100 YEARS OF SUPERCONDUCTIVITY: PRESENT UNDERSTANDING AND PERSPECTIVES

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Abstract. The phenomenon of superconductivity has not lost its appealing fascination ever since its discovery in 1911. Due to their unusual behavior, superconductors are interesting candidates for applications including power transmission, motors and generators and electronics. In this paper I shall summarize our present understanding of superconductivity and discuss present as well as perspective technological applications.

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1. INTRODUCTION

Superconductivity was discovered in 1911 by Heike Kamerlingh Onnes who had first liquefied He in 1908. He was awarded the Nobel Prize in 1913 for his contribution to low-temperature research. Kamerlingh Onnes found that the electrical resistivity of mercury abruptly vanishes when the sample is cooled below a temperature of ~4K [1] as shown in Fig. 1. Hundreds of metals are known to become superconducting below a critical temperature $T_c$ which is characteristic for a given material. Empirically, superconductivity was by and by established as a common low-temperature instability of metallic systems (see Fig.1). It is important to note that superconductivity is not exhibited by any of the magnetic elements. The superconducting elements have transition temperatures that lie between 1K and 10K. For the first generation of conventional superconductors the critical temperatures remained restricted to rather low values. The unusual properties displayed by superconductors were consistently explained in the 1950s and 1960s.

The interest in superconductivity was revitalized in 1986 when Bednorz and Müller discovered high-temperature superconductors [2]. These emergent materials obey the same general phenomenology as the classical superconductors, the underlying microscopic picture, however, is not yet settled.

The main purpose of the present paper is (i) to review the unique properties of superconductors, (ii) to describe our present understanding and (iii) to summarize major technical applications. It is organized as follows: In Section 2 the basic properties are described. The order parameter is introduced in Section 3. Section 4 is devoted to the consequences of...
macroscopic quantum coherence. The central assumptions and features of the microscopic theory are briefly summarized in Section 5. Section 6 deals with technical applications. Selected classes of novel superconducting materials are discussed in Section 7. The paper closes with a summary and an outlook in Section 8.

Fig. 1a. Left panel: Observation of superconductivity ([1] cited after [3]) Right panel: Periodic table with the distribution and $T_c$ [K] of chemical elements for which superconductivity has been observed without and with application of pressure (after [4] Chapter 1).

2. BASIC PHENOMENA

The first traditional hallmark of superconductivity is perfect conductivity. The complete disappearance of resistance is most sensitively demonstrated by experiments with persistent currents in superconducting rings which, in the absence of any driving field, have nevertheless shown no discernible decay. A lower bound of some $10^5$ years for the characteristic decay time has been established by measuring the decrease of the magnetic field produced by the circulating current.

The second hallmark is perfect diamagnetism discovered in 1933 by Meissner and Ochsenfeld [5]. If a normal metal in a magnetic field is cooled below its superconducting transition temperature the magnetic flux is suddenly expelled resulting in $B = 0$ inside the superconductor. This observation confirms that the superconducting state is a thermodynamic equilibrium state whose properties are independent of the history of its preparation. This can be seen as follows: When a normal metal is cooled below the superconducting transition in the absence of a magnetic field the infinite conductivity will prevent the magnetic induction inside the sample to change with time. If an external field is applied surface currents must be created to ensure $B = 0$ inside the sample.

As a consequence, the transition from normal to superconducting states can be considered as being thermodynamically reversible. The critical magnetic field $H_c(T)$ where superconductivity is destroyed at temperatures $T < T_c$ is related to the free-energy difference between the normal and superconducting states in zero field, the so-called condensation energy of the superconductor.
\[
\frac{H_c^2(T)}{8\pi} = f_a(T) - f_s(T)
\]

where \(f_a\) and \(f_s\) are the Helmholtz free energies per unit volume of the respective phases in zero field.

**Fig. 2.** Meissner effect (left): Magnetic flux is excluded from the interior of a superconductor. Levitation (right): A magnet levitates above a superconductor due to magnetic repulsion.

Complete expulsion of the magnetic flux (complete Meissner effect) occurs only for certain superconductors called type-I-superconductors. The elements Nb and V, most superconducting compounds and alloys have a different magnetic behavior. From these type-II-superconductors the magnetic flux is expelled only below a certain lower critical field \(H < H_{c1}\) while the zero-resistance state disappears at the upper critical magnetic field \(H > H_{c2}\). In the intermediate field regime some magnetic flux is trapped forming a periodic structure.

