Chapter 1

Introduction

Macroscopic quantum phenomena are effects, which reveal themselves on a macroscopic scale, although they are microscopically of quantum nature. Prominent examples are, for instance, superfluidity, Bose-Einstein condensation, quantum Hall effect, and giant magnetoresistance. In this lecture we analyze the various intriguing properties of the quantum phenomenon superconductivity. It occurs in a set of materials, where the electrical resistance vanishes and from which magnetic flux lines are expelled. Thus, a superconductor is at the same time an ideal metal and an ideal diamagnet.

1.1 Critical Temperature

Heike Kammerlingh Onnes achieved in Leiden in 1908 for the first time the liquidation of helium (He) as the last inert gas at the temperature 4.2 K. This achievement was the experimental requirement for investigating the properties of matter at low temperatures in general and to discover superconductivity in particular.

The electrical resistance ρ of a metal stems at low temperatures from the scattering of electrons at both lattice defects and phonons at low temperature. As both contributions have a different physical origin, they turn out to have a different temperature dependence, see Fig. 1.1a):

- The scattering of electrons at lattice defects yields an electrical resistivity, which is basically independent of the temperature. Therefore, it leads at absolute temperature $T = 0\,\mathrm{K}$ to the residual resistance ρ_0.
- Instead, the scattering of electrons at phonons strongly depends on temperature as the number of phonons increases with the temperature.

Both results are summarized by the rule of Matthiessen:

$$\rho(T) = \rho_0 + \Delta\rho(T)\,. \tag{1.1}$$

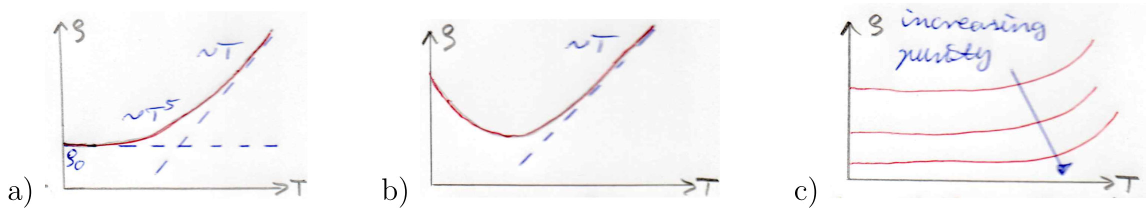

Figure 1.1: Electrical resistance of a solid: a) Without and b) with magnetic impurities at low temperatures. c) Residual resistance at absolute temperature $T = 0\,\mathrm{K}$ vanishes for an ideal pure crystal.

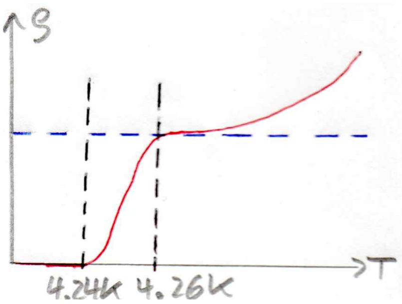

Figure 1.2: Electrical resistance of mercury in the vicinity of the critical temperature of superconductivity $T_c^{\mathrm{Hg}} = 4.2\,\mathrm{K}$.

Furthermore, at higher temperatures the electrical resistance $\rho(T)$ increases linearly with the temperature, as the electrical conductivity is then dominated by the free electrons, which scatter more and more at the atomic cores.

Note that the temperature dependence of the electrical resistance can deviate from this generic behaviour at low temperatures. This happens, for instance, when magnetic impurities are built in an originally non-magnetic metal. Due to the scattering of the conducting electrons at magnetic impurities the electrical resistance can increase, when the temperature is lowered, thus yielding a minimum, see Fig. 1.1b). This characteristic change of electrical resistivity with the temperature is called Kondo effect.

The original aim of Onnes was to experimentally test the assumption of the Matthiessen rule (1.1) that the residual resistance ρ_0 at absolute temperature $T = 0\,\mathrm{K}$ vanishes for an ideal pure crystal, see Fig. 1.1c). To this end metal probes with different purity degrees were investigated. Onnes used for these experiments the metal mercury (Hg). The reason was that, at the beginning of the 20th century, it was the only metal, which could be produced with the highest degree of purity by successive fractional distillations.

