance

The initial observation of the superconductivity of mercury raised a fundamental question about the magnitude of the decrease in resistance on entering the superconducting state. Is it correct to talk about the *vanishing* of the electrical resistance?

During the first investigations of superconductivity, a standard method for measuring electrical resistance was used. The electrical voltage across a sample carrying an electric current was measured. Here, one could only determine that the resistance dropped by more than a factor of a thousand when the superconducting state was entered. One could only talk about the vanishing of the resistance in that the resistance fell below the sensitivity limit of the equipment and, hence, could no longer be detected. Here, we must realize that in principle it is impossible to prove experimentally that the resistance has exactly zero value. Instead, experimentally, we can only find an upper limit of the resistance of a superconductor.

Of course, to understand such a phenomenon, it is highly important to test with the most sensitive methods to see whether a finite residual resistance can also be found in the superconducting state. So we are dealing with the problem of measuring extremely small values of the resistance. Already in 1914 Kamerlingh-Onnes used by far the best technique for this purpose. He detected the decay of an electric current flowing in a closed superconducting ring. If an electrical resistance exists, the stored energy of such a current is transformed gradually into joule heat. Hence, we need to only monitor such a current. If it decays as a function of time, we can be certain that a resistance still exists. If such a decay is observed, one can deduce

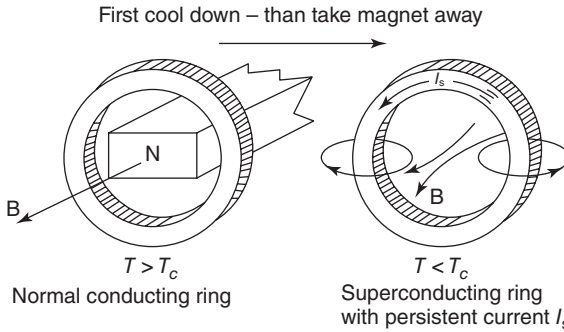


Figure 1.1 The generation of a permanent current in a superconducting ring.

an upper limit of the resistance from the temporal change and from the geometry of the superconducting circuit.

This method is more sensitive by many orders of magnitude than the usual current–voltage measurement. It is shown schematically in Figure 1.1. A ring made from a superconducting material, say, from lead, is held in the normal state above the transition temperature T_c . A magnetic rod serves for applying a magnetic field penetrating the ring opening. Now we cool the ring below the transition temperature T_c at which it becomes superconducting. The magnetic field¹⁾ penetrating the opening practically remains unchanged. Subsequently we remove the magnet. This induces an electric current in the superconducting ring, since each change of the magnetic flux Φ through the ring causes an electrical voltage along the ring. This induced voltage then generates the current.

If the resistance had exactly zero value, this current would flow without any change as a “permanent current” as long as the lead ring remained superconducting. However, if there exists a finite resistance R , the current would decrease with time, following an exponential decay law. We have

$$I(t) = I_0 e^{-(R/L)t} \quad (1.1)$$

Here, I_0 denotes the current at some time that we take as time zero; $I(t)$ is the current at time t ; R is the resistance; and L is the self-induction coefficient, depending only upon the geometry of the ring.²⁾

- 1) Throughout we will use the quantity \mathbf{B} to describe the magnetic field and, for simplicity, refer to it as “magnetic field” instead of “magnetic flux density.” Since the magnetic fields of interest (also those within the superconductor) are generated by macroscopic currents only, we do not have to distinguish between the magnetic field \mathbf{H} and the magnetic flux density \mathbf{B} , except for a few cases.
- 2) The self-induction coefficient L can be defined as the proportionality factor between the induction voltage along a conductor and the temporal change of the current passing through the conductor: $U_{\text{ind}} = -L(dI/dt)$. The energy stored within a ring carrying a permanent current is given by $(1/2)LI^2$. The temporal change of this energy is exactly equal to the joule heating power RI^2 dissipated within the resistance. Hence, we have $-(d/dt)((1/2)LI^2) = RI^2$. One obtains the differential equation $-(dI/dt) = (R/L)I$, the solution of which is Eq. (1.1).

For an estimate, we assume that we are dealing with a ring of 5 cm diameter made from a wire with a thickness of 1 mm. The self-induction coefficient L of such a ring is about 1.3×10^{-7} H. If the permanent current in such a ring decreases by less than 1% within an hour, we can conclude that the resistance must be smaller than $4 \times 10^{-13} \Omega$.³⁾ This means that in the superconducting state the resistance has changed by more than 8 orders of magnitude.