### 3. ORDER PARAMETER

Following Landau, we characterize the different kinds of long-range order by order parameters. In superconducting or superfluid phases the long-range order appears in a quantum-mechanical density matrix. In the case of fermionic superfluids/superconductors, the highly correlated superfluid phases in are characterized by long-range order in the two-particle density matrix which allows us to define order parameters \(\Psi_{ab}(x, x')\) which we shall refer to as pair amplitudes. They behave like two-fermion wave functions. The quantum numbers \(A\) and \(B\) denote (pseudo) spins in the case of electron systems or \(^3\)He, for ultra-cold atoms they refer to hyperfine states, whereas they include color, spin, and flavor indices in quark condensates. In the superconductors to be considered here, the pair amplitudes depend upon the fermion spins and positions which are conveniently expressed in terms of the center-of-mass and relative coordinates \(R = (x+x')/2\) and \(r = x-x'\). In homogeneous superconductors, the order parameter depends only on the relative coordinate, i.e. \(\Psi_{\sigma\sigma}(r)\). A superconducting order parameter is not the thermal expectation value of a physical observable, but rather a complex (pseudo) wave function describing quantum phase correlations on the macroscopic scale of the
superconducting coherence length. Its phase is a direct signature of the broken gauge invariance in the superconducting condensate.

The Pauli principle requires $\Psi_{\sigma\alpha}(\mathbf{r})$ to be antisymmetric under the interchange of particles, $\Psi_{\sigma\alpha}(\mathbf{r}) = -\Psi_{\sigma\alpha}(\mathbf{r})$. The superconducting order parameter which is represented by a $2 \times 2$ matrix in (pseudo) spin space can be decomposed into an antisymmetric "singlet" (s) and a symmetric "triplet" (t) contribution $\Psi = \Psi_s + \Psi_t$ whose parity is determined by the overall antisymmetry. The general classification scheme for superconducting order parameters proceeds from the behavior under the transformations of the symmetry group of the Hamiltonian. A comprehensive discussion is given e.g. in [6] and references therein. In the following discussion, we shall focus on even-parity (spin-singlet) superconductors belonging to a one-dimensional representation $\Gamma$ of the symmetry group. These states are characterized by a complex scalar function which can have zeros, symmetry-imposed or accidental, on the Fermi surface. If $\Gamma$ is the unity representation, the superconductor is called "conventional", otherwise we call it "unconventional". The long search for superconductors with anisotropic order parameters arrived in the 1980s finally at a small list of candidates for such "unconventional superconductivity" which had to be derived here in an indirect manner from the observation of anomalies in their physical properties.

4. CONSEQUENCES OF QUANTUM COHERENCE

For simplicity we shall consider here isotropic singlet superconductors which are characterized by a scalar function of the center of gravity variable. The many-particle condensate wave function $\psi(\mathbf{R}) = |\psi(\mathbf{R})| e^{i\phi(\mathbf{R})}$ which maintains phase coherence over macroscopic distances was originally introduced by Ginzburg and Landau [7] as an order parameter within Landau’s theory of second order phase transitions. It is related to the superfluid density through $n_s = |\psi|^2$. A fundamental assumption of the Ginzburg-Landau theory is that the supercurrent in the presence of a magnetic field derived from the vector potential $\mathbf{A}(\mathbf{R})$ is given by the ordinary quantum mechanical expression for particles of mass $m^*$ and charge $e^*$.

A direct consequence of the quantum coherence in a superconductor is the fluxoid quantization in a superconducting ring. Uniqueness of the wave function requires that the phase changes by integral multiples of $2\pi$ upon making a complete circuit, i.e., $\oint \nabla \phi \cdot ds = 2\pi$. Assuming that the gradient of the superfluid density can be neglected the supercurrent is given by

$$j = \frac{e^* \hbar}{m^* |\psi|} \left( \nabla \phi - \frac{e^*}{\hbar c} \mathbf{A} \right)$$

(2)

Appreciable currents can flow only near the surface of the superconductor. As a consequence, the condition $\oint j \cdot ds = 0$ must hold for any path encircling the aperture. The line integral of the vector potential along a closed path is directly related to the enclosed magnetic flux which must be quantized $|\Phi| = n (hc/e^*)$. 

4
The observation of flux quantization in units of the flux quantum or fluxoid \[ \Phi_0 = \frac{hc}{2e} = 2.0679 \times 10^{-7} \text{ gauss cm}^2 \] provides compelling evidence for the description of the superconducting state in terms of complex quantum mechanical wave functions for pairs of electrons.