In 1911 Onnes measured the temperature dependence of the electrical resistance of mercury. Surprisingly he found that the whole electrical resistance drops at about $4.2\,\mathrm{K}$ within a temperature interval of $20\,\mathrm{mK}$ to zero, see Fig. 1.2. Thus, mercury becomes superconducting at the critical temperature $T_c^{\mathrm{Hg}} = 4.2\,\mathrm{K}$. For this experimental discovery Onnes was awarded the Nobel Prize of Physics in 1913.

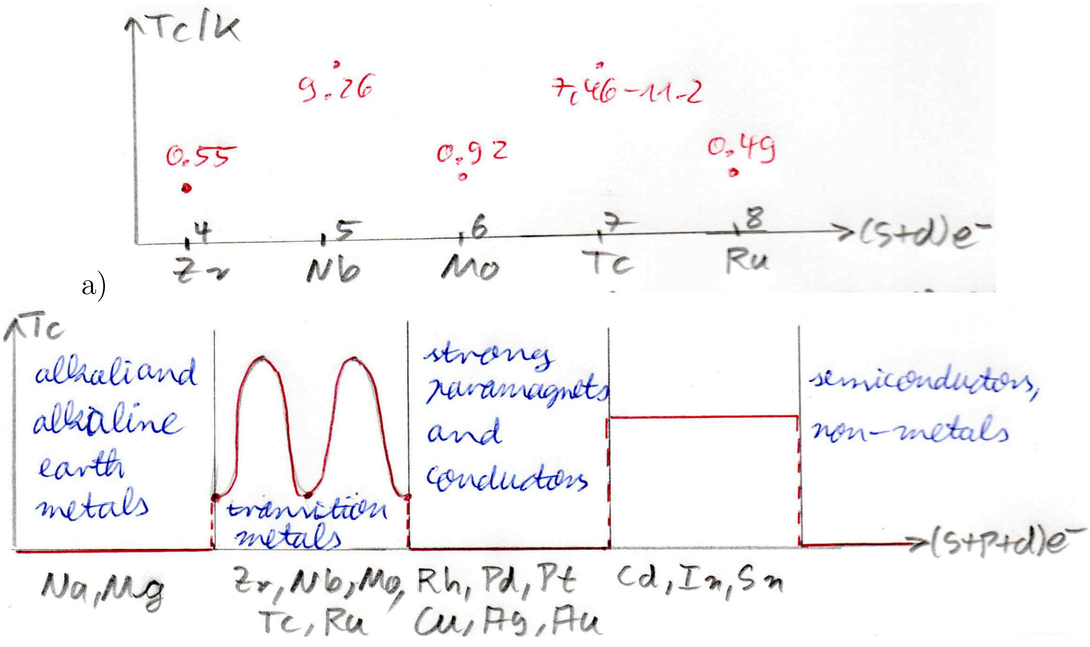

Figure 1.3: Dependence of critical temperature on number of valence electrons for a) transition metals and b) various elements.

1.2 Superconducting Materials

Although superconductivity is a quite omnipresent phenomenon, not all materials are superconducting. In the following we list some generic categories of elements, which are not superconducting. Among them are elements with spin order, which include ferromagnets, i.e. iron (Fe), nickel (Ni), and cobalt (Co), antiferromagnets like manganese dioxide (MnO_2), as well as ferrimagnets as, for instance, iron oxide (Fe_3O_4). But also elements with strong paramagnetism as rhodium (Rh), palladium (Pd), and platinum (Pt), or elements with a high electrical conductivity like copper (Cu), silver (Ag), and gold (Au) are not superconducting. And, finally, semiconductors like silicon (Si) or germanium (Ge) become superconducting only at very high pressures, typical measurement results are T_c^{Si} (120 kbar) = 6.7 K and T_c^{Ge} (115 kbar) = 5.35 K.