During such experiments the magnitude of the permanent current must be monitored. Initially [1] this was simply accomplished by means of a magnetic needle, its deflection in the magnetic field of the permanent current being observed. A more sensitive setup was used by Kamerlingh-Onnes and somewhat later by Tuyn [2]. It is shown schematically in Figure 1.2. In both superconducting rings 1 and 2, a permanent current is generated by an induction process. Because of this current both rings are kept in a parallel position. If one of the rings (here the inner one) is suspended from a torsion thread and is slightly turned away from the parallel position, the torsion thread experiences a force originating from the permanent current. As a result, an equilibrium position is established in which the angular moments of the permanent current and of the torsion thread balance each other. This equilibrium position can be observed very sensitively using a light beam. Any decay of the permanent current within the rings would be indicated by the light beam as a change in its equilibrium position. During all such experiments, no change of the permanent current has ever been observed.

A nice demonstration of superconducting permanent currents is shown in Figure 1.3. A small permanent magnet that is lowered toward a superconducting lead bowl generates induction currents according to Lenz's rule, leading to a repulsive force acting on the magnet. The induction currents support the magnet at an equilibrium height. This arrangement is referred to as a *levitated magnet*. The magnet is supported as long as the permanent currents are flowing within the lead bowl, that is, as long as the lead remains superconducting. For high-temperature superconductors such as $\text{YBa}_2\text{Cu}_3\text{O}_7$, the levitation can easily be performed using liquid nitrogen in regular air. Furthermore, it can also serve for levitating freely real heavyweights such as the Sumo wrestler shown in Figure 1.4.

The most sensitive arrangements for determining an upper limit of the resistance in the superconducting state are based on geometries having an extremely small self-induction coefficient L , in addition to an increase in the observation time. In this way, the upper limit can be lowered further. A further increase in the sensitivity is accomplished by the modern superconducting magnetic field sensors (see Section 7.6.4). Today, we know that the jump in resistance during entry into the superconducting state amounts to at least 14 orders of magnitude [3]. Hence, in the superconducting state, a metal can have a specific electrical resistance that

3) For a circular ring of radius r made from a wire of thickness $2d$ also with circular cross-section ($r \gg d$), we have $L = \mu_0 r [\ln(8r/d) - 1.75]$ with $\mu_0 = 4\pi \times 10^{-7}$ V s/A m. It follows that

$$R \leq \frac{-\ln 0.99 \times 1.3 \times 10^{-7} \text{ Vs}}{3.6 \times 10^3 \text{ Am}} \cong 3.6 \times 10^{-13} \Omega$$

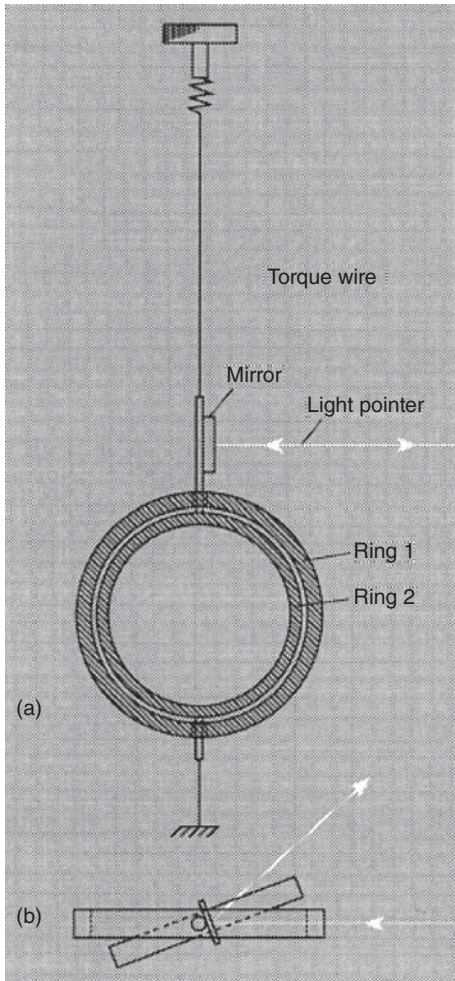


Figure 1.2 Arrangement for the observation of a permanent current. (a) side view, (b) top view. (After [2].) Ring 1 is attached to the cryostat.

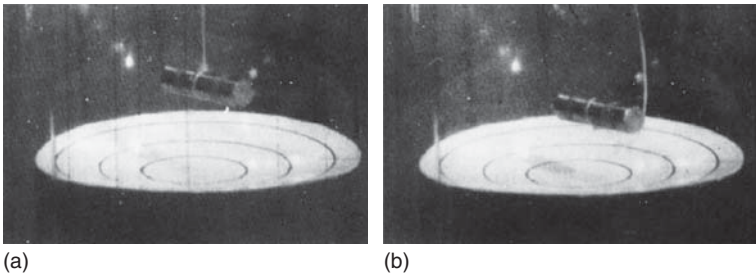


Figure 1.3 The "levitated magnet" for demonstrating the permanent currents that are generated in superconducting lead by induction during the lowering of the magnet. (a) Starting position. (b) Equilibrium position.