Further evidence is provided by several novel phenomena observed in junctions which are formed by two superconductors separated by a thin insulating barrier. They are collectively called Josephson effects [11]. The first of these phenomena is the flow of a zero voltage supercurrent through the junction

\[ I_s = I_c \sin \left( \frac{\Delta \phi}{\Phi_0} \int \mathbf{A} \cdot d\mathbf{s} \right), \]  

where \( \Delta \phi \) is the difference in phase of the order parameters in the superconducting electrodes. The integration is from one electrode of the weak link to the other. The critical current \( I_c \) denotes the maximum current the junction can support.

A second class of Josephson effects are based on the fact that a DC voltage \( V \) across the junction leads to a time-dependent phase difference between the order parameters of the electrodes and, concomitantly, induces an alternating supercurrent of amplitude \( I_c \) and frequency

\[ \omega_j = \frac{2eV}{\hbar}. \]  

It is important to note that the superconducting order parameter cannot be directly measured. Therefore it is difficult to unambiguously identify unconventional pair states. First convincing experimental evidence of d-wave exploits flux quantization. The experiments were performed on epitaxial c-axis oriented High Temperature Superconductor (HTS) thin films on
tri-crystal substrates. Such substrates are composed of three parts with different in-plane crystal. Suitable choice of the relative angles between these in-plane orientations leads to the formation of a magnetic vortex fixed right at the meeting point of these three film areas. As a consequence of the $\pi$-shift imposed by the boundary condition for connecting the superconducting order parameter of the three HTS subsystems (see Fig. 4 left), the flux of this vortex is restricted to half-integer multiples of the magnetic flux quantum $\Phi_0$, i.e. $\pm \Phi_0/2$ in ground state. Magnetic microscopy has arrived now at a flux resolution of a minute fraction of $\Phi_0$ which enables to distinguish the spatially clearly resolved $\Phi_0/2$ vortex at the meeting point of the three HTS film areas from the surrounding $\Phi_0$ vortices in the remaining film (see Fig. 4 right).

**Fig. 4.** Basic idea of tri-crystal experiments (left) and generally observed magnetic flux distribution (right) (after [4]).

### 5. MICROSCOPIC THEORY

The fundamental theory of superconductivity was developed by Bardeen, Cooper and Schrieffer in 1957[12]. It is called the BCS theory and all later theoretical work is based on it. It explains the observed unusual phenomena and the ordered state as consequences of fundamental laws of physics. A detailed presentation of the BCS theory is given in [13], for recent developments we refer to [14].

In the normal metallic phase the conduction electrons form a Fermi liquid whose ground state is characterized by a limiting momentum and energy, the Fermi wave vector $k_F$ and the Fermi energy $E_F$. They are directly related to the density of the fermions (conduction electrons) and set the length and time scales in the normal state through the Fermi wave length $\lambda_F = 2\pi / k_F$ and $t_F = \hbar / E_F$. Superconducting phenomena, on the other hand, occur on length and time scales set by the coherence length $\xi_0 >> \lambda_F$ and the gap frequency $\hbar / \Delta >> t_F$ which are much larger than their counterparts in the normal metallic. This fact implies that the dispersion of the electron states and their interaction are not significantly altered by the superconducting correlations and, consequently, the material-specific information can be evaluated in the normal state. The separation of length and energy scales is an important assumption underlying the BCS theory.

BCS demonstrated that the ground state of non-interacting fermions, the filled Fermi sea, is unstable against the formation of bound pairs for any attractive interaction. This is a direct consequence of Fermi-Dirac statistics. Thus they provided a foundation for the quantum
mechanical order parameter which had been postulated by Landau and Ginzburg. The energy gain of the superconducting state with respect to the normal state is the condensation energy of the pairs merging into a macroscopic quantum state which can be measured as an energy gap for single particle states.

At this point I should like to emphasize that the BCS theory assumes the existence of an attractive interaction and evaluates its consequences. It provides a qualitative explanation of the superconducting properties. Quantitative predictions, however, require a microscopic picture of the electron system in its normal state, in particular of the attractive interaction. Concerning the origin of the attractive interaction, it is generally accepted that lattice vibrations play the dominant role in “conventional” metals. In the novel “exotic” superconductors to be discussed in Section 7, magnetic degrees of freedom give rise to the attraction. In general, an attractive interaction between electrons close to the Fermi surface can arise from the exchange of any boson.

