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, Heike Kamerlingh-Onnes[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 [1]. 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, before long 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 effecting 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).

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

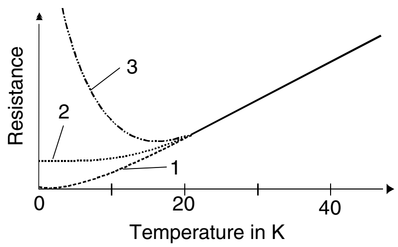

Fig. 1 Schematics of the temperature dependence of electrical resistance at low temperatures. See text for details of curves.

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 above. The value of this residual resistance depended upon 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.

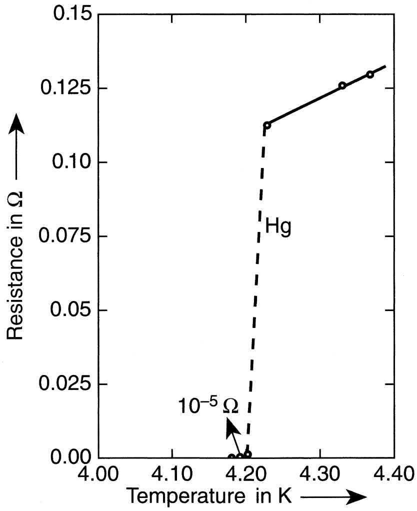

Fig. 2 The superconductivity of mercury (after [3]).

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 of resistance. The resistance change took place within a temperature interval of only a few hundredths of a degree and, hence, it resembled more 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, that had framed, bringing the resistance at once less than a millionth of its original value at the melting 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 the 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 quantized[3)] 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.

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 ^{4}He the lambda point is 2.17 K, and for ^{3}He 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 like 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 discov-

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). We have 1 Wb = 1 T m^2. If a loop is placed at a large distance around the axis of an isolated flux tube, we have $\Phi = \Phi_0$.

eries 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-Cu-O system" [9]. The authors had started from the hypothesis that substances with a pronounced Jahn-Teller effect[5)] could be superconductors with a particularly high transition temperature T_c. They first studied compounds based on nickel oxide, since Ni^{3+} in an octahedron of oxygen atoms displays a strong Jahn-Teller effect. However, within this group of substances they did not find any superconductors. Then they systematically turned to copper oxide. Cu^{2+} in an octahedron of oxygen also displays a large Jahn-Teller effect. After only a few months Bednorz and Müller had samples showing a steep drop of the electrical resistance already above 30 K. Had they found superconductors with T_c > 30 K? After more than 10 years of stagnation this would be a major breakthrough. 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.[6)] Hence, a convincing proof of superconductivity in these samples was still needed.

This proof was achieved by Bednorz, Müller, and Takashige by demonstrating the existence of the Meissner-Ochsenfeld effect [10]. 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, i. e. 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 [11]). They searched among the substances based on the

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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 The Jahn-Teller effect is understood as the displacement of an ion away from the highly symmetric position relative to its environment. In this case the degeneracy of the states of the ion is lifted and its energy is overall lowered. A strong Jahn-Teller effect indicates a strong electron-phonon interaction. So the hypothesis of Müller and Bednorz was well consistent with the BCS theory.

6 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 [R. A. Ogg Jr.: Phys. Rev. **69**, 243 and 668 (1946); **70**, 93 (1946)].

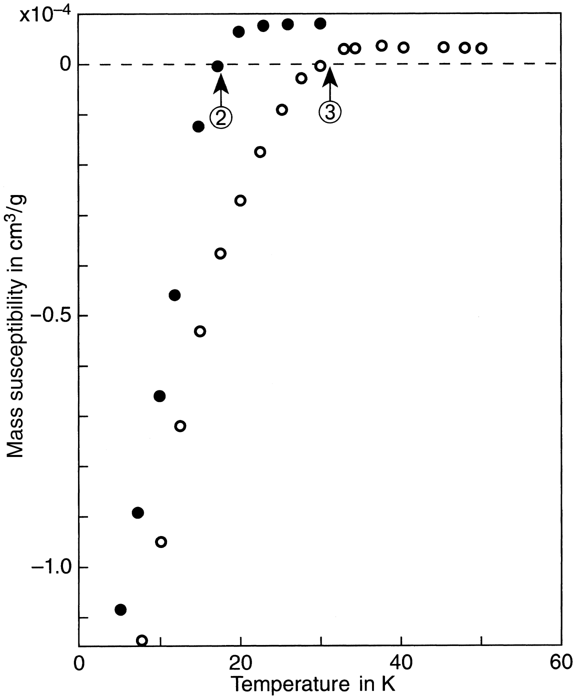

Fig. 3 The magnetic susceptibility of two samples of the Ba-La-Cu-O system versus temperature [10].