Figure 1.4 Application of free levitation by means of the permanent currents in a superconductor. The Sumo wrestler (including the plate at the bottom) weighs 202 kg.

The superconductor is $\text{YBa}_2\text{Cu}_3\text{O}_7$. (Photograph kindly supplied by the International Superconductivity Research Center (ISTEC) and Nihon-SUMO Kyokai, Japan, 1997.)

is at most about 17 orders of magnitude smaller than the specific resistance of copper, one of our best metallic conductors, at 300 K. Since hardly anyone has a clear idea about “17 orders of magnitude,” we also present another comparison: the difference in resistance of a metal between the superconducting and normal states is at least as large as that between copper and a standard electrical insulator.

Following this discussion, it appears justified at first to assume that in the superconducting state the electrical resistance actually vanishes. However, we must point out that this statement is valid only under specific conditions. So the resistance can become finite even in the case of small transport currents, if magnetic flux lines exist within the superconductor. Furthermore, alternating currents experience a resistance that is different from zero. We return to this subject in more detail in subsequent chapters.

This totally unexpected behavior of the electric current, flowing without resistance through a metal and at the time contradicting all well-supported concepts, becomes even more surprising if we look more closely at charge transport through a metal. In this way, we can also appreciate more strongly the problem confronting us in terms of an understanding of superconductivity.

We know that electric charge transport in metals takes place through the electrons. The concept that, in a metal, a definite number of electrons per atom (for instance, in the alkalis, one electron, the valence electron) exist freely, rather like a gas, was developed at an early time (by Paul Drude in 1900, and Hendrik Anton Lorentz in 1905). These “free” electrons also mediate the binding of the atoms in metallic crystals. In an applied electric field the free electrons are accelerated. After a specific time, the mean collision time τ , they collide with atoms and lose the energy they have taken up from the electric field. Subsequently, they are accelerated again. The existence of the free charge carriers, interacting with the lattice of the metallic crystal, results in the high electrical conductivity of metals.

Also the increase in the resistance (decrease in the conductivity) with increasing temperature can be understood immediately. With increasing temperature, the uncorrelated thermal motion of the atoms in a metal (each atom is vibrating with a characteristic amplitude about its equilibrium position) becomes more pronounced. Hence, the probability for collisions between the electrons and the atoms increases, that is, the time τ between two collisions becomes smaller. Since the conductivity is directly proportional to this time, in which the electrons are freely accelerated because of the electric field, it decreases with increasing temperature and the resistance increases.

This “free-electron model,” according to which electron energy can be delivered to the crystal lattice only due to the collisions with the atomic ions, provides a plausible understanding of electrical resistance. However, within this model, it appears totally inconceivable that, within a very small temperature interval at a finite temperature, these collisions with the atomic ions should abruptly become forbidden. Which mechanism(s) could have the effect that, in the superconducting state, energy exchange between electrons and lattice is not allowed any more? This appears to be an extremely difficult question.

Based on the classical theory of matter, another difficulty appeared with the concept of the free-electron gas in a metal. According to the general rules of classical statistical thermodynamics, each degree of freedom⁴⁾ of a system on average should contribute $k_B T/2$ to the internal energy of the system. Here, $k_B = 1.38 \times 10^{-23}$ W s/K is Boltzmann’s constant. This also means that the free electrons are expected to contribute the amount of energy $3k_B T/2$ per free electron, characteristic for a monatomic gas. However, specific heat measurements of metals have shown that the contribution of the electrons to the total energy of metals is about a thousand times smaller than expected from the classical laws.

Here, one can see clearly that the classical treatment of the electrons in metals in terms of a gas of free electrons does not yield a satisfactory understanding. On the other hand, the discovery of energy quantization by Max Planck in 1900 started a totally new understanding of physical processes, particularly on the

4) Each coordinate of a system that appears quadratically in the total energy represents a thermodynamic degree of freedom, for example, the velocity v for $E_{\text{kin}} = (1/2)mv^2$, or the displacement x from the equilibrium position for a linear law for the force, $E_{\text{pot}} = (1/2)Dx^2$, where D is the force constant.

atomic scale. The following decades then demonstrated the overall importance of quantum theory and of the new concepts resulting from the discovery made by Max Planck. Also the discrepancy between the observed contribution of the free electrons to the internal energy of a metal and the amount expected from the classical theory was resolved by Arnold Sommerfeld in 1928 by means of the quantum theory.