But one observes that many metals are superconducting. The critical temperatures vary between several hundredth of Kelvin (wolfram: $T_c^{\mathrm{W}} = 10^{-2}\,\mathrm{K}$) up to about 10 K (niobium: $T_c^{\mathrm{Nb}} = 9.26\,\mathrm{K}$). Within the periodic table of elements one can recognise essentially two groups of superconducting elements. On the one hand, there are non-transition metals of the group IV, V, VI, among them are the high-pressure phases of silicon and germanium. On the other hand, we have transition metals, where in each row with increasing order number in the periodic table inner electron shells are filled up. Bernd Theodor Matthias, who was said to have discovered more elements and compounds with superconducting properties than any other scientist, formulated the following rule. The number of valence electrons, i.e. the electrons not belonging to closed shells, are decisive for the occurrence of superconductivity. It turns out that an odd

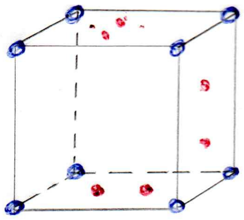

Figure 1.4: β-wolfram A15 structure of Nb_3Sn or Nb_3Ge: Blue dots (red dots) represent Sn or Ge (Nb) atoms at the corners (pages) of each cuboid.

perovskite-like metal oxide	$(LaBa)_2CuO_4$	$YBa_2Cu_3O_7$	$Bi_2Sr_2CaCu_2O_8$	TlBaCaCuO
critical temperature in K	35	83	110	125

Table 1.1: Critical temperatures of high-temperature superconductors.

(even) number of valence electrons leads to a higher (lower) critical temperature. For instance, for elements of the second row of the transition metals the respective critical temperatures are depicted in Fig. 1.3a). Plotting the critical temperature of superconductivity over the number of valence electrons, one yields periods of superconducting and not superconducting elements as shown in Fig. 1.3b).

Among the intermetallic superconductors those with a so called β-wolfram A15 structure have the highest critical temperature: $T_c(Nb_3Sn) = 18.05\,K$, $T_c(Nb_3Ge) = 22.7\,K$. Here the tin (Sn) or germanium (Ge) atoms form a cubic lattice (blue dots in Fig. 1.4). And two niobium (Nb) atoms (red dots in Fig. 1.4) lie at the pages of each cuboid in the main directions [100], [010], and [001]. Thus, we have one Sn/Ge atom and three Nb atoms per elementary cell. It turns out that the electrical conductivity occurs along the Nb chains, which represent a one-dimensional electronic system.

In 1986 Bednorz and Müller analyzed at the IBM Research Laboratory in Zurich so-called perovskite structures. For the substance lanthanum barium copper oxide ($La_{1.85}Ba_{0.15}CuO_4$) they discovered superconductivity at the critical temperature of 35 K, which was larger than the so far known highest critical temperature of 22.7 K for Nb_3Ge. For this milestone discovery Bednorz and Müller were awarded the Nobel Prize of Physics in 1987. Later on even higher critical temperatures were found for other perovskite-like metal oxides, see Tab. 1.1. The common feature of all those perovskites are layers of copper oxide. Exemplarily Fig. 1.5 shows different elementary cells of thallium barium calcium copper oxide. It is found that the critical temperature of superconductivity increases with the number of copper oxide layers.

Until now the physical mechanism for those high critical temperatures of superconductivity is unknown. Therefore, this lecture does not deal with those high T_c-superconductors and focuses instead on the class of classical superconductors, which are well understood even on a quantitative level.

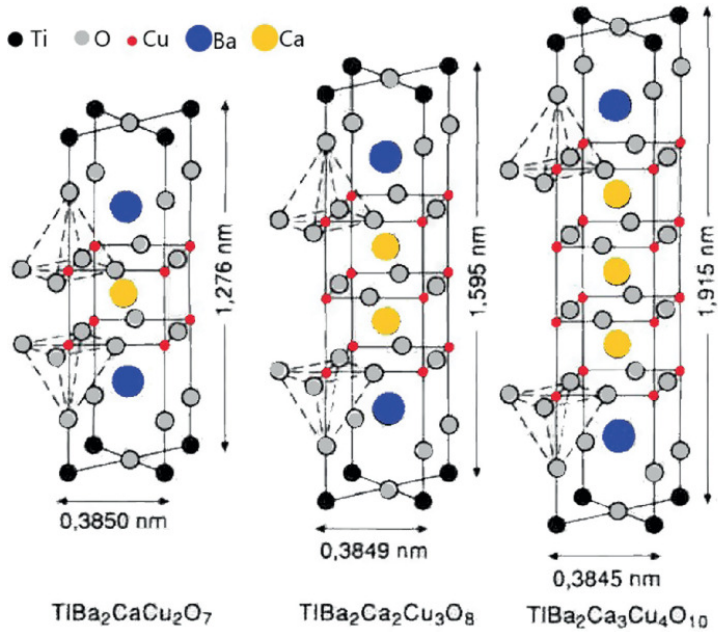

Figure 1.5: Thallium barium calcium copper oxide, or TBCCO, which is pronounced "tibco", represents a family of high-temperature superconductors with 2, 3, and 4 layers of copper oxide from left to right.