6. APPLICATIONS

Superconductivity is a unique and powerful phenomenon of nature. Nearly a century after its first discovery, its full commercial potential is just beginning to be exploited. The applications are based on the unusual properties described in the present paper such as dissipation-free current flow, macroscopic quantum effects and highly non-linear I-V curves for the superconducting transition. Superconductors offer unique advantages in both large-scale applications as well as electronics. We do not attempt at giving a complete overview over already existing and emerging commercial applications but rather mention selected important examples.

The foundation of the large-scale applications is a new generation of wire, capable of carrying vastly (on the order of 100+ times) higher currents than conventional copper wires of the same dimension, with zero or negligible resistive losses. Today, refined NbTi and Nb3Sn conductors are the basis of a billion dollar industry which delivers magnets, e.g., for Magnetic Resonance Imaging (MRI) systems and High-Energy Physics (HEP) particle accelerators. MRI has become the "gold standard" in diagnostic medical imaging. The typical field values required for MRI cannot be achieved using conventional magnets. Just as importantly, high homogeneity and stability of the magnetic field are essential to achieve the resolution, precision and speed required for economical clinical imaging, and superconductors provide a unique solution to these requirements. The rings of particle accelerators are made of superconducting magnets, strung together like beads on a necklace. In the Large Hadron Collider (LHC), two concentric rings are made up of thousands of superconducting magnets. The high energies required could not be economically achieved without superconducting magnets. Superconductors play a critical enabling role in the International Thermonuclear Experimental Reactor (ITER) project by generating the high magnetic fields needed to confine and shape the high temperature plasma. Turning to commercial applications, superconductor magnets enable the large magnetic separators used for industrial processing. An important example is the kaolin clay industry.
Another recent progress of HEP accelerators comes from Nb-based rf-cavities with extremely high quality factor which transfer much more acceleration energy to the particle bunches than conventional cavities. Miniaturized microwave filters are at present the most advanced HTS electronics application: The low loss of HTS resonators allows a complex coupling of a large number of resonators which enables sharp frequency cut-offs.

Superconductors are expected to be used in power transmission in the near future. Today’s advanced superconductor cable designs enable controllable power flows and the complete suppression of stray electromagnetic fields. Superconductor power cables transmit 3-5 times more power than conventional copper cables of equivalent cross section, enabling more effective use of limited and costly rights-of-way. Three major in-grid demonstrations have been completed in the US including the world’s first superconducting power transmission cable system in a commercial power grid which is capable of transmitting up to 574 megawatts (MW) of electricity, enough to power 300,000 homes.

Superconductivity can leverage the advantages of electrified transportation of various types, ranging from high-speed trains to advanced ship propulsion systems. The incorporation of superconductor technology into transportation system design can improve the efficiency and performance, reduce the weight and fuel consumption, and extend the range of transportation systems of all types. Superconductor motors and generators are much smaller and lighter; operating prototypes are one-third the size and weight of their conventional copper-wound counterparts and quieter. The elimination of rotor losses results in much higher efficiency, especially under partial-load conditions, where many ships operate for the great majority of their operating hours. Magnetically levitated trains have attained top speeds in excess of 500 km/h. Superconductor magnets are essential to this application because of their dramatically lighter weight and lower power requirements. At present, maglev train lines operating in Japan, Germany and China make use superconductor technology.

Let us now turn to electronics applications. Josephson junctions, well-defined weak links of superconducting regions, can be coupled to “Superconducting QUantum Interferometric Devices” (“SQUIDs”), magnetic flux detectors with quantum accuracy which are the most sensitive magnetic field detectors presently available. Nb/AlOₓ/Nb junctions represent by now the highest technical standard of Josephson junctions. Due to their accuracy, superconducting devices are used for realizing the electrical unit of “Volt.

The transition edge bolometer exploits the abrupt change of the electrical resistance at the superconducting transition. Here the temperature increase due to absorption of radiation in the antenna structure allows for broad-band radiation detection. In combination with a THz filter one obtains THz detectors. The latter are used in security checks to search for hidden metal pieces. In radioastronomy, they allow to set up temperature maps of remote galaxy clusters.

In the 1970s and 1980s, IBM tested the fast switching of Josephson junctions from the superconducting to the normal state with respect to a post-semiconductor computer generation. Unfortunately, the switching step from the normal to the superconducting state turned out to limit the practical performance instead of theoretical ~1THz to several GHz Meanwhile, new device concepts based on the transport of single magnetic flux quanta reestablished the
possibility of THz operation. The hottest topic of present Josephson circuit investigations is the realisation of quantum bits ("Qubits") by means of the superconducting wavefunction guided around µm-sized loops including exactly one flux quantum. In contrast to other demonstrated Qubit realizations, superconductive electronics implementation has the largest potential of upscalability to the several kQubit-size with only comparatively moderate lithographic requirements.