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 1986/87 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 [12]. Only a few weeks later transition temperatures above 80 K were observed in the Y-Ba-Cu-O system [13, 14]. 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 $YBa_2Cu_3O_7$ (also "YBCO" or "Y123") and $Bi_2Sr_2CaCu_2O_8$ (also "BSCCO" or "Bi2212"), which display

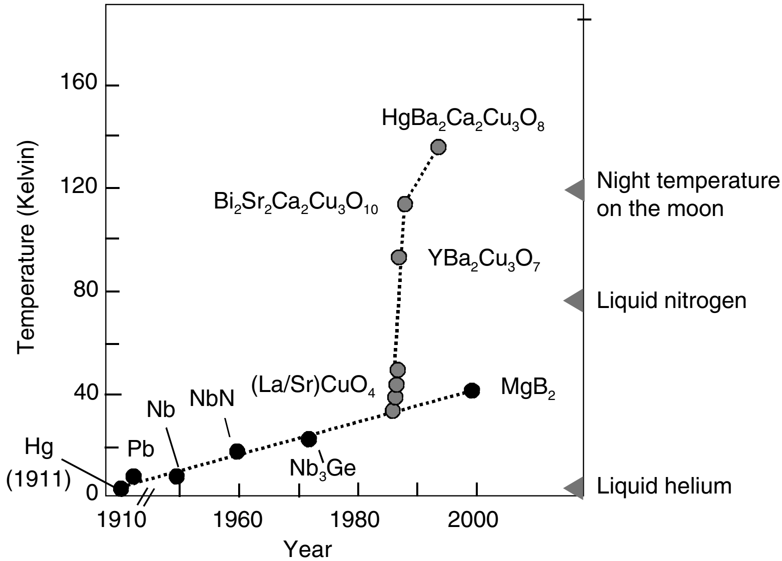

Fig. 4 Evolution of the superconducting transition temperature since the discovery of superconductivity (after [15]).

maximum transition temperatures around 90 K. Many compounds have transition temperatures even above 100 K. The record value is claimed by $HgBa_2Ca_2Cu_3O_8$, having at atmospheric pressure a T_c value of 135 K and at a pressure of 30 GPa a value as high as $T_c = 164$ K. 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 Fig. 4 we have also included the metallic compound MgB_2, for which surprisingly superconductivity with a transition temperature of 39 K was detected only in 2000, even though this material has been commercially available for a long time [16]. This discovery also had a great impact in physics, and many essential properties of this material have been clarified already in the subsequent years. It turned out that MgB_2 behaves similarly to the "classical" metallic superconductors.

In contrast to this, many properties of the high-temperature superconductors (in addition also to other superconducting compounds) are highly unusual, as we will see many times during the course of this book. Even more than 15 years after the discovery of the oxide superconductors it is still unclear how Cooper pairing is accomplished in these materials. However, it seems likely that magnetic interactions play an important role.

Due to the discovery of the cuprates, the phenomenon of superconductivity is not restricted any more to a temperature range far away from that relevant for all organic life. One hopes that one day materials are found showing this phenomenon also 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 [17, 18].[7] 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.

Already, for some time, with liquid helium as the cooling agent, we have utilized metallic superconductors in the medical field, for the generation of high magnetic fields in nuclear spin tomography, or in magnetic field sensors. In field tests, magnetic field sensors made from $YBa_2Cu_3O_7$ are employed for the non-destructive testing of materials or for detecting magnetic cardiac signals. In the field of energy technology, the first prototypes of cables made from high-temperature superconductors are already operating. High-temperature superconductors can be kept in a well-stabilized state above or below strong magnets. In this way a contact-free bearing and motion nearly without any friction can be achieved, which is highly attractive in many fields 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.

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

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