1.3 Phase Transitions

In the following we briefly discuss some elementary properties of superconductors from the point of view of phase transitions. All these properties will later on be worked out in more detail.

1.3.1 First-Order Phase Transitions

A first-order phase transition is characterized by a discontinuity of a first derivative of the thermodynamic potential. For instance, a discontinuity of the entropy S leads to the latent head $\Delta Q = \Delta S\, T_{\mathrm{c}}$. Here ΔS denotes the entropy change from one to the other phase and T_{c} represents the critical temperature. Examples for first-order phase transitions are the phase transition from a liquid to a solid or from a normal conductor to a superconductor for a non-vanishing magnetic field.

1.3.2 Second-Order Phase Transitions

For a second-order phase transition all first derivatives of the thermodynamic potential are continuous. For instance, the entropy is continuous so that a latent heat does not exist. But, instead, a second derivative of the thermodynamic potential is discontinuous. One example is provided by the transition from a paramagnet to a ferromagnet, as the magnetic susceptibility

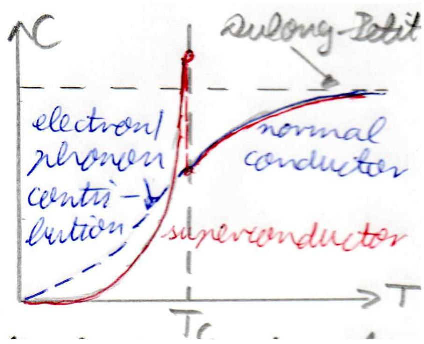

Figure 1.6: Temperature dependence of heat capacity for superconductor and normal conductor.

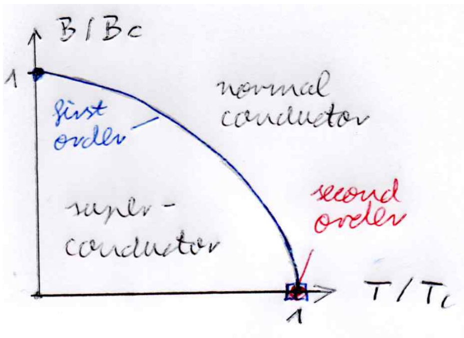

Figure 1.7: Phase diagram of a superconductor.

makes a jump at the critical temperature. Another example is the transition from normal conducting to superconducting at a vanishing magnetic field, which is revealed, for instance, by the temperature dependence of the heat capacity as depicted in Fig. 1.6. At the critical temperature the heat capacity suddenly increases in the superconducting state. At low temperatures the heat capacity does not vary polynomially with the temperature as in a normal conductor but reveals a characteristic exponential dependence:

$$C(T) \sim e^{-\Delta/k_{\rm B}T} \,. \tag{1.2}$$

Whereas a polynomial temperature dependence would indicate a polynomial density of states, the exponential dependence (1.2) signals that the density of states has an energy gap Δ. This means that one needs a finite energy Δ per electron in order to excite it.

1.3.3 Phase Diagram

In the plane spanned by the control parameters of the magnetic induction B and the temperature T one finds experimentally a phase diagram as depicted in Fig. 1.7. There is a transition line between a normal conducting phase, which is paramagnetic, and a superconducting phase, which turns out to be diamagnetic. The latter means that the magnetic field lines are expelled from the superconductor. The boundary between both phases is empirically described quite

superconductor	Nb	Nb_3Sn	high T_c's
$B_c(0)$ in T	0.2	25	~ 100

Table 1.2: Critical magnetic fields of superconductors.