7. CHALLENGE: NOVEL MATERIALS

As shown in the preceding section, superconductors provide fascinating and rather unique opportunities for applications. The major disadvantage is, however, that refrigeration is needed. In addition, superconductors have to compete with well-established technologies. An undispensable requirement for commercial application is that the production of superconductors with sufficiently high transition temperatures becomes cost-efficient. The search for new classes of superconducting materials plays an important role. The evolution with time of the maximum critical temperature is displayed in Fig. 5.

![Fig. 5. Evolution with time of maximum Tc (left). Typical schematic temperature vs carrier concentration x phase diagram of emergent superconductors (right).](image)

Current superconductor material science focuses on “emergent” materials. Prominent examples are the cuprate high-temperature superconductors. In contrast to the “deep” Fermi sea of free electrons in the case of classical metals there is only a “shallow” reservoir of charge carriers in these layered cuprate compounds which has to be introduced into the parent stoichiometric antiferromagnetic insulators by means of appropriate doping. The released charge carriers bring about a “bad metal” as genuine normal state where strong Coulomb correlations connect charge transport and magnetic degrees of freedom. The intimate proximity of metal-to-insulator, magnetic and superconducting transitions presents a challenge to theory which is sensibly more complicated than the classical superconductivity problem. A schematic phase diagram is displayed in Fig. 5. In the present section I shall give a briefly review the
properties of three selected classes of materials which are technologically relevant. For a broader review, we refer to [4] and references therein.

Cuprate High-Temperature Superconductors play an outstanding role in the scientific development and for the present understanding of superconductivity. Probably with the only exception of semiconductors, no other class of materials has been investigated so thoroughly by a huge number of researchers worldwide. The new dimension in the development of HTS materials, in particular in comparison with the case of silicon, is that HTS are *multi-element* compounds based on complicated sequences of *oxide layers*. The crystal structures are shown schematically in Fig. 6.

![Fig. 6. Crystal structure of the high-Tc cuprates LaSrCuO (left) and YbCuO (middle). The general structure of HTS cuprates is shown schematically in the right panel.](image)

Today, reproducible preparation techniques for a number of HTS material species are available which provide a first materials basis for applications.

![Fig. 7. Crystal structure of quasi-2D organic superconductors (ET salts). The in-plane structure is denoted by greek latters.](image)

Since the discovery of an organic superconductor in 1980 [15] remarkable critical temperatures $T_c > 10$K have been achieved. Similar to HTS the restriction of the effective dimensionality and strong Coulomb repulsion effects push the systems towards metal-to-insulator transitions. Today more than 100 organic superconductors are known. The vast
majority of them is based on the bis-ethylene-dithia-tetra-thiafulvalene molecule abbreviated as BEDT-TTF or simply ET. The charge transfer molecules form layered structures with large in-plane electrical conductivity. This makes them similar to the HTS in many respects. For the crystal structure see Fig. 7.

![Crystal structure of iron pnictide superconductors](image)

**Fig. 8**: Crystal structure of iron pnictide superconductors (left) and variation with (chemical) pressure of the transition temperature in $\text{Ba(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2$ (right).

High temperature superconductivity in iron pnictides, with a critical temperature $T_c$ in excess of 55ºK, was discovered in early 2006 [16]. For a recent review see [17]. The enormous impact of this discovery upon the scientific community was comparable to that of the discovery of the high-$T_c$ cuprates in 1986. There are important similarities between Fe pnictides and cuprates. Both are layered systems, both have $d$ electrons playing a crucial role, and both feature close proximity of antiferromagnetic order and superconductivity in their respective phase diagrams.

8. SUMMARY AND OUTLOOK

The superconducting phase discovered a century ago continues to be a fascinating state of matter. The unusual properties which are remarkably well understood form the basis for important applications. A number of theoretical ideas have close parallels in other fields of physics, in particular in contemporary particle physics. Examples are the Meissner effect which is closely associated with the Higgs mechanism and the concept of topological conservation. An even more exciting potential application of superconductors lies in the area of foundations of quantum mechanics.

Turning now to the future of superconductivity, an important area of research and development will be the field of material science. Emergent materials will certainly continue to play a crucial role for applications as well as for experimental and theoretical research. The present unsatisfactory microscopic understanding of these systems reflects our insufficient knowledge about materials with strongly correlated electrons.
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REFERENCES