The quantum theory is based on the fundamental idea that each physical system is described in terms of discrete states. A change of physical quantities such as the energy can only take place by a transition of the system from one state to another. This restriction to discrete states becomes particularly clear for atomic objects. In 1913, Niels Bohr proposed the first stable model of an atom, which could explain a large number of facts hitherto not understood. Bohr postulated the existence of discrete stable states of atoms. If an atom in some way interacts with its environment, say, by the gain or loss of energy (e.g., due to the absorption or emission of light), then this is possible only within discrete steps in which the atom changes from one discrete state to another. If the amount of energy (or that of another quantity to be exchanged) required for such a transition is not available, the state remains stable.

In the final analysis, this relative stability of quantum mechanical states also yields the key to the understanding of superconductivity. As we have seen, we need some mechanism(s) forbidding the interaction between the electrons carrying the current in a superconductor and the crystal lattice. If one assumes that the “superconducting” electrons occupy a quantum state, some stability of this state can be understood. Already in about 1930, the concept became accepted that superconductivity represents a typical quantum phenomenon. However, there was still a long way to go for a complete understanding. One difficulty originated from the fact that quantum phenomena were expected for atomic systems, but not for macroscopic objects. In order to characterize this peculiarity of superconductivity, one often referred to it as a *macroscopic quantum phenomenon*. Below we will understand this notation even better.

In modern physics another aspect has also been developed, which must be mentioned at this stage, since it is needed for a satisfactory understanding of some superconducting phenomena. We have learned that the particle picture and the wave picture represent complementary descriptions of one and the same physical object. Here, one can use the simple rule that propagation processes are suitably described in terms of the wave picture and exchange processes during the interaction with other systems in terms of the particle picture.

We illustrate this important point with two examples. Light appears to us as a wave because of many diffraction and interference effects. On the other hand, during the interaction with matter, say, in the photoelectric effect (knocking an electron out of a crystal surface), we clearly notice the particle aspect. One finds that independently of the light intensity the energy transferred to the electron only depends upon the light frequency. However, the latter is expected if light represents a current of particles where all particles have an energy depending on the frequency.

For electrons, we are more used to the particle picture. Electrons can be deflected by means of electric and magnetic fields, and they can be thermally evaporated from metals (glowing cathode). All these are processes where the electrons are described in terms of particles. However, Louis de Broglie proposed the hypothesis that each moving particle also represents a wave, where the wavelength λ is equal to Planck's constant h divided by the magnitude p of the particle momentum, that is, $\lambda = h/p$. The square of the wave amplitude at the location (x, y, z) then is a measure of the probability of finding the particle at this location.

We see that the particle is spatially "smeared" over some distance. If we want to favor a specific location of the particle within the wave picture, we must construct a wave with a pronounced maximum amplitude at this location. Such a wave is referred to as a *wave packet*. The velocity with which the wave packet spatially propagates is equal to the particle velocity.

Subsequently, this hypothesis was brilliantly confirmed. With electrons we can observe diffraction and interference effects. Similar effects also exist for other particles, say, for neutrons. The diffraction of electrons and neutrons has developed into important techniques for structural analysis. In an electron microscope, we generate images by means of electron beams and achieve a spatial resolution much higher than that for visible light because of the much smaller wavelength of the electrons.

For the matter wave associated with the moving particle, there exists, like for each wave process, a characteristic differential equation, the fundamental Schrödinger equation. This deeper insight into the physics of electrons must also be applied to the description of the electrons in a metal. The electrons within a metal also represent waves. Using a few simplifying assumptions, from the Schrödinger equation we can calculate the discrete quantum states of these electron waves in terms of a relation between the allowed energies E and the so-called wave vector \mathbf{k} . The magnitude of \mathbf{k} is given by $2\pi/\lambda$, and the spatial direction of \mathbf{k} is the propagation direction of the wave. For a completely free electron, this relation is very simple. We have in this case

$$E = \frac{\hbar^2 \mathbf{k}^2}{2m} \quad (1.2)$$

where m is the electron mass and $\hbar = h/2\pi$.

However, within a metal the electrons are not completely free. First, they are confined to the volume of the piece of metal, like in a box. Therefore, the allowed values of \mathbf{k} are discrete, simply because the allowed electron waves must satisfy specific boundary conditions at the walls of the box. For example, the amplitude of the electron wave may have to vanish at the boundary.

Second, within the metal the electrons experience the electrostatic forces originating from the positively charged atomic ions, in general arranged periodically. This means that the electrons exist within a periodic potential. Near the positively charged atomic ions, the potential energy of the electrons is lower than between these ions. As a result of this periodic potential, in the relation between E and \mathbf{k} ,