Figure 1.8: Illustration of a Cooper pair, which consists of two electrons of opposite momentum and spin.

well by the formula of Kok:

$$\frac{B_c(T)}{B_c(0)} = 1 - \left(\frac{T}{T_c}\right)^2 . \tag{1.3}$$

As this phase boundary can be written in reduced physical quantities, it is universal, i.e. it is valid for all classical superconductors. This finding of universality indicates that there is an underlying physical mechanism, which is responsible for classical superconductivity irrespective of the underlying material. Note that for $B_c(T) > 0$ ($B_c(T) = 0$) the phase transition is of first (second) order as indicated in Fig. 1.7. Furthermore, we remark that the critical magnetic field at absolute temperature $B_c(0)$ varies strongly, see Tab. 1.2. For the sake of comparison we mention that the magnetic induction of the earth is of the order of about $30\,\mu$T.

1.3.4 BCS Theory

The microscopic theory for classical superconductors was worked out by John Bardeen from the Bell Telephone Company in New Jersey as well as Leon Cooper and John Schrieffer from the University of Illinois in 1957. As it explains all properties of classical superconductors quantitatively, the theory is abbreviated by the initial letters of their discoverers and is called BCS theory. Bardeen, Cooper and Schrieffer were awarded the Nobel Prize of Physics in 1972.

According to the BCS theory the main mechanism for superconductivity is the pairing of two electrons with opposite momentum and spin, see Fig. 1.8. Note that this pairing occurs not in real but in momentum space, so the distance between two electrons is with about 1000 Å quite large in comparison with the distance between two atoms in a metal, which is of the order of Å. The electrons pairs, which are also called Cooper pairs, are mainly created at the Fermi surface. Therefore, they create at the Fermi surface an energy gap Δ for the density of states of single electrons, which leads to the exponential low-temperature dependence of the specific heat (1.2). Scattering processes, which are possible for single electrons, are no longer possible for Cooper pairs. Thus, they can transport electric current without resistance.

As a consequence of the Cooper pairing, the BCS theory yields for the critical temperature of superconductivity in good approximation the following explicit result:

$$T_{\rm c} = 1.13\,\frac{\hbar\omega_{\rm D}}{k_{\rm B}}\,e^{-2/N(E_{\rm F})\,g}\,. \tag{1.4}$$

Here $N(E_{\rm F})$ denotes the density of states of single electrons at the Fermi energy $E_{\rm F}$. Furthermore, g stands for the strength of the effective electron-electron interaction. Note that, originally, two electrons repel each other due to the Coulomb interaction. But due to the interaction of the electrons with the phonons, i.e. the quantized lattice vibrations, a residual effective attractive electron-electron interaction emerges. Thus, for a large (small) product $N(E_{\rm F})\,g$ the critical temperature of superconductivity is large (small). This explains a posteriori several observations from above:

- On page 3 elements with high electrical conductivity are considered. Here the electron-phonon scattering and, thus, the effective electron-electron attraction g are so small that the critical temperature basically vanishes.
- On page 4 the Matthias rule is discussed. For an odd (even) number of valence electrons the density of states $N(E_{\rm F})$ and, thus, $T_{\rm c}$ are large (small).
- On page 4 the intermetallic materials Nb_3Sn, Nb_3Ge are explained to be 1D electronic systems. Therefore $N(E_{\rm F})$ is large and $T_{\rm c}$ turns out to be large as well.

Apart from the exponential factor, the critical temperature $T_{\rm c}$ scales in (1.4) with the Debye frequency $\omega_{\rm D}$, which is the cut-off frequency for phonons. On the one hand, this dependence underlines that the electron-phonon interaction is crucial for superconductivity. On the other hand, the Debye frequency $\omega_{\rm D}$ and, thus, also $T_{\rm c}$ depend via $1/\sqrt{M}$ on the atom mass M. This dependence was experimentally discovered for the first time in 1950 and is called isotope effect:

$$T_{\rm c}\,\sqrt{M} = \text{const}\,. \tag{1.5}$$

It is noteworthy that this isotope effect represents a key result of the BCS-theory, which turns out to be not fulfilled for high-temperature superconductors. But before we can work out the microscopic BCS theory, we have to describe in more detail the physical properties of superconductors. To this end we describe in the next chapters superconductivity on a phenomenological level. In Chapter 2 we summarize the magnetic properties and in Chapter 3 the thermodynamic properties of superconductors.